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Sol Gel Synthesis and Preparation of Macroporous Glass: Effect of Sodium Nitrate Addition

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Abstract: The aim of this study is to prepare gel glasses derived via acid catalyst sol-gel method based on SiO₂-CaO-P₂O₅ and SiO₂-CaO-Na₂O-P₂O₅. The synthesized gel glass powder was compacted into pellets and sintered at 1000 °C for 3 hours. The initial characteristics and sintered properties for both glasses then were analyzed. It was found that, the addition of sodium nitrate in the glass leads to foaming effect which occurred during sintering process. Thus, enables the formation of macroporous structure and expansion in thickness experienced by the glass. The pore size was approximately 300 µm by varying the sodium to calcium composition, whereas glass without sodium content only contained nanopores. The fluxing effect that occurred during sintering also caused vitrified bodies which reduced the glass porosity percentage. Glass with sodium content formed sodium related phases such as Na₅.27Ca₃(Si₆O₁₈) which increased the glass crystallinity. From this study, it shows by addition of sodium nitrate into the glass composition, macroporous glasses can be produced which potentially being used as a scaffold material.

Keywords: Bioglass, Sol-gel, Macropores, Synthesis;

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1. INTRODUCTION

Bioglass with macroporous structure is highly needed when being used as a scaffold. Minimum size required for interconnected macroporous structure to promote tissue in growth is at 100 µm while larger pore size at 300 µm enable bone in growth as well as the formation of capillary to occur [1,2]. Bioglass with macroporous structure within this range of pore size is required to fulfill the requirement as an implant scaffold. This can be achieved by preparing porous bioglass by using various methods [3-7]. Thermal treatment has the ability to influence the structural transformation and the final phase of a glass which is also important in order to improve the mechanical properties of a glass scaffold. Nevertheless, the ideal sintering temperature is much closer to the glass crystallization temperature [8]. Crystallization is said to decline the bioactivity of glass due to lower ionic dissolution in vitro. Besides, the highly porous nature of sol-gel glass may decline their sinter ability [9]. By the way, bioglass powder has to be sintered for production of high porous scaffolds or as coatings of implant materials. However, only few papers addressed this issue due to limitations as stated above. Melt derived bioglass, commonly used Na₂O to reduce the melting temperature [10,11].
However, low processing temperature of sol-gel method eliminates the needs of Na$_2$O. Because of that, simple composition of bioglass such as in binary system of SiO$_2$-CaO can be prepared by sol-gel technique. By the addition of network modifier cations such as sodium (Na$^+$) and calcium (Ca$^{2+}$), non-bridging oxygen (NBO) bonds can be introduced through the disruption of structure. This NBO bonds may improve the dissolution and bioactivity of bioglass [3,4]. Thus, the component of Na$_2$O in the sol-gel glass is still considered to be relevant. Apart from that, our observation has found that glasses with macroporous structure together with good mechanical properties can be prepared by synthesis ternary glass with the presence of specific Na$_2$O content prepared by sol-gel method. As it potentially used as scaffold material, further investigation needs to be carried. Thus, the aim of this study is to investigate the effect of sodium nitrate addition on the initial characteristic and sintered properties of ternary glass composition made by sol-gel method. In this study, the comparison between without sodium oxide containing glass and sodium oxide containing glass will be discussed.

2. MATERIALS AND METHODS

Bioglass in the ternary system of SiO$_2$-CaO-P$_2$O$_5$ and quaternary system of SiO$_2$-CaO-Na$_2$O-P$_2$O$_5$ were prepared for comparison. Bioglass without sodium nitrate content in ternary system was labeled as SiCa$_4$P and bioglass with the addition of sodium nitrate content in quaternary system was labeled as SiCaPNa$_3$.

Mixing of reagents was involved during synthesis of bioglass powder for both systems via sol-gel method. This sol-gel method involved series addition of reagents where 40 ml of deionized water was mixed with 1 ml of nitric acid (HNO$_3$, 1M, Sigma Aldrich) and a precursor contained 10 ml of tetraethyl orthosilicate (TEOS, Si(O$_2$CH)$_4$, Sigma Aldrich). This mixture was stirred using magnetic stirrer and it was allowed to react for 40 min before added with 2 ml of tetraethyl phosphate (TEP, OP(O$_2$CH)$_4$, Merck). After 30 min stirring, 8 g of calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$, 4H$_2$O, Merck) then added into the solution mixture and it was allowed to react for another 40 min. For the preparation of bioglass in quaternary system, it was differentiated by adding 5 g of calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$, 4H$_2$O, Merck) and the solution mixture was allowed to react for 20 min before added with 3 g of sodium nitrate (NaNO$_3$, Merck) and it was allowed to react for another 20 min. The final solution that obtained then casted into plastic container and gel formation was observed after solution was left at ambient temperature for three days. Aging process then took placed for 24 hours at 60 $^\circ$C before proceed to drying process for another 2 days at 120 $^\circ$C. The dried powder obtained was directed to the thermal stabilization process in muffle furnace for 3 hours at 600 $^\circ$C with heating rate of 5 $^\circ$C/min in order to remove any residues that contained in the powder. A fine gel glass powder was obtained by grinding using agate and mortar and preliminary analysis of the powder which involved Thermal Gravimetric Analysis (TGA, Rigaku Thermo plus Evo) and Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer) were carried out.

The powder was then compacted into cylindrical pellet with diameter and thickness of about 12.00 mm and 3.00 mm respectively. The compacted pellets were sintered at 1000 $^\circ$C with soaking time and heating rate of 3 hours and 5 $^\circ$C/min respectively. Further analyses such as Scanning Electron Microscopy (SEM, JOEL Model JSM-6460LA), X-ray Diffraction (XRD, BRUKER D2 PHASER), FTIR and Archimedes test (HR-250AZ) were carried out.

3. RESULTS AND DISCUSSION

3.1 Initial characterizations.

Fig. 1 (a) and (b) show the TGA and FTIR analysis for gel glass powder thermal stabilized at 600 $^\circ$C respectively. The increment of sodium nitrate content resulted increased in nitrate residual within the glass matrix as indicated by infrared spectrum. This lead to the highest decomposition to occur at temperature range between 600 $^\circ$C to 900 $^\circ$C for the sample with presence of sodium nitrate in their glass matrix as shown.
on TGA graph. Samples contained sodium nitrate was observed to be effectively stable above 900 °C due to the decomposition of by product occurred. This was approved by Arcos et al. which showed nitrates decomposed approximately at 680 °C [12]. Increase in the sodium nitrate content lead to the increment of Si-O- Ca non-bridging oxygen (NBO) bond which indicated by FTIR [12-14]. This NBO bond should be advantages for bioactivity property of a scaffold.

![Fig. 1](image)

**Fig. 1** (a) TGA and (b) FTIR analyses of gel glass for (i) SiCa₄P, (ii) with addition of sodium nitrate and (iii) with addition of more sodium nitrate (SiCaPNa₃) thermal stabilized at 600 °C

### 3.2 Physical and morphological properties.

Table 1 displays the dimensional changes in thickness and diameter as well as porosity and densification using Archimedes principle for gel glass pellets sintered at 1000 °C. The SiCa₄P shrank in both thickness (9.85 %) and diameter (9.93%) due to the densification of the particle that occurred upon sintering process. Meanwhile, SiCaPNa₃ shrank in diameter (4.35%) but expanded in thickness (60.53%). Scanning electron microscopy (SEM) reveals the SiCa₄P existed in nanoporous sized while SiCaPNa₃ was in macroporous sized with pore size approximately achieved 300 µm throughout both surface and cross section of the sintered gel glass pellet. This phenomenon of macroporous formation occurred due to the gas released and eventually created such foaming effect once the gel glass pellet undergo sintering process at this temperature. This factor also caused the expansion in thickness of sintered SiCaPNa₃.

For Archimedes test, water is used as the medium. SiCa₄P showed 41.1374% porosity which is higher compared to SiCaPNa₃ at only 6.8346%. The presence of sodium nitrate content in SiCaPNa₃ showed this sample experienced partially melted on its surface due to the fluxing effect and lead to vitrified body after sintered. This factor lead to the major reduction in porosity percent of the sintered gel glass due to the SiCaPNa₃ that was impermeable to water and it only allowed water to passes throughout the pores. These indicated that SiCa₄P was able to absorb more water than SiCaPNa₃. This suggested that, Archimedes principle using water as a medium is not very suitable in order to determine the porosity percent of these samples.
Table 1 Dimensional changes, porosity and densification analyses for sol-gel glass pellet sintered at 1000 °C

<table>
<thead>
<tr>
<th>Properties</th>
<th>SiCa₄P</th>
<th>SiCaPNa₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness shrinkage (%)</td>
<td>9.85</td>
<td>60.53</td>
</tr>
<tr>
<td>(Expand)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter shrinkage (%)</td>
<td>9.93</td>
<td>4.35</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>1.3971</td>
<td>1.1383</td>
</tr>
<tr>
<td>Apparent porosity (%)</td>
<td>41.1374</td>
<td>6.8346</td>
</tr>
<tr>
<td>Densification (%)</td>
<td>58.8626</td>
<td>93.1654</td>
</tr>
</tbody>
</table>

Fig. 2 Surface morphology for (a) SiCa₄P and (b) SiCaPNa₃ and cross section morphology for (c) SiCa₄P and (d) SiCaPNa₃ sintered at 1000 °C

3.3 Phases and structural properties.

Fig. 3 shows the diffractograms of gel glass powder sintered at 1000 °C. The percent of crystallinity for SiCa₄P was 66.6% while for SiCaPNa₃ was 71.5%, which indicate an increased in sample crystallization with the presence of sodium content. The SiCa₄P contained calcium silicate (CaSiO₃) as the main phase (40.7%) meanwhile for SiCaPNa₃ is tetracalcium catena-hexaphosphate(V) (Ca₄(P₆O₁₉)) phase (39.2%). For SiCa₄P, all the phases formed were related to calcium such as dicalcium silicate (Ca₂(SiO₄)), dicalcium diphosphate(V) (Ca₂(P₂O₇)), decalcium hexakis(phosphate(V)) oxide (Ca₁₀(PO₄)₆O) and calcium silicate (CaSiO₃). However, for SiCaPNa₃ most of the phases formed were sodium-related such as sodium calcium cyclo-hexasilicate (Na₅.27Ca₃(Si₆O₁₈)), sodium peroxide (NaO₂) and disodium dicalcium disilicate (Na₂Ca₂(Si₂O₇)). This indicates the formation of new phases as sodium nitrate was added into the sol-gel glass matrix. This sodium related
phase proved the presence of Na₂O in SiCaPNa₃. With the presence of sodium related phases, bioactive glass monolith with enhanced mechanical strength and adequate biodegradability would be achieved [15].

Fig. 3 XRD analysis for (a) SiCa₄P and (b) SiCaPNa₃ sintered at 1000 °C

Fig. 4 FTIR spectrum for (a) SiCa₄P and (b) SiCaPNa₃ sintered at 1000 °C
4. SUMMARY

Fig. 4 shows the Fourier transform infrared (FTIR) spectrum of gel glass sintered at 1000 °C. In both samples, peak related to P-O bond were observed to correspond with XRD spectra. This proved the presence of phosphate crystalline phase in both samples. It was found that, peak that related to nitrate was fully decomposed as indicated by TGA analysis. From the graph, silicate (Si-O) and phosphate (P-O) spectral band intensity were reduced. This is caused by the addition of sodium nitrate into the glass matrix increased the non-bridging oxygen (NBO) structure thus reducing those glass networking structures. This would enhance the in vitro bioactivity property of this glass monolith.

5. CONCLUSION:

Macroporous monolith with the additions of sodium nitrate into ternary sol-gel derived glass composition (SiO₂-CaO-P₂O₅) was successfully prepared. The initial properties of sodium-contained glass were compared to the typical ternary glass composition. The macroporous structure formation can be related to foaming effect occurred during sintering. The addition of sodium nitrate in this ternary glass composition leads to the formation of macro-sized pores, formed sodium-related phases which increased glass crystallinity besides decreased the glass networking structures. Thus, it was possible to prepare macroporous glass structure by addition of sodium nitrate, which replaced calcium oxide content in the sol-gel composition with sintering at 1000 °C.

REFERENCES

1522.


The Formulation Parameter Influence on PHB Hollow Colloidosomes Formation Prepared via Two Step Solvent Evaporation Method

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ABSTRACT. This study demonstrates polyhydroxybutyrate (PHB) as a potential polymer to produce colloidosomes through two step solvent evaporation method. In this study, the surfactant concentrations, molecular weight and oil phase volume were varied which proven that a range of average diameter, $D_{ave}$ and higher yield of PHB colloidosomes can be successfully achieved. The $D_{ave}$ increased slightly by 0.03 µm when surfactant concentration decreases from 1.2 wt.% to 0.5 wt.%. However, $D_{ave}$ increases significantly from 1.33 to 8.68µm when the average molecular weight, $M_w$ of surfactant used increases from 13,000 to 130,000. In addition, the colloidosomes yield also increases as the surfactant average $M_w$ increases. This study also displayed the simplicity of the method, where it is straightforward and used commercially available materials.

Keywords: PHB, Colloidosomes, Encapsulation, Solvent evaporation method;

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1. INTRODUCTION

Colloidosomes are hollow particles whose shells are composed of a closed-packed layer of colloidal particles [1]. The work on colloidosomes was first reported by Velev and colleagues in 1996 [2] although the term was introduced later by Dinsmore et al.[1]. This hollow particle plays significant roles in microencapsulation: a process in microscopic formation of thin coatings of wall material around an active ingredient [3] This process has been used in varies applications such as controlled release of drugs [4], aroma [5], food industries [6] and protection of biologically active species [7]. Microcapsules preparation methods can take several steps which might be complex, time consuming and in need of binders [1,8]. A study by Thompson et al. [9] reported that latex colloidosomes prepared via thermal annealing might be unfavorable to thermal sensitive active ingredient such as fragrances or drugs. Layer-by-layer (LbL) method usually uses solid templates. The desired materials are self-assembled layer-by-layer onto the pre-produced colloidal particles which will be removed at the end of the process to achieve the hollow structures [10]. However, LbL’s drawback is the multistep processes which is time consuming [9]. Therefore, the two-step solvent evaporation method was chosen as preparation method because it is simple, straightforward and less time consuming.

Polyhydroxalkanoates (PHA) polymers are natural polymers which are produced by bacteria and PHB is the most researched members of the PHA family [11]. PHB particularly has attracted considerable interests for its applications as delivery system or as scaffolds in tissue engineering. This is owing to its advantages of excellent biocompatibility, biodegradability and easy processability. Due to these favorable properties of PHB, this study proposed PHB as potential structural polymer to prepare hollow colloidosomes via two-step solvent evaporation method.
2. MATERIALS AND METHODS

2.1 Colloidosomes Preparation.

The terms PHB(x)/PVA(y) was used to indicate the colloidosomes formulation. The terms PHB(x)/PVA(y) is referring to structural polymer/surfactant, where x and y are referring to the structural polymer and surfactant concentration (wt.%) respectively and z is referring to the average molecular weight, M_w of the surfactant used to prepare the sample. The mixture of the oil and water phase will form emulsions.

Here, O/W emulsion preparation route was used. The oil phase consists of PHB in CH_2Cl_2 is fed to the water phase which consists of polyvinyl alcohol, PVA (98% hydrolysed) in deionized water whilst homogenized at 9000 rpm for 30 min using IKA T18 Digital Ultra Turrax homogenizer. The emulsion will be immediately rotary evaporated to trigger the colloidosomes formation. All polymers and surfactant were purchased from Sigma Aldrich and used as received.

2.2 Physical Measurements.

A Leica DM750 microscope was used to obtain optical images. For this work, the analyser was fixed at 90°. For a given sample, a drop of fully evaporated emulsion was placed on a microscope slide and viewed immediately. The objective lenses used had magnifications of ×10, ×40, and ×60. The average diameter, D_{ave} were determined by counting at least 100 microparticles. Zeiss Supra 55VP field emission scanning electron microscopy (FESEM) was used to study the morphology of the colloidosomes. The samples were dried at room temperature overnight prior to measurement. All samples for characterization are washed three times by centrifugation at 3000 rpm. Table 1 shows the colloidosomes formulation of PHB/PVA and the resulting sizes.

**Table 1** The formulation used in this study to prepare the PHB/PVA colloidosomes

<table>
<thead>
<tr>
<th>Entry</th>
<th>System</th>
<th>D_{ave} / µm</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>PHB(1.5)/PVA13k(1.2)</td>
<td>1.30</td>
</tr>
<tr>
<td>2*</td>
<td>PHB(1.5)/PVA13k(1.2)</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>PHB(1.5)/PVA13k(0.5)</td>
<td>1.33</td>
</tr>
<tr>
<td>4</td>
<td>PHB(1.5)/PVA30k(0.5)</td>
<td>1.37</td>
</tr>
<tr>
<td>5</td>
<td>PHB(1.5)/PVA130k(0.5)</td>
<td>8.68</td>
</tr>
</tbody>
</table>

* Only entry 2 use higher oil volume

3. RESULTS AND DISCUSSION

The formulation for PHB colloidosomes started from the optimized PCL(1.5)/PVA13k(1.2) system (Entry 1 in Table 1) reported in previous study by Shahidan et al. [8]. Fig.1 shows that PHB has the potential to be prepared as colloidosomes. However, optimum condition for PHB/PVA13k system need to be investigated. The results shows that the average size, D_{ave} are small (D_{ave}=1.30µm) and the yield is low (Fig.1(a)) compared to PCL/PVA13k system (inserted images) under optical microscope. Interestingly, the PHB/PVA colloidosomes morphology shows that PHB colloidosomes are more porous (Fig. 1(b)) compared to PCL hollow colloidosomes (Fig. 1(c)). In addition to PHB’s advantages stated previously, highly porous morphology is one of the important 3D scaffolds features for tissue engineering application [12].

In order to increase the colloidosomes yield, we increased the oil volume from 75ml to 125ml (Entry 2, Table 1). However, the increasing oil volume induced flakes formation which indicated that the surfactant might not be enough to stabilize the emulsion and resulting aggregation which lead to flakes formation (not shown). Therefore, we reduced the oil volume to 75ml and reduce surfactant concentration from 1.2wt.% to 0.5wt.% to increase the system D_{ave} (Entry 3, Table 1). Fig.2(b) shows colloidosomes prepared at lower PVA concentration. The result shows the D_{ave} for PVA concentration of 1.2wt.% and 0.5wt.% is not significantly...
different ($D_{ave} = 1.30$ and $1.33 \mu m$ respectively). However, the small flakes are no longer visible. The insignificant $D_{ave}$ difference between entry1 and 3 shows that, in order to stabilize the emulsion, higher molecular weight might be needed to increase the stearic repulsion.

**Fig. 1** Shows hollow colloidosomes prepared using PHB(1.5)/PVA13k(1.2) system and PCL(1.5)/PVA(1.2)13k system under (a) optical microscope (insert shows the PCL/PVA system), (b) and (c) FESEM for the system respectively. Images for PCL/PVA system

**Fig. 2** (a-d) shows PHB/PVA system formulation in entry 1,3 to 5, respectively. The insert in each figure shows crossed polarised colloidosomes. Entry 4 and 5 (Fig.2(c) and (d)) shows colloidosomes prepared using higher molecular weight surfactant. The $D_{ave}$ increased from 1.33 to 1.37 $\mu m$ when the surfactant average $Mw = 13k$ increased to 30k. The $D_{ave}$ increased significantly to 8.67 $\mu m$ when surfactant with average $Mw = 130k$ was used in the preparation. The increased average $Mw$ reduced the number of surfactant molecules. This could be seen that the $D_{ave}$ increases as average $Mw$ increases. However, they are more effective to
stabilize the emulsion for particle/colloidosomes formation. Their images under polarized microscope are more visible as the increasing average $M_w$ increases $D_{ave}$ (insert Fig. 2 (a-d)).

Fig. 3 (a-c) shows the colloidosomes morphology prepared using formulation in entry 1, 3 and 4 respectively. The FESEM images below each system show an enlarged surface morphology.

Fig. 4(a-d) shows the colloidosomes morphology prepared using formulation in entry 5. Fig. 4(b') and (c') are the enlarged images of (b) and (c) respectively. Red arrows show the smoothen area due to higher average $M_w$ surfactant used.

The colloidosomes morphology prepared at different polymer concentration and average $M_w$ of the surfactant is shown in Fig 3. The PHB(1.5)/PVA13k(1.2) system show highly porous morphology. When PHB(1.5)/PVA(0.5) system was used, the morphology are less porous and further smoothed (Fig. 3 (b) and (c) respectively). It is proposed that PHB(1.5)/PVA130k(0.5) system are porous. However, the remaining higher average $M_w$ of the surfactant used might covered the porous surfaces as evidence of the smoothen colloidosomes surface (red arrows in Fig 4)) which might also be the case for PHB(1.5)/PVA30k(0.5) compared to PHB(1.5)/PVA13k(0.5) system.
4. SUMMARY

It is proven that PHB could be the potential polymer structure to prepare hollow colloidosomes via two-step solvent evaporation method. This study also shown that the formulation control of surfactant concentration and molecular weight and oil phase volume could be altered to produce higher yield of hollow colloidosomes and varies their sizes.

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REFERENCES

Effects of Anthocyanin Pigment from Purple Cabbage in Food Packaging
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ABSTRACT. In developing countries, food spoilage and increase in pollution of solid waste, especially from food packaging. Basically, this problem does not only affect the damaging to human being, but also towards environment. Purple cabbage that contain high amount of anthocyanin can be utilized in food packaging production as it bring unlimited number of economic and environmental benefits to the industrial of food. The purposes of this research are to extract anthocyanin pigment in purple cabbage and to study the effect of anthocyanin in food packaging towards storage condition, food product and mechanical properties. Two different types of solvents were used to compare the amount of anthocyanin extracted. Fourier transform infrared (FTIR) and UV-vis region spectra showed compatibility of anthocyanin in plastic film matrix. Based on the effect on food sample, the pH indicator film showed color changes from purple to pink, whereas for the effect of storage; when temperature increases, the physical properties of deteriorates. Overall, pH indicator films that contain anthocyanin from purple cabbage extract has high potential to be used as one of the material in food packaging in order to detect food spoilage since they have reliable response to pH and temperature.

Keywords: Anthocyanin, Extraction, Food packaging, Purple cabbage;

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1. INTRODUCTION

At present time, food packaging becomes the major concern within the consumer because the function of food packaging itself must act as a protector towards food products. As growth of technology increase, the changes in consumer preferences and demand for safe and high quality food products also increases. This situation leads to innovative developments and improvement of packaging materials. Food packaging is often used as marketing tool to differentiate a product and the materials used must be in environmental considerations [1]. For example, the packaging itself does not produce any adverse effect on the quality of the product through chemical reactions, leaching of packaging materials or absorption. The important factor that should be considered is low in cost, ease of fabrication, availability and regulatory acceptance of the materials.

In this research, purple cabbage extract had been chosen as natural sources that will added during food packaging production. This cabbage contain very low in saturated fat, cholesterol and a source of thiamin but providing large amounts of anthocyanin and giving high antioxidant properties that can decrease the risk of cardiovascular diseases, brain disorders and cancer [2].

2. MATERIALS AND METHODS

Potato starch powder and purple cabbage were bought at the Giant supermarket, Seksyen 7, Shah Alam. This potato starch powder comes from local product which contain 315 kcal energy, 79.0 gm carbohydrate, 0.05 gm protein and 0.05 gm total fat per 100 gm. Extraction of purple cabbage was divided based on two different solvents which was hundred percent distilled water and a mixture of ethanol-distilled water with ratio one to one. For the extraction using distilled water, purple cabbage was cut into small size and boiled
using hot plate. The ratio of purple cabbage and distilled water is 1:2. After the solution was boiled, the solution was cooled down for a few min before filter using muslin cloth into scotch bottle. Then, the scotch bottle was wrapped with aluminium foil to avoid the colour diminish before stored in chiller with 4-5 °C.

Same goes when extracting using a mixture of ethanol-distilled water. The molarity used for ethanol was 40% that was diluted with distilled water from 95% molarity that available in laboratory. For extraction process, the ratio used was 1:1. Purple cabbage was cut into small in size and blend using a blender. This process cannot be boiled to avoid ethanol being vaporize since its boiling point is lower than water which is around 78 °C compared to water 100 °C. The solution was filtered using muslin cloth, wraped with aluminium foil to avoid the colour diminish and stored in chiller with 4-5 °C.

2.1 Preparation of film as food packaging.

The procedure was started by preparing the water bath method. 250 ml of extract solution was pour into a beaker and heat until 40 °C. Then, 7.5 g of potato starch powder was added into the solution for about 10 min for starch to dissolve. After that, the temperature was increased up to 80-95 °C to ensure the starch solution gelatinize completely. Next, 1.93 ml glycerol was added which act as plasticizer to the plastic film. After 10 min, the solution was cooled down and 20 ml solution was poured into each of petri dish. Finally, all the petri dish were put into the oven with temperature 35 °C for 24 hours.

2.2 Fourier transform infrared (FTIR) spectroscopy.

FTIR analysis was carried out using a Perkin Elmer with model Spectrum One. FT-IR spectra of pH indicator films (with and without purple cabbage extract) were measured between 4000 and 515 cm⁻¹ wave number range.

2.3 Colour response analysis of pH indicator films on Strawberry Fruit.

The colour changes of food packaging will be observed with different temperature. The temperature were varied from cold temperature (4 °C), room temperature (25 °C) and warm temperature (60 °C).

2.4 UV-vis Spectroscopy of pH indicator film.

UV-vis spectra of plastic films (with and without purple cabbage extract) were measured using a Perkin Elmer UV-vis spectrophotometer (Shelton, CT 06484, USA) with model 750 lambda. The spectra of pH indicator films in pH values of 6 to 7 were measured in the range of 400 to 700 nm after the pH films were undergo analysis on food sample. A standard curve of anthocyanin extract was used to compare and confirm the incorporation of purple cabbage extract into those pH indicator films.

3 RESULTS AND DISCUSSION

3.1 Fourier transforms infrared (FTIR) spectroscopy.

Fig. 1 shows a few of peaks in absorbance wavenumbers spectrum range from 4000 cm⁻¹ to 515 cm⁻¹. From the result obtained, all samples have broad absorption range between 3200 cm⁻¹ and 3400 cm⁻¹ showed the chemical has intermolecular hydrogen bond (H-bond) which is stretching vibration of free, inter and intra-molecule. Almost all the samples have sharp absorption between 1600 cm⁻¹ and 1650 cm⁻¹, shows that C=C stretching vibration was conjugate.

By comparing both curves, curve that used ethanol as solvent has deformation of alkane group and there was C-O-C stretching vibration of ester acetates. This deformation will help in plastic film production. While, curve that used distilled water do not have much deformation of alkane. Another difference between those curves is at wavelength 1217.25 nm from ethanol curve. At this peak, there is anthocyanin which is flavonoid, under phenolic compound. In organic chemistry, sometimes phenolic also called phenol. It is a class of
chemical compounds consisting of a hydroxyl group bonded directly to an aromatic hydrocarbon group. Basically, this anthocyanin plays an important role to colour the purple cabbage.

![Graph of FTIR on extraction of purple cabbage solution with two different type of solvents](image)

**Fig. 1** Graph of FTIR on extraction of purple cabbage solution with two different type of solvents

3.2 *Colour response analysis of pH indicator films on strawberry fruit.*

Anthocyanin that comes from extract purple cabbage can also act as pH indicator to food packaging technology. In other words, this food packaging not only biodegradable, edible but also can help consumers during product selections. The analysis was carried out by wrapping a strawberry as food sample using different type of solvent with different storage temperature. The result and observations of the analysis was tabulated in the Table 1 below. The pH of all packaging in this analysis are around 6, while the pH of purple cabbage is around 6 to 7.5. Strawberries are acidic and the pH for ripe strawberries are around 3.3 to 3.6 [3]. Packaging that contain purple cabbage extract is said will change its original colour based on the pH of materials. If the materials is in neutral state, the colour is purple and if the materials in alkali state, its colour is blue and for the strongest alkali is green. Lastly, if the element is in acid state, the colour is pink and for the strongest acid is red. Purple cabbage can be used as a pH indicator because it turns red in acid and blue in basic solutions [4].

From this table, once the strawberries get spoilt, the packaging that contain extract of purple cabbage turns colour from purple to pink-purple. It can be conclude that extraction of anthocyanin from purple cabbage is one of the important material that can be used in food packaging. This is because anthocyanin play an important role to detect the spoilage of food. But not for packaging without extraction of anthocyanin. Even though the strawberry inside that food packaging get spoilt, the colour of packaging is still in good condition. That is mean anthocyanin can help consumers to notify the spoilage of food sample. The changes in colour of the pH indicator film is a good diagnostic tool in order to detect the food safety and quality [4].

**Table 1** Result of plastic film as food packaging. (a) plastic film with purple cabbage extract using distilled water-ethanol as solvent, (b) plastic film with purple cabbage extract using distilled water as solvent, (c) plastic film without purple cabbage extract
The strawberry is in fresh and good condition for all temperature.

- The colour of plastic films are in neutral colour, where (a) and (b) is purple colour and (c) is colourless.
- The purple colour of (a) is darker compare to (b), means that more anthocyanin extract contain inside that film.

Besides, as temperature increase, the appearance of packaging changed. As we can see, at the end of the experiment which is at day 5, the packaging in the cold storage still in a good condition. Those packaging is still in their original colour and the texture of those packaging is still soft and glossy in appearance. Compared to packaging in hot storage, the colour of all of the three packaging changed from purple to brown. This changes occurred might be cause by denaturing of protein in purple cabbage. Besides that, the texture of those packaging changed which is turned hard and rough due to high temperature applied to those packaging. Thus, it shows that the optimum storage temperature for package strawberry is in cold storage.

### 3.3 UV-vis Spectroscopy of pH Indicator Film

The pigment in purple cabbage comes from a group of compounds called anthocyanin, which is an antioxidant behavior of their phenolic groups. Anthocyanins are important antioxidant where part of a larger group of flavonoids structures. The pigment that come from these anthocyanins are responsible to colour the plant for example red, purple, blue and so on. The colour changes of films with purple cabbage extract were tested in order to verify the use of the extract as a pH indicator dye. Fig. 2 shows a graph of UV-vis spectra of
pH indicator films with and without purple cabbage extract after performing analysis on strawberry as a food sample in cold storage condition which is in their optimum storage condition.

The colour concentration in that mixture is proportionally to its absorbance at that wavelength it absorb light [4]. From the result obtained, at wavelength 554 nm, the absorption peak for plastic film with anthocyanin extract using distilled water-ethanol as their solvent and plastic film with anthocyanin extract that using distilled water as their solvent is 0.9111 and 0.9549 respectively. Meanwhile at wavelength 569 nm, the absorption peak for plastic film with anthocyanin extract that using distilled water-ethanol as their solvent and plastic film with anthocyanin extract that using distilled water as their solvent is 0.8748 and 0.9549 respectively.

The different of absorption peak between those two types of pH indicator films is due to the different in pH of that film. Plastic film with anthocyanin extract that using distilled water-ethanol as their solvent has pH 6.1 while plastic film with anthocyanin extract that using distilled water as their solvent has pH 6.5. After that plastic films being analysis on food sample, plastic film that contain ethanol in its solvent change colour to pink more quickly than the other plastic. That is why its pH is low and its absorption peak is lower compare to packaging that do not contain ethanol as solvent.

![Absorbance vs Wavelength](image)

**Fig. 2** UV-vis spectra of pH indicator films with and without purple cabbage extract

### 4 SUMMARY

Film with high light absorbance could be an excellent barrier to prevent light-induced lipid oxidation and it is useful to be applied in food technology [5]. Overall, plastic film with purple cabbage extract had a high potential which can be used in pH sensitive dye due to its sensitivity to color variations where the colour had change from purple to pink as a result of pH changes. From the UV-vis spectra above, we can see that pH indicator films which contain purple cabbage extract have a strong absorption peak in the UV-vis region. Whereas film without purple cabbage extract do not have absorption peaks in the UV-vis spectrum. This variation happened because of the presence of anthocyanin from those extractions. A conclusion can be made which is purple cabbage extract was incorporated into agar and starch films.
ACKNOWLEDGEMENT

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Effect of Leaching Agent Composition on Morphology, Thermal and Mechanical Properties of Bioglass® Reinforced Polyurethane Scaffold

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ABSTRACT. In this preliminary study, Bioglass® (BG) reinforced Polyurethane (PU) composite scaffolds with different composition of leaching agent were fabricated. Salt leaching technique was used to prepare the scaffolds by using different percentage of NaCl and NaHCO\textsubscript{3} as leaching agent to create the pore. Morphological characteristic, thermal properties and mechanical properties of the scaffold were investigated by field emission scanning electron microscope (FESEM), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). As revealed by FESEM images, as the percentage of NaHCO\textsubscript{3} increased the pore structure of the scaffold changed drastically. As the content of NaHCO\textsubscript{3} increased from 50%, the pore become less uniform with micropore majorly formed within the scaffold. Considering the result obtained from TGA, NaHCO\textsubscript{3} entrapped in the scaffold did not change the properties of the PU matrix itself. However, high percentage of NaHCO\textsubscript{3} greatly influenced the mechanical properties of the scaffold due to NaHCO\textsubscript{3} entrapped in scaffold might act as filler which further increased the storage modulus of the scaffold. Based on morphology analysis of 100C and 75C25H scaffolds, future work would attempt to consider 0-25% amount of NaHCO\textsubscript{3}able to further improve the microstructure of the scaffold.

Keywords: Polyurethane, Bioglass®, Salt leaching, Scaffold; NaCl, NaHCO\textsubscript{3}

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1. INTRODUCTION

Scaffold fabrication and design are crucial in biomaterials aspect as it plays unique role in bone tissue regeneration and repair [1]. Scaffold is defined as a 3D substrate for cells and tissue regeneration template [2]. Ideal scaffold for bone template should have the following requirements: (i) highly porous structure with interconnected pore network to allow cell penetration, as well as transport of nutrients and metabolic waste [1], (ii) biocompatible and bioresorable with synchronize degradation rate and cell/tissue growth in vitro and in vivo [3], (iii) compatible surface chemistry for cell attachment, proliferation and differentiation [3], (iv) mechanical properties mimic with the natural bone tissue [4], (v) able to bond to host tissue as well as prevent the invasion of scar tissue [1]. Polyurethane (PU) has attracted great attention for clinical and surgical application as it has unique segmented structure [5]. Tunable soft and hard segment properties of PU make it possible to tailor its mechanical properties, thermoplasticity and durability depending on its application [6]. Therefore, there were urged among researchers to fabricate polymer scaffold reinforced with bioactive materials such as Bioglass® (BG), bioglass-ceramic and calcium phosphate ceramic [7] which is one of the alternatives to improve the bioactivity of the PU scaffold. Hence, Bioglass® 45S5 discovered by Hench in
1969-1971 with the Na₂O-CaO-SiO₂-P₂O₅ system high in calcium content with a composition closed to the Na₂O-CaO-SiO₂ diagram [8] become one of the promising candidates to improve the bioactivity of PU scaffold.

A wide variety of techniques to fabricate 3D biodegradable polymeric scaffold including thermal induced phase separation [9], salt leaching [10], freeze drying [4], solid-liquid phase separation [11] and electro spinning [12]. Salt leaching method has been chosen to construct the scaffold due to ease of fabrication, controllable pore size and porosity by varying the size and concentration of leaching agent [5], do not imply any high temperature that preserve the polymer properties and on top of that leaching agent do not release dangerous ions for the human body if trapped in the scaffold [10].

Salt leaching had been widely applied by other scholars to prepare the scaffold by means this method is effective in controlling the porosity and pore size. The leaching agent used usually sodium chloride (NaCl) salt or of an organic compound such as saccharose to create pores [13]. Cannillo et al. [10] carried out preliminary study to define the best NaCl and/or NaHCO₃ able to optimize the pore structure of the polycaprolactone scaffold. It is believed the blend of leaching agent NaCl and NaHCO₃ able to create open pore with controllable pore size as NaHCO₃ aids to form interconnected structure for the scaffold. Hence, the scaffold obtained by salt leaching technique with different percentage of salt mixtures should be further investigated as the scaffold will exhibit different structural and physical properties that will further affect the mechanical behavior of the scaffold itself. In this work, 25-100% of NaHCO₃ had been combined with NaCl as leaching agent to fabricate PU-BG scaffold and the effect of different composition of leaching agent on morphology, thermal and mechanical properties of the scaffold was studied.

1. MATERIALS AND METHODS

1.1 Synthesis of Bioglass® (BG).

Bioglass® 45S5 with the 45.0 wt.% SiO₂, 24.5 wt.% Na₂O, 24.5 wt.% CaO and 6 wt.% P₂O₅ were synthesized by melt quenched technique [8]. High purity powder SiO₂, Na₂CO₃, P₂O₅ (Sigma-Aldrich) and CaCO₃ (MERCK Milipore) were weighed and melted in a crucible by two melting stages at temperature 1200 °C and 1400 °C for seven hours with a heating rate 10 °C/min to ensure a homogeneous molten glass can be produced. After melting, a molten glass was quenched immediately in deionized water bath at room temperature.

1.2 Fabrication of PU-BG composite scaffold.

The PU-BG scaffold was fabricated by solvent casting / salt leaching technique followed the flow procedure by Lim et al. [14]. Neat PU (PEARLTHANE 11T80 from Duplas Marketing Sdn. Bhd.) beads were weighed and dissolved in Tetrahydrofuran (THF) (Sigma Alrich) at a concentration of 10 w/v% for 1.5 hours at 50 °C to form PU solution. Then, 10 wt.% of synthesized BG powder (mean particle size < 8µm) was added to the PU dispersion then stirred continuously for 1.5 hours to allow homogeneous dispersion of BG. Leaching agent NaCl and NaHCO₃ (MERCK Milipore) were then added into the dispersion with the ratio of 1:5 of polymer to leaching agent and mixed homogeneously for another 15 min. The dispersion was then transferred into a mold and dried in room temperature for two days to allow complete THF evaporation. The
salt in the sample was then washed out by immersing the sample in deionized water for three days. The water was refreshed every six hours to ensure salt was leached out from the sample. Finally, the obtained scaffold was dried in an oven at 80 °C for one day. Thus, five types of sample were fabricated using leaching agent NaCl, labelled as ‘C’ meanwhile NaHCO₃ labelled as ‘H’. Table 1 tabulated the samples code with different composition of leaching agent.

Table 1 Samples of PU-BG with different composition of leaching agent

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Composition of leaching agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>100C</td>
<td>100% NaCl</td>
</tr>
<tr>
<td>75C25H</td>
<td>75% NaCl and 25% NaHCO₃</td>
</tr>
<tr>
<td>50C50H</td>
<td>50% NaCl and 50% NaHCO₃</td>
</tr>
<tr>
<td>25C75H</td>
<td>25% NaCl and 75% NaHCO₃</td>
</tr>
<tr>
<td>100H</td>
<td>100% NaHCO₃</td>
</tr>
</tbody>
</table>

1.3 Characterization.

Field emission scanning electron microscope (FESEM) (SUPRA 35VP, ZEISS) equipped with energy dispersive X-ray spectroscopy (EDX) was performed on scaffolds to observe the pore structure of the scaffold. Thermal properties of scaffold were carried out by both thermogravimetric analysis (TGA) (1 STAR® System, Mettler Toledo) to analyze degradation profile of scaffolds. The degradation process was analyzed from room temperature until 800 °C at a controlled heating rate of 10 °C/min under nitrogen gas. Compression test by dynamic mechanical analysis (DMA) was carried out on cylinder shaped specimens with dimensions of 9 mm height and 20 mm radius. This testing was carried out using mechanical analysis (DMA) Mettler Toledo. The temperature-dependent storage modulus of each material was evaluated with a temperature sweep of 0 °C to 100 °C, at a compression frequency of 1 Hz, 20 μm amplitude, 0.3% strain, and 0.01N static force. The storage modulus (E) value was recorded as a function of frequency.

2. RESULTS AND DISCUSSION

FESEM images of the scaffold in Fig. 1 reveal the open pore and interconnectivity of the cross-sectional structure of the scaffold. FESEM images reveals that, different ratio of salt composition gives a significant effect on the properties of the pore. Shape and size of the pore changed significantly as the proportion of the
leaching agent varied. It can be observed that, scaffold with high percentage of NaCl (100C) had slightly rounded shape and pore size around 84-326 µm. Meanwhile, as the composition of NaHCO$_3$ increases, the structure of the pore changes drastically as the pore becomes less uniform with irregular pore shape within the scaffold. This observation can be distinguished from the scaffolds 25C75H and 100H which had pore size range 84-281 µm and 54-143 µm respectively. Irregular macropore exists in scaffold 25C75H and 100H was caused by the agglomeration of smaller particle of NaHCO$_3$ which did not dispersed homogeneously besides caused the pore wall to rupture. However, as reviewed by Karageorgiou et al. [15], general minimum pore size required to generate mineralized bone is considered ~100 µm. Although macroporosity (pore size > 50 µm) has big impact in osteogenic outcome, microporosity (pore size < 10 µm) and pore wall roughness play an important role as well to induce bone formation [16]. It seems that scaffold 100C is the best scaffold in this work since the scaffold exhibited a lot and well-developed porosity with pore size covers a very wide range, from tens of microns to hundreds of microns. Macropores within the range 100-400 µm are considered the ideal size for bone tissue formation meanwhile pore between 150-900 µm allows for nutrient supply and waste removal of cells grown on the scaffold [9]. Even though the pore structure for 75C25H scaffold was not well-built with a slight rupture of the pore wall, however this scaffold can be a promising candidate as it was able to create micropore as interconnected pore within the pore wall. Thus, it was suggested to continue investigating the effect of salt composition between the scaffold 100C and 75C25H.

TGA characterization was performed to monitor the weight loss of the material due to the formation of volatile compound under degradation owing to the heating and temperature rising. Fig. 2 presents the

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**Fig. 1** FESEM images of the composite scaffolds, (a) 100C, (b) 75C25H, (c) 50C50H, (d) 25C75H, and (e) 100H
degradation profile of PU-BG scaffold with different composition of NaCl and NaHCO₃. Based on Fig. 2, around temperature 76 until 106 °C, all scaffolds except 100C start to degrade due to the decomposition of NaHCO₃ into Na₂CO₃, water and carbon dioxide. Second step degradation was around 130 until 170 °C which can be attributed to the completion degradation of NaHCO₃ into Na₂CO₃ mostly occur around 200 °C. Eq. 1 shows the reaction of NaHCO₃ into Na₂CO₃, water and carbon dioxide [17]. Another degradation step befalls around temperature 240 to 480 °C which is due to the degradation of urethane bond of PU. This can conclude that, excess leaching agent entrapped in the scaffold did not alter the properties of the PU.

\[
2 \text{NaHCO}_3(s) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g) + \text{Na}_2\text{CO}_3(s)
\]  

(1)

The excess of NaHCO₃ entrapped in the scaffold had been proved by the EDX result in Fig. 3. The amount of sodium (Na) contain in the sample 100H is much higher (12.68 wt.%) as compared to sample with 100C (0.80 wt.%). High percentage of Na in 100H scaffold indicates the presence of NaHCO₃ which did not fully leached out during the immersion in deionized water. This finding suggested the difficulty to leached out NaHCO₃ as NaHCO₃ had lower water solubility which is only 96 g/L as compared to NaCl with 358 g/L (according to SDS provided by Merck Milipore).
Fig. 3 FESEM images and EDX analysis for scaffold (a) 100H and (b) 100C

Fig. 4 represents the storage modulus for PU-BG scaffold at 27 °C and 37 °C. Such temperatures were selected to investigate the behavior of the samples at room temperature and human body temperature since the application is related to bone tissue engineering. According to Fig. 4, the data showed scaffold 100H exhibits the highest storage modulus compared with others scaffold which do not show a significant difference in storage modulus. Due to the smaller particles size of NaHCO₃, micropores were formed in the 100H scaffold resulted with higher density scaffold. In addition, the presence of leaching agent NaHCO₃ that had not been completely leached out during immersion in deionized might act as filler and improved the storage modulus of the PU-BG scaffold. Scaffold 50C50H and 25C75H used NaHCO₃ leaching agent 50 and 75% respectively, however the value of storage modulus of 50C50H (14.5 kPa) is higher than 25C75H (9 kPa) suggesting that the formation of more homogeneous foam structure in scaffold 50C50H had allowed for higher resulting storage modulus of the scaffold. Other study also demonstrated storage modulus of PU scaffold within the similar range with the obtained result [18].
Fig. 4 Storage modulus of PU-BG scaffold with different composition of leaching agent

3. SUMMARY

In this study, porous Bioglass® (BG) reinforced Polyurethane (PU) scaffolds were fabricated using salt leaching technique with different composition of NaCl and NaHCO₃ as leaching agents. It was found that, the composition of leaching agent gives a profound impact on the scaffold morphology and mechanical properties. As the composition of NaHCO₃ increased, pore formation changed drastically with irregular shape of pore formed and smaller pore size. The 100C scaffold showed better morphology with a well-developed pore structure compared with others composite. However, 75C25H scaffold showed promising candidate as it was able to create micropore as interconnected pore within the pore wall. Thus, further study should be conducted to investigate the effect of salt composition within the range 100C and 75C25H. It was also found that, scaffolds with higher composition of NaCl aid to the leaching process as TGA analysis showed no traces of leaching agent left at the final product of scaffold. Storage modulus of the scaffold indicate that, scaffold using high percentage of NaHCO₃ composition possessed higher value of storage modulus resulted from the smaller pore size of the scaffold besides the entrapped leaching agent may act as filler that increased the storage modulus.

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Studies on Alkaline Pretreatment of Sugarcane Bagasse and Rice Straw Hydrolysis for the Recovery of Reducing Sugar

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ABSTRACT. Preliminary screening was performed to investigate the effects of different types of alkaline solution (2\%, w/v NaOH and Ca(OH)\textsubscript{2}) on total reducing sugar (TRS) recovery. The results showed that usage of Ca(OH)\textsubscript{2} yields higher TRS as compared to NaOH. Therefore, Ca(OH)\textsubscript{2} was chosen for further studies in this effort. One-Factor-A-Time (OFAT) approach was employed to determine possible optimum ranges of chosen independent variables (i.e., pre-treatment temperature, concentration of Ca(OH)\textsubscript{2} and reaction time). It is found that for both biomasses, rice straw gives the higher yield of TRS. The optimum temperature for rice straw and sugarcane bagasse are 70 °C and 80 °C, respectively. Increasing the concentration of Ca(OH)\textsubscript{2} and reaction time gives an overall negative effect on the yield of TRS.

Keywords: Alkaline pre-treatment, sugarcane bagasse, rice straw, acid hydrolysis;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Lignocellulosic materials such as sugarcane bagasse and rice straw are largely produced in tropical countries. These lignocellulosic materials are largely waste, and if these waste materials are fully utilized, 205 GL of bioethanol could be annually produced from fermentable sugar obtain through pre-treatment and hydrolysis, globally \[1\]. The main obstacle in hindering the advances of widespread uses of lignocellulosic biomass as primary renewable energy source is the recalcitrant natural characteristics of these materials. Lignocelluloses are made up of three primary compounds; cellulose, hemicellulose and lignin, along with several minor inorganic materials. The cellulose microfibrils which lead to its formation of crystalline structure enable cellulose to become highly resistant to enzymatic action in nature. The presence of lignin also serves as a protective barrier against the attack of enzyme or acid. In order to obtain fermentable sugar from lignocelluloses, the crystalline structure of cellulose needs to be disrupted to increase the accessibility of chemical or enzymatic attack on the cellulose structure [2]. Chemical pre-treatment involving alkaline hydrolysis is one of the most efficient treatments in reducing crystallinity of cellulose compared to other pre-treatment method [3]. It involves the use of bases such as sodium hydroxide, calcium hydroxide (lime), potassium hydroxide and ammonia to break the ester and glycosidic side chain resulting in structural...
changes in lignin. The mechanism is said to be saponification of intermolecular ester bonds cross-linked with hemicelluloses and lignin [4]. The present research work aims to determine the optimal conditions of alkaline pre-treatment for two types of biomass waste i.e., sugarcane bagasse and rice straw.

2. MATERIALS AND METHODS

2.1 Biomass preparation. Rice straw samples were obtained from a paddy farm locally in Padang Besar, Perlis. Samples were collected on March, 2015. Sugarcane bagasse samples were collected from a local stall in Perlis where the juices from sugarcane were pressed. Both samples were dried in the oven at temperature 80 °C.

2.2 Alkaline Pre-treatment. Alkali pre-treatment was conducted by weighing 5 g of each biomass. A 1:20 solid to liquid loading ratio was used for all the alkaline pre-treatment. Conical flasks containing samples and chosen alkaline solutions were placed in a water bath where constant temperature was maintained. Two alkaline reagents were used, NaOH and Ca(OH)₂ with various concentrations. The best alkaline treatment, in terms of producing high yield of TRS was chosen for further experiments. Table 1 shows the parameters investigated in the initial pre-treatment study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>60 °C, 70 °C, 80 °C, 90 °C, 100 °C</td>
</tr>
<tr>
<td>Alkaline concentration (w/v)</td>
<td>1%, 2%, 3%, 4%, 5%</td>
</tr>
<tr>
<td>Pre-treatment time (hours)</td>
<td>1, 2, 3, 4, 5</td>
</tr>
</tbody>
</table>

The pre-treated samples were separated from the pre-treatment solution by filtration. Samples were then washed extensively with distilled water to reduce the pH close to neutral (pH 7-8). Pre-treated solid residues were dried in an oven overnight at 80 °C before subjected to acid hydrolysis for sugar conversion. The difference in mass of sample before and after pre-treatment indicates the percentage of lignin removal.

2.3 Acid hydrolysis. Glucose conversion was achieved by subjecting the pre-treated samples to acid hydrolysis using 6% HNO₃ at 90 °C for 90 min. Filtration was done using filter paper to separate solid residues from liquid. Liquid separated underwent neutralisation by adding NaOH. The neutralised liquor was analysed for amount of total reducing sugar using DNS assay while the solid residues that had been washed until pH close to 7 were dried overnight in an oven until constant weight was achieved. All biomass and liquid samples were sealed and stored at 4 °C until further analysis.

2.4 Total reducing sugar determination. The neutralised liquor from acid hydrolysis was determined for their sugar content using DNS assay [5]. 2 mL of DNS reagent is added to 2 mL of liquor in the test tube. Mixture was heated for 15 min at temperature of 95 °C. After cooling to room temperature, mixture was
measured at wavelength of 540 nm using Shimadzu Scientific UV-1800 UV-vis spectrophotometer. Total reducing sugar concentration was then obtained from the standard glucose calibration curve.

2.5 Scanning electron microscopy (SEM). Morphologies of both samples, before and after pre-treatment, were observed using SEM (JEOL JSM-6460LA). Pre-treated rice straw and sugarcane bagasse were sputter-coated with platinum. Scanning electron images that were obtained were compared.

3. RESULTS AND DISCUSSION

3.1 Pre-treatment studies. SEM images were scrutinized to show the effect of pre-treatment on the structure and surface of samples. The surface structures of raw (before treatment) rice straw and sugarcane bagasse samples are seen in Table 2, images (a) and (b). Comparing those two images with images (c) and (d) together with (e) and (f), it is clearly shown that alkaline pre-treatment with NaOH and Ca(OH)$_2$, respectively, is effective. Significant morphological changes can be observed in comparison with the images of the samples of before and after pre-treated with both alkaline solutions. Under such comparison, it is hard to determine which pre-treatment solution is perhaps better. Thus, an analysis of the content of TRS in the pregnant alkaline solution is done.

Fig. 1 displays the yield of TRS for sugarcane bagasse and rice straw for both alkaline solutions. The results indicates that Ca(OH)$_2$ gives higher concentration of TRS in the pregnant solution than NaOH. This is especially true for sugarcane bagasse; a difference of nearly 2 g/L was observed if the two alkaline solutions were compared in terms of TRS concentration. Therefore, further studies of this work focuses on the usage of Ca(OH)$_2$ in pre-treatment, with relation to the effect of chosen operating conditions, i.e., temperature, Ca(OH)$_2$ concentration and reaction time.

Table 2 Morphology of raw material of sugarcane bagasse and rice straw, pre-treated with NaOH and pre-treated with Ca(OH)$_2$

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>Sugarcane bagasse</th>
<th>Rice straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without pre-treatment</td>
<td><img src="a" alt="Image" /></td>
<td><img src="b" alt="Image" /></td>
</tr>
</tbody>
</table>

Enche Ab Rahim et al., 2018
Fig. 1 Yield of total reducing sugar (TRS) with the effect of different alkaline solution choice with different biomass
3.2 Effect of temperature. Fig. 2 shows the overall TRS yield of sugarcane bagasse and rice straw with the effect of pre-treatment temperature. Generally, for both biomasses, TRS values initially increase along with pre-treatment temperature but then subsequently declined. This finding is agreeable with Idrees and co-researchers [6] and Sakdaronnarong et al. [7]. Mohd Shukri et al. [8], in their findings, mentioned that increase in pre-treatment temperature will cause increment in hemicellulose content; therefore, overheating at high temperatures of biomass burns the biomass surface. This result also was reported by Goh et al. [9], where in their findings, temperature did not significantly influence TRS recovery. In this study, it is observed that temperatures of 70 and 80 °C are perhaps optimum, for rice straw and sugarcane bagasse, respectively, to recover highest concentrations of TRS.

![Graph showing the effect of temperature on TRS yield](image)

**Fig. 2** Yield of total reducing sugar (TRS) with the effect of pre-treatment temperature for rice straw (RS) and sugarcane bagasse (SB)

3.3 Effect of Ca(OH)₂ concentration. The effect of Ca(OH)₂ concentration in the pre-treatment of both biomasses are shown in Fig. 3. For both samples, the concentration of TRS are seen rising with increasing Ca(OH)₂ concentration, up to 2% w/v. The increasing trend of TRS might be due to the lignin removal with the increased Ca(OH)₂ (alkaline) concentration from 1% v/w to 2v/w%. Rice straw was found to yield higher concentration of TRS. However, for both biomasses, the concentration of TRS started to drop when concentrations of Ca(OH)₂ increases above 2v/w%.
Fig. 3 Yield of total reducing sugar (TRS) with the effect of pre-treatment using different Ca(OH)$_2$ concentration for rice straw (RS) and sugarcane bagasse (SB)

3.4 Effect of reaction time. For both biomass samples in general, increasing the reaction time will increase the concentration of TRS. However, increasing the reaction time for more than 3 hours will give a negative effect on the recovery of TRS. This is because of longer reaction time might cause the initially exposed cellulose tends to be solubilized and degraded into furfural compounds. The presence of furfural and others inhibitors hinders the hydrolysis process to produce fermentable sugar [8].

Fig. 5 Effects of residence time on sugarcane bagasse and rice straw from 1-5 hours. Pre-treatment conditions: respective optimum temperature found (70 °C for rice straw-RS, 80 °C for sugarcane bagasse-SB) with optimum alkaline concentration of 2% Ca(OH)$_2$)
4. SUMMARY

In this study, pre-treatment of sugarcane bagasse and rice straw were commenced using two chosen alkaline solutions. The results obtained show that Ca(OH)$_2$ gives higher yield of TRS. Further studies using that Ca(OH)$_2$ for both biomasses, reveals that TRS concentrations increases with pre-treatment temperature but then subsequently declined above 70 °C (for rice straw) and 80 °C (for sugarcane bagasse). Increasing Ca(OH)$_2$ concentrations and reaction time in pre-treatment process will increase the yield of TRS until 2v/w% and 3 hours (optimum condition). Increasing the conditions above these values, results in reduced TRS yield.

REFERENCES


The Effect of Different Urea Composition on Production of Porous Stainless Steel type 316L through Powder Metallurgy Technique

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ABSTRACT. Recently, there has been renewed interest in fabrication of porous metals and metallic foams as biomedical implants. Metal foams have great properties such high stiffness, great mechanical strength and high energy absorption that cannot be obtained from ceramic and polymer foams. The present study aims to fabricate the porous stainless steel by using urea as space holder material through powder metallurgy technique. Stainless steel (SS316L) powders was used as metallic material were mixed with urea and polyethylene glycol (PEG) as binder using ball milling machine and then compacted at 8 tons. The composition of urea particles into the formulation are 45 wt.%, 50 wt.%, 55 wt.%, and 60 wt.%. The two-stages sintering process was performed which at the first stage, the temperature applied was 400 °C for 2 hours to remove the urea particle in the green compacts and the second temperature at 1100 °C for 2 hours to sinter the steel. The characterization of the samples after sintering process was carried out by performing density and porosity test and scanning electron microscopy (SEM) was conducted to identify the morphology characteristic. The findings show that, the sample with 40 wt.% of urea composition produced high density value of about 4.36 g/cm3. The sample with 60 wt.% of urea composition produced larger pores in their structure and obtained high porosities value of about 56.22%.

KEYWORDS: Cellular metals, Urea, Space-holder technique, Sintering;

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1. INTRODUCTION

The combination properties of metals which are tough and thermally and electrically conductive and porous which synonym to lightweight behaviour will produce the unique characteristics of porous metals [1,3]. Porous metals can be classified into closed-cell and open-cell foams. In closed-cell foams, the pores was separated by a metal thin wall, whilst in open-cell foams the pores was interconnected in each metallic strut frames [3,4]. Porous metals have gained the attention from researchers due to their interesting properties such low densities, high bending strength, thermal and electrical conductivity and great acoustic properties [5]. Porous metals are well known as lightweight structures that usually applied in aerospace and automotive industries, as functional application such filters, electrode, catalyst, as well as dental and orthopaedic devices in biomedical application [6]. Porous metals with adjustable density, high porosity and excellent combination of properties have great potential for biomedical application as bone implant. However, there is major challenging concerning porous metals as bone implant. Mismatch of Young's moduli between implant and the surrounding bone lead to implant loosening and may cause stress shielding of bone [6]. In order to overcome these problems, it is important to form highly porous implants which can provide better biological fixation and enhanced bone in growth into the pores network of the implants [7].

Numerous research has been successfully used metals as bio implant for many years and cobalt-chrome based alloys and stainless steel are the first metals that successfully used in orthopaedic application during the twentieth century [8]. Stainless steel in one of the principal metals that usually choose for structural application such as orthopaedic implants and shoulder due to properties like ability to bear significant loads, high fracture toughness, biocompatibility and high corrosion resistance [3,10].
Numerous fabrication methods have been studied in order to produce and develop porous metals efficiently. Solid state methods via powder metallurgy technique based on space holder method are the most promising method for manufacturing porous metals. The advantage of this technique is the process variables can be easily control, the pore size and the structures can be designed, and the fabrication process can be performed at lower temperature thereby decrease the severe chemical reactions [10]. By performing this technique, the shape, size and volume fraction of porosity can be controlled which the range of porosity in about 60-80% can be formed. The space holder method starts by mixing the metallic powder along with space holder materials and binder homogenously. Then, the mixtures were compacted using uniaxial pressing machine and the resulting product called as green compact. Heat treatment was apply to the green compact at relatively low temperature in order to remove the space holder material from the compact, and the next stage the compact is sintered at high temperature [11].

This study set out to produce the porous stainless steel type 316L foams by using compaction method with different composition of urea particles as space holder materials. The green compact was sintered in two-stages sintering process using tube furnace under high purity Argon atmosphere. The characterization of the sintered porous SS316L was analyzed by performing density and porosity testing and the morphology analysis of the foams was evaluated by using SEM apparatus. The influence of the composition of urea on the formation of stainless steel foam and the pore distribution was studied.

2. MATERIALS AND METHODS

The sintered powder compacts were prepared using stainless steel type 316L powder with the particle size of 7.157 µm (D50) purchased from Maju Scientific Sdn. Bhd. The spherical SS316L powders with the composition of 40, 45, 50, 55, and 60 wt.% was mixed with urea with the particle size of 200 µm and 1 wt.% of PEG by using ball milling machine at 60 rpm for about 15 min. The samples of 14 mm diameter and 26 mm thickness in size were compacted in cylindrical die by using Carver pressing machine at a pressure of 8 tons. Urea particles was removed in a tube furnace at a temperature of 400 °C for 2 hours and then was sintered at temperature of 1100 °C for 2 hours with heating and cooling rate of 2 °C/min in high purity of argon (Ar) atmosphere with flow rate was maintained at 51 ml/min. The physical properties of the samples was analyzed by performing density and porosity test by applying Archimedes' principle and morphology analysis was analyzed by using JEOL scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

The microstructural analysis was conducted to determine the pore size and strut produced. The pores and struts inside the porous structure of porous SS316L for 60, 55, 50, 45, and 40 wt.% of the urea samples were observed by SEM. The sizes of the pores are in the range 169.99 µm to 198.90 µm and can be categorized as large size pores (50-400 µm) [8,9]. Fig. 1 shows an overview of pores and slag generated from the samples of all compositions with the sintering temperatures of 1100 °C for the sintered samples performed in argon environment by using the tube furnace. All samples have clearly produced pores and struts.

Fig. 1 (a) presents the sample with 60 wt.% of urea content has open pores and well-developed of struts but the surface was too rough. This may be due to the amount of the space holder was too excessive than SS316L powder, causing it to become unable to coat the grain particle of space holder effectively. In fact, it is very tough to control the process in different metal and space holder powders [14].

In addition, it is difficult to control the cell size and its distribution practically especially for micro porous metal [15]. As shown in Fig. 1. (c,d), for 55 wt.% of urea content, non-uniform pore distribution was formed on the sample structure. This is caused by the irregular shape and non-uniform size of the space holder particles [12]. As shown in Fig. 1 (e,f), the pore distribution of the sample with 50 wt.% of urea content can be categorized as clustered and the cluster pores are apart from each other. Fig. 1 (g,h) displays the SEM image for stainless steel foam with composition of 45 wt.% of urea content. It can be seen from the Fig. 1 (h) the
formation of large pore is less likely to occur and small pores was formed in the sample structures. It is possible that the decreasing the composition of urea into the formulation may reduce the formation of large pores. Fig. 1 (i,j) displays the structure of the sample with 40 wt.% of urea content. The closed pores were generated and a thicker structure of struts increased comparing to other compositions. It is proven by the average of the bulk density in this composition is higher compared to other. The details of bulk density of the samples are as shown in Fig. 2.

Fig. 2 presents the graph of sintered density and apparent porosity versus compositions of SS316L powders. The highest density value at the sample with 40 wt.% of urea content was recorded. The result shows that the sintered density of the porous SS316L increase with the decreasing of composition of urea content due to the less formation of pores and lead to the densification occurred during the sintering process. These results is consistent with data obtained in previous research that stated that sintered density increase with the decreasing of urea content added up to the samples formulation [16].

In contrast, the porosity of the samples is decreased with increasing of SS316L powders into the formulations. The highest apparent porosity value at the sample with 40 wt.% of stainless steel powder was observed. The increasing amount of urea influence the apparent porosity of the samples [11]. The formation of larger pores due to the urea particles accumulated in one area and fully burnt off during the first stage of sintering process. This happens because the accumulated urea particles breaking the necks grow between particle contacts of stainless steel particles to form the larger size of pores thus increase the apparent porosity of the foams [11].

**Fig. 1** Comparative SEM image for porous SS316L at composition of (a, b) 60 wt.%, (c, d) 55 wt.%, (e, f) 50 wt.%, (g, h) 45 wt.% and (i, j) 40 wt.% of urea content.
4. SUMMARY

Porous SS316L is successfully fabricated via space-holder technique and urea was used as a space holder material. Porous SS316L with 40 wt.% composition recorded the highest sintered density value of 4.36 g/cm$^3$ due to the decreasing of urea content into the formulation and allow densification occur between stainless steel particles. In contrast, porous SS316L with 60 wt.% of urea content produce highest apparent porosity of 56.22% compared to other compositions due to the highest amount of space holder into the formulation. It can be seen that the morphology of stainless steel foam with composition of 60 wt.% also forms larger pores with the struts clearly formed in the foams structures which is encouraging the cell in growth between the implant and the bones and thus have potential to be applied in biomedical application.

ACKNOWLEDGEMENT

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REFERENCES


Comparison Thermal and Hardness of CaO-MgO-Al₂O₃-SiO₂-B₂O₅ Glass from Different Sources of Kaolin Minerals as Main Raw Mineral

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ABSTRACT. In this paper, all the raw materials used to synthesis glass specimen has been characterized to obtained elemental composition. In this work, silica, dolomite, colemanite, limestone, and 2 different sources of kaolin were characterize using XRF to obtain elemental composition analysis. The composition of each raw materials were calculated and synthesis glass specimen by XRF result. Different sources of raw materials have different chemical composition. Two sources of kaolin were obtained from Kota Tinggi Johor, Malaysia (LK) and China (KC) as raw minerals and having different chemical composition, thus it is important to modification and recalculation of composition after XRF result obtained in order to meet the standard specification of glass. The element composition in different kaolin minerals contain different impurities or traces thus promote different properties. Synthesized glass specimen was subjected to thermal analysis and hardness testing and found that the glass samples with kaolin china as raw mineral (glass KC) having same trend of DTA results and having higher weight loss compare to glass using local kaolin as raw mineral (glass LK). Furthermore, the hardness of glass KC is higher than glass LK because present of TiO₂.

Keywords: Glass, X-ray fluorescence, Thermal analysis, Vickers hardness;

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1. INTRODUCTION

Many industries synthesis glass by using KC as main mineral because of consistence composition as well as dolomite, colemanite, limestone and silica. Ronget al. [1] and Memon et al. [2] investigated KC have consistence of SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, K₂O, TiO₂ and P₂O₅ compound. The consistency of chemical composition in China caused most of the industry in Malaysia imported kaolin from China as raw material for many kind of product such as glass fiber grade, sheet glass, tiles and etc. Ceramics from China dominated the trade of ceramic findings in Malaysia. The use of LK as main mineral would result in reducing transportation cost and increase job opportunities thus increase the profit of glass industries in Malaysia. The main oxide for glass specimen predominantly contain oxides of boron, sodium, calcium, aluminium and silicon. Minerals that generally used in production of glass and ceramic product are kaolin, dolomite, colemanite, limestone and silica. Minerals from different sources contained different in oxide composition due to its impurities [3]. In order to synthesis glass specimen and meet the standard specification of glass, characterization of all minerals were carried out by XRF for composition determination. After composition determination, recalculated and modification of oxide composition of all the minerals to synthesis glass specimen. In this research, we emphasized the analysis of the differences in thermal behaviour and hardness of synthesized glasses. Thermal behaviour and hardness of both glasses were characterized using DTA/TG and Vickers hardness test.

2. MATERIALS AND METHODS

The starting raw minerals for glass specimen were silica, dolomite, colemanite, limestone, and 2 different sources of kaolin ((i) KC and (ii) LK). All the raw materials were supplied by Nippon Electric Glass. The glass
was produced based on standard chemical specification of glass. The composition of the raw materials used was recalculated and modified based on the standard specification of the glass specimen from the industries. Element composition of each minerals were analysis by XRF in order to obtain elemental results. All raw minerals were analysed by X-ray Fluorescence Spectrometers (XRF): Benchtop EDXRF Spectrometer, Qualitaxto obtain elemental composition. The weight percent of minerals powder used in this present work were based on the standard specification of glass. After obtaining the weight of each minerals, all minerals were mixed together.

Wet milling method was used to mix the raw powders. Alumina ball was used to mix the powder homogeneously at 350 rpm for 8 hours and dried at 100°C overnight. The homogenized mixture of raw minerals was melted in alumina crucibles at 1400 °C for 4 hours. The molten glass was quenched in water immediately to form glass LK and glass KC. Glass frit was characterized to compare the thermal behaviour and hardness by using Vickers hardness test. A square base pyramid shaped diamond is used as indicator in this method. Test load used was 49.03N and dwell time was set for 10 s. Sample was place perpendicular to the indicator and test started. The test was done five times to get a correct reading by its average hardness value.

3. RESULTS AND DISCUSSION

3.1 Elemental analysis

Elemental composition of all raw materials which were measured by XRF was tabulated in Table 1. LK contains 47.4% of SiO₂ and 36.8% of Al₂O₃. Others oxide that were present in LK is Fe₂O₃ (0.50%), TiO₂ (0.50%), CaO (0.01%), MgO (0.10%), K₂O (2.00%) and P₂O₅ (0%). Amount of LOI of LK is 12.55% due to the evaporation of water content. Chemical composition of KC contain SiO₂ and Al₂O₃ are 43.0% and 36.2%. The main impurities that present in KC such as Fe₂O₃ (0.59%), TiO₂ (1.02%), CaO (1.90%), MgO (0.54%), K₂O (0.18%) and P₂O₅ (0.06%). Others compound as traces that contain % in KC. KC also has 16.13% of LOI. Traces contain in KC is higher than LK. The different impurities contain in KC and LK give different properties to the synthesized glass. The elemental analysis was done to confirm each of the raw materials with its chemical composition for modification and recalculating the weight percent needed to produce glass specimen.

3.2 Thermal Analysis

Thermogravimetric analysis was used in the thermal analysis of synthesized glass. Fig. 1 demonstrated the DTA curve for glass LK and glass KC. The two curve is the same in trend. There are an exothermic peak for both glass at temperature about 300°C that can explain with the oxidation occur inside the glass samples. When temperature reach 1100°C, there are another peak occur that is endothermic slope. The endothermic peak demonstrated the glass melting at the temperature 1100°C. Although excess of CaO and MgO in KC as fluxes will promote to a lower melting point but in DTA curve of glass KC does not shift the endothermic peak to lower temperature but showed same thermal behaviour.

Fig. 2 shows the TGA curves of glass samples after synthesized using different raw minerals which are LK and KC. The weight gain of glass sample using KC is known as glass KC is about 0.07mg from total weight of 10.39mg, less than 0.1wt.% at room temperature until about 400°C. Attila investigated that is likely due to the oxidation reaction occur in molten glass [4]. There is a weight loss of about 0.03mg from its original weight starting at temperature about 1200°C. A similar behaviour is seen in the TGA curve of glass sample using LK (glass LK). The weight gain is increase moderately until 0.06mg from room temperature and stop at about 1200°C and undergo a weight loss of 0.02mg from its original weight of about 0.02wt.% until 1400°C. The total weight loss for both are match to the result of TGA individual for KC and LK.
Table 1 Chemical compositions of KC and LK (wt.%)

<table>
<thead>
<tr>
<th>Compound</th>
<th>KC</th>
<th>LK</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>43.0</td>
<td>47.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>36.2</td>
<td>36.8</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.59</td>
<td>0.50</td>
</tr>
<tr>
<td>MgO</td>
<td>0.54</td>
<td>0.10</td>
</tr>
<tr>
<td>CaO</td>
<td>1.90</td>
<td>0.01</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.18</td>
<td>2.00</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.02</td>
<td>0.51</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>Traces</td>
<td>0.38</td>
<td>0.13</td>
</tr>
<tr>
<td>LOI</td>
<td>16.13</td>
<td>12.55</td>
</tr>
</tbody>
</table>

Fig. 1 DTA curve for glass LK and glass KC

Fig. 2 TGA results for glass samples synthesized by different raw minerals, glass LK and glass KC.
3.3 **Vickers Hardness Analysis.**

Vickers hardness analysis has been done on two types of glass fiber grade specimen using 2 different kaolin sources. The applied load used was 49.03N. The hardness value obtained were shown in Fig. 3 boxplot and tabulated in Table 4.8. Fig. 3 shows that the hardness of the glass LK and glass KC. The hardness of glass KC is higher than glass LK. The average hardness of glass KC is 704.6HV and the glass LK is 665.6HV.

![Fig. 3 Vickers hardness results for glass KC and glass LK](image)

The higher value of hardness is due to the excess impurities content in the raw materials. XRF result demonstrated in the kaolin china content of excess TiO\textsubscript{2}, NiO\textsubscript{2}, ZrO\textsubscript{2}, and CuO that promote excess hardness to the fiber glass grade specimen. Beside that the alkalis such as Na\textsubscript{2}O, K\textsubscript{2}O and Li\textsubscript{2}O in glass composition will decrease the hardness of glass [5]. Result from XRF can proved that the traces in the glass LK content excess alkalis such as potassium oxide K\textsubscript{2}O that showed 0.78wt.% compare to glass KC that contained only 0.09wt.%.

The higher percentage of K\textsubscript{2}O in glass give a lower hardness and it is matched with the result of Vickers hardness test.

**Table 2 Vickers hardness of two different types of fiber glass**

<table>
<thead>
<tr>
<th>Vickers hardness reading (HV)</th>
<th>Glass KC</th>
<th>Glass LK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reading 1</td>
<td>635.9</td>
<td>677.3</td>
</tr>
<tr>
<td>Reading 2</td>
<td>691.4</td>
<td>668.9</td>
</tr>
<tr>
<td>Reading 3</td>
<td>687.3</td>
<td>643.9</td>
</tr>
<tr>
<td>Reading 4</td>
<td>730.7</td>
<td>658.1</td>
</tr>
<tr>
<td>Reading 5</td>
<td>777.5</td>
<td>680.2</td>
</tr>
<tr>
<td>Average</td>
<td>704.6</td>
<td>665.6</td>
</tr>
</tbody>
</table>

4. **SUMMARY**

From the comparison of glass KC and glass LK, it can be conclude that the glass KC have the same trend on thermal behaviour and only small weight loss of 0.02mg of glass KC compare to glass LK. For the present
of TiO$_2$ compound in KC, the glass KC having higher hardness compared to glass LK. Thus, this present study substitution of LK to synthesis glass is in same thermal properties but lower in hardness.

REFERENCES


Degradation of Methyl Orange Using N-TiO$_2$ Synthesized via Hydrothermal Treatment

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**ABSTRACT** In this work, urea (0.1 to 1.7 wt.%) is incorporated with TiO$_2$ using hydrothermal treatment for 3 hours at temperatures of 180°C. The influence of urea content on the crystalline TiO$_2$ and their photocatalytic activity are investigated. The samples are characterized by using X-ray diffraction (XRD), energy dispersive X-ray (EDX), field emission scanning electron microscope (FESEM) and UV-Visible spectroscopy (UV-Vis). XRD results indicate that all samples are anatase phase while FESEM images shows agglomeration with average grain size approximately of 30 to 46 nm. The photocatalytic activity shows that TiO$_2$ with 0.5 wt.% of urea give the highest performance with 67% degradation after 4 hours visible light irradiation.

**Keywords:** TiO$_2$, Hydrothermal, Photocatalytic activity, Methyl orange;

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1. INTRODUCTION

One of the biggest issues in the world nowadays is air pollution. The polluted air can contribute to the unhealthy environment resulting to chronic diseases such as heart disease, lung cancer, and both chronic and acute respiratory diseases, including asthma [1,2]. World health organization(WHO) reported that 92% of the world population was living in places where the WHO air quality guidelines levels were not met. Ambient (outdoor air pollution) in both cities and rural areas was estimated to cause 3 million premature deaths worldwide in 2012 [3]. In order to address this issue, many researches have been conducted such as the used of ozonation [4], bio-monitoring [5] advanced oxidation process (AOP) and others. Among these, AOP is an environmental friendly technology for air purification as it can degrade and recalcitrant organic compounds into harmless materials. AOPs are based on the production of highly reactive and oxidizing hydroxyl radical (·OH) with a potential oxidation of 2.85V [6]. Photocatalysis is one of AOP technology that are widely used to detoxify organic pollutants in air and water [7-9]. The complex organic compounds can be break down by the generation of potent oxidation radicals such as ·OH and O$_2$· [10].

TiO$_2$ is widely used as photocatalyst as it has the highest stability, high ultraviolet absorption, commercial availability and cheap. Furthermore, TiO$_2$ has high photoactivity and very suitable to use for removing pollutants in water and air. Despite the promising properties, TiO$_2$ application is limited to the UV region which only 4% of the entire solar system whereas 45% of the solar energy corresponds to the visible light. More practical application can be possible if the photocatalytic active region can be expanded to the visible...
light region (400-700 nm), and the photoenergy can be used more efficiently. TiO$_2$ doped with metal and nonmetal element within certain limits can prolong the lifetime charge carriers of TiO$_2$ and change the optical properties towards visible light region [11-13]. In general, the TiO$_2$ doped showed higher photocatalytic activities compared than the pure ones.

In this work, we introduces a novel ceramic processing technology for the preparation of photocatalytic materials. The process involves the use of urea with various content (0.1 to 1.7 wt.%) incorporated with TiO$_2$ via hydrothermal treatment to obtain a nanostructure product. In addition, this paper describes the characteristic of N-TiO$_2$ and their performance as photocatalysts to degrade methyl orange dye compound under visible irradiation.

2. MATERIALS AND METHODS

The N-TiO$_2$ was synthesized using a modification procedure in previous study [14]. A determined urea mass was dissolved in water and stirred until complete dissolution. Titanium isopropoxide was dissolved in isopropanol alcohol and distilled water to obtain a 1 M solution. A determined volume of urea solution was drop wise added to the mixture under vigorous stirring and subsequently followed by hydrothermal treatment for 3 hours at temperatures of 180°C. The obtained solid was separated and dried at 80°C overnight. TiO$_2$ without nitrogen was also synthesized by the same procedure without the presence of urea to produce the hydrolysis of the alkoxide. The X-ray diffraction (XRD) measurements were performed using Bruker D8 Advance with CuKα as the X-ray source. The crystallite sizes of samples were calculated using Debye-Scherrer equation with correction for instrumental line broadening. The morphologies of the samples were observed by using high resolution field emission environmental scanning electron microscope (FESEM, JSM-7600F). The optical properties of samples were measured on a Shimadzu UV-VIS spectrometer (UV-1800) in the wavelength of 300-800 nm.

The photocatalytic activity of as-prepared N-TiO$_2$ were evaluated by degradation of methyl orange (MO) under visible light. A metal halogen lamp was used as light source and a UV-filter was employed to eliminate spectral range radiation below 400 nm. 5 mg of the as-prepared sample were dispersed and stirred in 10 ppm MO in the dark. After that, the solutions were irradiated up to 4 hours and the aliquot samples were collected in every one hour interval time. The concentration of degraded MO was measured by means of its corresponding to absorption intensity.

3. RESULTS AND DISCUSSION

The phase structure and purity of the as-prepared samples are determined by using XRD. Fig. 1 shows the XRD patterns of TiO$_2$ and N-TiO$_2$ synthesized via hydrothermal treatment. From Fig. 1, all the peak at an angle 2θ (20 <2θ <90) are anatase phase, corresponding to no. JCPDS: 00-021-1272. The peaks are located at 25.3°, 37.8°, 48.1°, 53.9°, 55.1°, 62.7°, and 68.8°, corresponding to the plane (101), (004), (200), (105), (211), (204), (116), and (220), respectively. The size of the crystallites are summarized in Table 1 and calculated by using Debye-Scherrer equation as shown in Eq.1.

\[ d = \frac{\lambda}{\beta \cos \theta} \]  

Where d is the crystallite size, θ is the Bragg angle, β is the diffraction peak width at half of the maximum intensity, λ is the X-ray wavelength which is 0.15406 nm and k represents as constant form factor which is 0.89. It is found that the crystallite size of TiO$_2$ was decreased from 25.3 nm to 8.5 nm. The crystallite size was decreased due to the incorporation of N with TiO$_2$ which is an agreement with other result in previous study [15]. Furthermore, the ionic radius of N$^-$ (0.171nm) is close to that of O$^2-$ (0.144nm), so N$^-$ can be incorporated into the TiO$_2$ lattice by substitution of O$^2-$.
Fig. 1 XRD pattern for sample (a) 0.1 wt.% N-TiO₂, (b) 0.5 wt.% N-TiO₂, (c) 0.9 wt.% N-TiO₂, (d) 1.3 wt.% N-TiO₂, (e) 1.7 wt.% N-TiO₂ and (f) pure TiO₂

Table 1 Crystallite size pure TiO₂, 0.1 wt.%, 0.5 wt.%, 0.9 wt.%, 1.3 wt.%, and 1.7 wt.% N-TiO₂

<table>
<thead>
<tr>
<th>Samples</th>
<th>Urea content (wt.%)</th>
<th>Crystallite size (nm)</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO₂</td>
<td>0</td>
<td>25.3</td>
<td>Anatase</td>
</tr>
<tr>
<td>0.1 wt.% N-TiO₂</td>
<td>0.1</td>
<td>10.0</td>
<td>Anatase</td>
</tr>
<tr>
<td>0.5 wt.% N-TiO₂</td>
<td>0.5</td>
<td>11.4</td>
<td>Anatase</td>
</tr>
<tr>
<td>0.9 wt.% N-TiO₂</td>
<td>0.9</td>
<td>8.5</td>
<td>Anatase</td>
</tr>
<tr>
<td>1.3 wt.% N-TiO₂</td>
<td>1.3</td>
<td>15.5</td>
<td>Anatase</td>
</tr>
<tr>
<td>1.7 wt.% N-TiO₂</td>
<td>1.7</td>
<td>14.3</td>
<td>Anatase</td>
</tr>
</tbody>
</table>

The morphology and size of the synthesized products are observed using FESEM. Fig. 2 shows the images of the synthesized samples prepared with various urea content. All samples are found to be agglomerated with grain size estimated from 32 to 46 nm. The agglomeration may due to several reasons such as the presence of capillary absorption, solid bridge, Van der Waals and hydrogen bond [16].

The photocatalytic performance of the as-prepared N-TiO₂ photocatalyst can be evaluated by degradation of MO solution under visible light irradiation. To achieve the adsorption equilibrium, the solution including MO and photocatalyst was stirred in dark for 30 min without light irradiation. Fig. 3 shows the result.
obtained after the photocatalytic activity conducted under visible light for 4 hours irradiation time. The photocatalytic activity was evaluated using the following (Eq. 2):

\[
MO \text{ Degradation} \% = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]  

(2)

![Fig.2 Grain size of (a) pure TiO$_2$ (b) 0.1 wt.% (c) 0.5 wt.% (d) 0.9 wt.% (e) 1.3 wt.% and (f) 1.7 wt.% N-TiO$_2$](image)

![Fig. 3 MO degradation under visible light irradiation](image)
Where $C_0$ is the original concentration of methyl orange and $C$ is the concentration of methyl orange after irradiation. Based from Fig 3, it is found that the performance of photocatalytic activity from high to low is as follows: %, 0.5 wt.% N-TiO$_2$ > 0.1 wt.% N-TiO$_2$ > pure TiO$_2$ > 0.9 wt.% N-TiO$_2$ > 1.3 wt.% N-TiO$_2$ > 1.7 wt.% N-TiO$_2$. The highest photocatalytic activity is sample with 0.5 wt.% urea (67%) which is three times higher than 1.7 wt.% urea (21%). It is believe that the optimum amount of N in TiO$_2$ has reached the optimal value at 0.5 wt.% urea. In addition, the decreased of crystallite size may result to the increment of photocatalyst surface area. It is well known that materials with larger surface area can absorb more organic pollutants on their surface, leading to more reaction with electrons in photocatalytic process. It also resulted in higher efficiency in the photocatalytic activity. In another study, Kalantari et al. [15] suggested that the average transfer time of photocatalyst can be reduced by reducing the crystallite size N-TiO$_2$. Accordingly, there combination rate of photogenerated electron-hole pairs for N-TiO$_2$ is reduced and its photocatalytic activity increases.

4. SUMMARY

N-TiO$_2$ was successfully synthesized via hydrothermal treatment at 180 °C. It is found that the morphology, structural, optical property of the synthesized materials influence on the photocatalytic activity. The structural and morphological analysis showed that all samples have anatase framework and agglomerated. It is revealed that the photocatalytic activity of N-TiO$_2$ is greater compared to pure TiO$_2$ under visible light irradiation. The highest performance was contributed by 0.5 wt.% urea incorporation with TiO$_2$. Based on the results, N-TiO$_2$ can be regarded as an efficient visible-response photocatalyst which have a great significance in environmental purification including for air and wastewater treatment.

REFERENCES


Deposition of TiO$_2$ on Macroporous Cordierite Substrate for Wastewater Treatment

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ABSTRACT. In this paper, the titanium dioxide (TiO$_2$) which act as the photocatalyst was synthesized and deposited on macroporous cordierite (MC) (carrier substrate) by using sol-gel and dip-coating method. The TiO$_2$/MC in this study were characterized by XRD, SEM, densitometer and UV-Vis spectrometer. The effect of calcination temperature at 700 °C, dipping cycles of TiO$_2$/MC and UV light irradiation on photodegradation of organic pollutant (methyl orange (MO)) were studied. The results showed that TiO$_2$/MC with 5 cycles of dipping parameter have the highest removal efficiency after 7 hours while without drop-off present in wastewater treatment process. Conversely, further increasing the dipping cycles at 7 reduced the photocatalytic activity. Under UV light irradiation, all samples have been photo-activated to decolorized MO except sample MC which do not have photocatalyst.

Keywords: Titanium dioxide, Photocatalyst, Sol-gel method, Dip-coating method, Cordierite;

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1. INTRODUCTION

Nowadays, the rate of environment pollutants is increasing sharply. Water pollution is one of the main concern of human health. Azo dyes, one type of the most concerned contaminants in refractory wastewater treatment due to carcinogenic and mutagenic properties. Moreover, the azo bonds (-N=N-) in the dye are difficult to be removed as they are adherent and long lasting. Heterogeneous photocatalysis, a classification from photocatalysis is belonged to advanced oxidation processes (AOPs) which works at near-ambient temperature and pressure. Powerful oxidizing radical species such as •OH were produced through AOPs for complete decomposition of organic contaminants into non-toxic products like H$_2$O, CO$_2$ and inorganic salts [1,2]. Photocatalyst materials such as titanium dioxide (TiO$_2$) can be a good candidate in photocatalytic activity due to its strong oxidizing power of its holes, high photostability and redox selectivity [3,4]. However, conventional TiO$_2$ powder gives disadvantages of agglomeration and difficulty to separate between final particles and fluid for the catalyst recycling [5]. In addition, the small size of titania particles would make photocatalytic slurry reactors impractical and caused the difficulty in separation stage such as filtration [6]. There are a few types of carriers or catalyst supports such as alumina (Al$_2$O$_3$) and zirconia (ZrO$_2$) which used for water treatment process. Cordierite ceramics (2MgO-2Al$_2$O$_3$-5SiO$_2$) have been found to be alternative catalyst support due to high mechanical strength, good thermal stability and low thermal expansion coefficient [7,8]. In addition, it has lower sintering temperature than Al$_2$O$_3$ which give advantages of reducing processing time and cost. In order to accelerate the degradation reaction, porous ceramic cordierite is promoted due to its higher photocatalytic surface area. Furthermore, good performance in higher contact area with fluid required high fraction of open porosity. In this study, the deposition of high amount of photocatalyst TiO$_2$ on macroporous cordierite were prepared by sol-gel method and it was further deposited by dip-coating method.

2. MATERIALS AND METHODS

Titanium (IV) isopropoxide (purity: >98%) and MO were purchased from ACROS as a precursor in the synthesis of TiO$_2$ and dye in this study. Acetic acid (purity: 99.8%), absolute ethanol (purity: 95%) and deionized water were used to prepare the TiO$_2$ sol. Hydrochloric acid (Fisher Scientific) and deionized water
used to pre-wash substrate. Macroporous cordierite (MC) (96.4 wt.% α-cordierite) was used as a photocatalyst support in this study.

2.1 Synthesis of TiO\textsubscript{2} and Deposition Method

In this study, TiO\textsubscript{2} sol was prepared by sol-gel method with volume ratio of Ti(OC\textsubscript{3}H\textsubscript{7})\textsubscript{4}:H\textsubscript{2}O:C\textsubscript{2}H\textsubscript{5}OH:CH\textsubscript{3}COOH is 1:2:1:0.53. The TiO\textsubscript{2} sol was stirred vigorously at 80 °C for 30 min followed by aging process for 3 hours. Then, the MC samples were pre-washed with HCl and H\textsubscript{2}O with ratio 1:25 and dried in hot oven at 70 °C for 10 min. Sample C0 was prepared in the absent of TiO\textsubscript{2} while sample C1, C2, C3 and C4 of TiO\textsubscript{2}/MC were prepared by the dip-coating method in different dipping cycles of 1, 3, 5 and 7 respectively. Each dipping cycle process was carried out by dipping cordierite in TiO\textsubscript{2} sol for 3 min then dried in a hot oven at 70 °C for 10 min. After that, the TiO\textsubscript{2}/MC samples were calcined at 700 °C for 4 hours.

2.2 Materials Characterization

The samples were analyzed with X-ray diffractometer (XRD) model D/max-III, Rigaku using Cu-K\textalpha radiation in the range of 2θ = 5-80° at a scan speed of 2°/min and step size of 0.02°. Rietveld refinement was performed by Xpert HighScore Plus software. The sample’s morphologies were observed by scanning electron microscopy (SEM) from JEOL (Model: JSM 6460 LA). Auto fine coated from JEOL (Model: JFC 1600) was used to coat the surface of the samples with a thin platinum layer. The conductive layer formed coating process is required to improve the imaging of the samples and reduce thermal damage. Bulk density and total porosity of TiO\textsubscript{2}/MC were measured by densitometer.

2.3 Experiments of Photocatalytic Degradation of MO Dye

In this study, 10 ppm of MO dye solution with pH 7.5 was used for photodegradation. Samples TiO\textsubscript{2}/MC are prepared in dimension of 1.5 cm × 1.5 cm × 1.5 cm and 8 pieces in each dipping parameter. Set of different dipping parameter cordierites was immersed into a beaker which contains 200 ml of MO solution and placed under UV light. The 5 ml of dye solution was sampled every hour and analyzed by UV-Vis spectrometer (Perkin Elmer Lambda 35). The absorption and reduction in wavelength were evaluated according to the absorbance at a maximum wavelength of 465 nm. The removal efficiency was measured by Eq. 1.

\[
\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\%
\]

Where \(C_t\) is the final concentration at reaction time (t) in hours and \(C_0\) is the initial concentration.

3. RESULTS AND DISCUSSION

Fig. 1 demonstrates the XRD pattern of TiO\textsubscript{2}/MC. It has shown that the cordierite ceramic with the present of anatase and a small fraction of rutile phase which indicates TiO\textsubscript{2} has been successfully coated on the MC. The highest intensity anatase was located at 25.3368° at (011) crystal plane with d-spacing of 3.5124. This indicates that TiO\textsubscript{2}/MC have a high concentration of anatase phase or availability of active TiO\textsubscript{2} compound [9,10].

For uncoated cordierite, C0 (Fig. 2(a)), it has large surface area but with an uneven and rough surface with a low percentage of shrinkage in the substrate. While after dipping process and heat treatment, the TiO\textsubscript{2} was successfully deposited on the substrate as shown in Fig. 2(b-e). However, the TiO\textsubscript{2} thin films have uneven rough surfaces and contain some cracks on the surface of the substrate (spotted by the red circle). According to Yao et al. [11], the crack happened due to the difference in heat dissipation between the cordierite substrate and the TiO\textsubscript{2} coating. Moreover, the relieve stress after the calcination process was one of the reasons the coated foam were struck. In addition, there are some holes in the thin film for each substrate (labelled by the blue circle). This is due to the insufficient amount of TiO\textsubscript{2} coated or the high viscosity of TiO\textsubscript{2} sol during dip coating process. For Fig. 2(e), there are some excess TiO\textsubscript{2} coated on the surface of the substrate (spotted by the yellow circle). The higher the dipping cycles resulted in severe agglomeration of particles, thus higher the content of TiO\textsubscript{2} coated on the substrate [9]. However, too many dipping cycles such as sample T4 have caused the excess TiO\textsubscript{2} to attach weakly at the surface. Furthermore, the bulk density of sample C4 is lower than samples C2 and C3 by bulk density of 0.0191 g/cm\textsuperscript{3} and 0.0371 g/cm\textsuperscript{3} as shown in Fig. 3.
Fig. 1 XRD diffraction pattern for TiO$_2$/MC (c-cordierite; a-anatase; r-rutile)

Fig. 2 SEM morphology of TiO$_2$ deposited macroporous cordierite with different dipping cycles (a) before dip-coating, C0, (b) C1, (c) C2, (d) C3, and (e) C4 under magnification of 1000x. As shown in Fig. 3, the bulk density increased as the dipping cycles increased from 1 to 5 as more amount of TiO$_2$ coated on the cordierite. However, there was a change in the trend of the bulk density and total porosity with the increases of dipping cycle. Sample C4 with 7 dipping cycles gave the lowest bulk density of 0.3009 g/cm$^3$ and highest porosity of 86.1% as compared with C2 and C3 samples. Lowest bulk density related to the edges which made by the excess TiO$_2$ coated on cordierite not finely interlocked or mechanically bonded with cordierite. Hence, result in dropped off material and lower the bulk density of sample C4. Archimedes principle indicates that sample C3 are the best product which finely coated with a high content of TiO$_2$ in this study due to the highest bulk
density as compared to the others, no dropped off while the total porosity was in optimum pore size value of macroporous cordierite which was larger than 50 nm.

**Fig. 3** Graph of bulk density and total porosity of deposited cordierite under different dipping cycles

Fig. 4(a) showed the relationship of dipping parameters effect on removal efficiency of MO. The trend of the photodegradation of all samples was increased over irradiation time. This may due to the •OH and O₂•⁻ as mentioned by Ho et al. [12]. There is no photocatalytic reaction acted on sample C0 with absent of photocatalyst. Sample C3 with a value of 58.1% are higher than others. This trend was similar with the bulk density as discussed in section 3.3. The orange color of MO had been gradually changed into colorless as denotes the destruction of chromophoric group (-N=N-) and photodecomposition of organic dye. According to Guttei and Amar [13], the removing efficiency of the process strongly depended on the catalyst amount. As the amount of photocatalyst increased, the availability of the active sites such as •OH radicals increased which able to remove organic compound in the MO dye and rapid attack pollutants [14,15]. From Fig. 4.4(b), there was two significant peaks located at 270 nm in UV region and 464 nm in the visible region. It can be noted that the absorption of visible bands was decreased over irradiation time. The rapid decrease in the spectrum at 464 nm indicates the decoloration of MO solution. This indicates the cleavage of azo bond (-N=N-) in this water treatment application testing [16]. In this study, the azo bond has been attacked by most of the photocatalyst active site. Although the total removal efficiency was not achieved in 100%, it was believed that the photodegradation could continuous happen even after 7 hours.

**Fig. 4.** (a) Removal efficiency of different dipping parameter over period of photodegradation activity under UV light radiation and (b) UV-Vis spectrum for photodegradation of 10 ppm MO solution by C3 upon different irradiation time
4. SUMMARY

In summary, TiO₂/MC with optimum dipping cycles of 5 which is C3 has the best photocatalytic performance as compared to the others. This is due to the highest photocatalyst amount whereas the higher the amount of photocatalyst, the higher the number of active sites available in the photodegradation process. Further dipping cycles which more than 5 times would result in the poor coating and TiO₂ dropped-off from MC. Dropped-off of photocatalyst does not achieve the objective of using photocatalyst support as the drop-offs must be filtered in a secondary process after treatment. The photodegradation was increased over UV irradiated time as increased formation of •OH and O₂••. In this study, the trend of the removal continuous increasing as a function of time and doesn’t decrease in its rate of removal MO. Thus, the photodegradation process would be carry on even after 7 hours and need longer irradiation time to reach its limit.

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Effect of Calcination Temperature on Microstructural Evolution of Electrospun ZnO Fibers

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\textbf{ABSTRACT.} Development of portable or wearable devices demands for flexible, lightweight or even foldable materials for fabrication. In this respect, electrospinning offers a cost-effective, high throughput, versatile and scalable route for the production of flexible micro/nanofibers on almost all kinds of surfaces. In this work, semiconducting ZnO fibers of high aspect ratios were electrospun from organic precursor of ZnO solution. The effect of calcination temperature on the microstructures of the electrospun fibers was investigated. Simultaneous thermal analysis (STA) was used to monitor the temperature at which the organic precursor was removed to form ZnO. X-ray diffraction (XRD), on the other hand, was used to monitor the phase formations at various heating stages. Field emission scanning electron microscope (FESEM) equipped with energy dispersive spectrometry (EDX) was employed for morphological study of the ZnO produced. Continuous single phase ZnO fibers started to form at a temperature of around 460 °C and evolved through various stages of microstructural formations, from tubular-like structures to segmentation of granular structures and hierarchical structures at further increases in calcination temperatures. The ZnO fibers experienced increasing crystallinity and stoichiometry change during the heating process. When mechanically bent, the fibers were able to generate current pulses of between 0.1 to 10 nA.

\textbf{Keywords:} Zinc oxide, Electrospinning, Calcination;


\textit{Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.}

1. \textbf{INTRODUCTION}

ZnO is an n-type semiconductor that possesses richness in growth geometries, from rod, tube to more complex morphologies such as hexagonal plate-like or flower-like structures [1-3]. Due to its unique properties such as large excitation binding energy (60 meV) at room temperature, wide band gap (3.37 eV), thermal stability, large piezoelectric coefficient and irradiation resistance, it has been used as the building blocks in various solid state devices such as sensors, cosmetics, liquid crystal displays, optoelectronics, photovoltaic and piezoelectric devices [4-6]. Moreover, ZnO has a polar crystalline structure which produces a noncentrosymmetric charge gradient in the crystal lattice when subjected to an external force. Such property has made ZnO nanofibers good candidate materials for piezo generators as these nanostructures are ultrasensitive in converting mechanical forces to high output voltages due to their high degree of flexibility for deformation [7].

ZnO fibers can be fabricated using electrospinning, a simple, cost effective and high throughput technique that uses electric field to provide sufficient tensile force to overcome the surface tension of a polymer fluid so that it can be ejected through an electrically charged needle to form fibers onto an electrically grounded collector [8]. Advantages of electrospun fibers are that they are flexible, lightweight,
ultra-long and has various thicknesses and shapes for applications in wearable or implantable devices [9]. Using an appropriate collector design, the one-dimensional fibers can be uniaxially aligned or randomly oriented to form a two-dimensional mat. As microstructures play a significant role in the performance of the fibers in devices, it is important to characterise the microstructures at various stages of heat treatment for the formation of ZnO from its polymer precursor. This work focused on the study of microstructural evolution experienced by the electrospun fibers under different calcination temperatures ranging from room temperature to 800 °C. XRD and FESEM equipped with EDX were employed to characterize the microstructures, morphologies, phases, dimensionality and chemistry of the nanostructures obtained while STA was used to monitor the thermal processes involved, such as changes in weight and heat exchange. The synthesized fibers were encapsulated and their piezoelectric performance was evaluated and compared by applying external mechanical forces to the fibers.

2. MATERIALS AND METHODS

A precursor solution was prepared by mixing 1.5 M zinc acetate (Zn(CH₃COO)₂·2H₂O) with 10% polyvinylpyrrolidone (PVP, Mw = 1300000) in ethanol at a volume ratio of 1:9. It was then loaded into a plastic syringe. A voltage of 16 kV was applied between the needle tip of the syringe and a rotating wire collector separated by a distance of 16 cm. Electrospinning was performed at a flow rate of 0.03 ml/min with rotating speed of the wire collector fixed at 600 rpm. The rotating wire collector allowed the formation of uniaxially aligned fibers. The as-synthesised zinc acetate/PVP composite fibers were then transferred to a silicon substrate and calcined at temperatures of 400 °C, 500 °C, 600 °C, 700 °C and 800 °C for 4 hours to form crystalline ZnO fibers, respectively. Both the PVP/zinc acetate and ZnO fibers were characterized using XRD (PANalytical XPert Pro MPD), FESEM (Carl Zeiss Gemini SEM 500) equipped with EDX (Oxford Instrument) and STA (Netzsch 449F3 Jupiter).

3. RESULTS AND DISCUSSION

Fig. 1 shows a typical optical image of the aligned fibers electrospun at 16 kV. The average diameter of the as-spun fibers was found to be (125 ± 70) nm as determined digitally using the ImageJ software.

Fig. 1 Optical image of the aligned electrospun PVP/zinc acetate fibers

A fiber sample with initial weight of 14.9 mg was placed in an alumina pan and heated from 25 °C to 900 °C at a rate of 10 °C min under nitrogen purging of 50 ml/min. Fig. 2 shows the simultaneous TGA and DSC curves obtained during thermal process. The initial step of weight loss in the TGA curve was observed at 140 °C and continued till 320 °C. This was associated with an exothermic peak in the DSC curve in the same temperature range. This weight loss was attributed to sample dehydration and release of volatile PVP solvent. A major drop in weight was found at 460 °C, which was associated with burnt-out of organic components that constituted about 54% of the total weight of the sample. During this process, breakout of the organic bonds of the CH₃COO component of zinc acetate occurred. This was followed by the nucleation of
ZnO crystallites which was completed at 500 °C as may be evidenced from the intense exothermic peak observed in the same temperature range. With further increases in temperature, there was a gradual drop in weight and an associated exothermic peak. This was due to the occurrence of the second crystallization event, which was the formation of non-stoichiometric ZnO$_x$ ($x > 1$), as evidenced from the difference in percentage weight composition (from EDX analysis) between the fibers calcined at 800 °C (Zn: 53%; O: 47%) and those calcined at 700 °C or lower (Zn: 77%; O: 23%). Using X-ray photoelectron spectroscopy (XPS) as the characterization tool, Baek et al. [10] also observed that the process of calcination promoted the oxidation state of Zn species in their calcined electrospun ZnO fibers.

![Fig. 2 DSC/TGA thermograms of the electrospun ZnO fibers](image)

![Fig. 3 Comparison of X-ray diffractograms of the electrospun ZnO fibers calcined at different temperatures.](image)

(The dotted stick pattern represents the peak positions of ZnO taken from JCPDS No: 00-001-1136 and * represents the peak positions of zinc acetate from JCPDS No.00-001-0089)
To evaluate the phase change in the sample, X-ray diffractograms of the electrospun fibers were obtained after heat treatment at different temperatures (Fig. 3). No characteristic peak of ZnO is observed for the fibers before heat treatment. With its polymeric components, the fibers were amorphous. After calcined at 400 °C, ZnO diffraction peaks start to emerge, with crystalline phase of zinc acetate coexisting in the sample. When calcination temperature was increased to 500 °C, the diffraction peaks of ZnO become more intense. Typical ZnO peaks of Miller indices 100, 002 and 101 of wurtzite crystal structure (JCPDS No: 00-001-1136) have been identified. After calcined at 800 °C, the diffraction peaks of ZnO are shifted to the positions of larger interplanar distances. The expansion of the lattice parameters is in accordance with the formation of non-stoichiometric ZnO$_x$ (x >1).

Fig. 4 FESEM images of electrospun ZnO fibers calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C and (e) 800 °C
Fig. 4 shows the microstructures of the fibers obtained at different calcination temperatures. After calcined at 400 °C, the fibers were found to be discontinuous due to the removal of majority polymer contents (Fig. 4a). When calcined at temperature of 500 °C or more, the fibers started to reconstruct to form continuous structures with the nucleation and growth of ZnO crystallites. At early stage of crystallization, partially hollow structures were formed, as shown by their tubular structure when calcined at 500 °C (Fig. 4b). Fibers calcined at 600 °C were, however, able to exhibit continuous solid structures (Fig. 4c). At 700 °C, the fibers were segmented into granular structure with microgaps between the grains and the sample no longer had a fibrous structure (Fig. 4d). Further heating of the samples produced larger ZnO grains, resulting from the merging of the grains, as well as branching of smaller ZnO nanorods from the granular cores to yield hierarchical structures (Fig. 4e).

To evaluate their piezo response, aligned ZnO fibers calcined at 600 °C were used. The fibers were transferred to a Kapton film by lift-off technique. Silver pastes were applied to both ends of the fibers as the Schottky electrodes for connection to an external circuit via a source measure unit (SMU) (Keithley 2600). A flexible PDMS layer was coated on the fibers. Fig. 5 shows the schematic diagram of the fabricated piezoelectric generator and the current pulse generated when the fibers were flexed by fingers.

![Fig 5](a) Schematics of a ZnO piezo generator and (b) The current pulse produced when the fibers were bent and released

When the fibers were bent by external force, piezoelectric potential was created when the crystal symmetry was broken and electrons were driven from one electrode to another via the external circuit. Electrons were also accumulated at the interface between the fibers and the electrode. When the force was released, the piezo potential disappeared and the accumulated electrons were then flown back in the opposite direction, generating a negative pulse. A current pulse was thus generated by applying and releasing the force. A.C. pulse was generated and a maximum output current pulse of 10 nA was demonstrated for an approximate effective working area of 1 cm² of fibers. The presence of Schottky contact was important to enhance the output signal from the generator to be above the noise level by preventing the electrons to flow into the ZnO fibers through the interface [11].

4. SUMMARY

ZnO fibers calcined at different temperatures showed different microstructures and morphologies. Continuous single-phase ZnO fibers started to form at a temperature around 460 °C and evolved through various stages of microstructural formation from tubular-like structures to segmentation of granular structures and hierarchical structures. The ZnO fibers also experienced a stoichiometry change when heated to 800 °C. Continuous ZnO fibres calcined at 600 °C have been demonstrated to be able to generate a maximum current pulse of 10 nA cm⁻² when mechanically bent.
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Effect of Calcination Temperature on the Silica Ceramic Membrane Synthesized via Sol-gel Dip-coating Method

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ABSTRACT. Ceramic membranes became one of the most important ceramic products because of their numerous benefits to many applications especially in gas separation processes. The attractive features offered by this technology include high energy efficiency, simplicity design and construction of membrane modules and environmental compatibility. The aim of this project is to get the optimum calcination temperature thus will give the optimize pore size for separation gas without cracking or pinholes the membranes. Therefore, the silica ceramic membrane was fabricated via sol-gel dip-coating method and the effect of calcination temperature on the membrane pore size was investigated. The ceramic support was dipped in the mixture solution of tetraethyl orthosilicate (TEOS), distilled water, ethyl alcohol and nitric acid with the desired molar ratio followed up by the calcination process at 400 °C, 500 °C and 600 °C. For X-ray diffraction (XRD) results, the fabricated silica ceramic membrane shows the existence of silicate hydrate when calcined at 400 °C, 500 °C and 600 °C. The XRD analysis showed the highest peak intensity at 22.5° which proved the presence of silica. From the field emission electron microscopy (FESEM) images, the pore size of the ceramic support was around 0.5 to 0.6 μm. After the silica ceramic membranes were fabricated, the pore size no longer visible under the FESEM proves that the pore size of the membranes was reduced. Fourier transform infrared spectroscopy (FTIR) showed adsorption spectra of the fabricated membranes with different calcination temperature. The broad band in the region around 1060 to 1090 cm⁻¹ correspond to the O-Si-O bond of mesoporous silica altogether confirming the existence of silica. Based on the result analysis, the suitable calcination temperature at 500 °C with less crack and more consolidated surface membrane.

KEYWORDS: Silica, Ceramic membrane, Calcination temperature, Sol-gel, Dip-coating

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1. INTRODUCTION

Currently, the interest in application of membranes for various gas separation has increased significantly in term of economic importance as compared to other conventional methods. Due to the increase of environmental regulation, membranes are favourable as it reduces waste disposal expenditure and allow the recovery and recycling of the materials which results in economic advantage [1]. Membranes categories can
be divided into organics, inorganics and mixed matrix membranes [2]. Inorganic membranes have received great attention as it overcomes the limitation of organic membranes in term of chemical and thermal resistance [3]. Inorganic membranes can be divided into two categories, which are porous and nonporous [4]. The porous inorganic membrane is favourable as they can tolerate higher temperatures and limit the connection between permeability and selectivity [5]. Ceramic inorganic membranes possess the characteristics of high stability, resistance to chemical and solvents, long term durability and high mechanical strength [1].

There are various ways to prepare ceramic membrane based on material used and also required characteristic (porosity, pore size, thickness) [4]. Dip-coating method are the most preferable process for ceramic membrane fabrication as it possessed many advantages, such as preparation of materials with exceptional purity and homogeneity and well-defined distribution of pore size [6,7]. Dip-coating method is used to fabricate ceramic membrane when reduction of pore size is required [4]. Example of ceramic membrane that can be fabricated using the dip-coating method is silica membrane, which then resulting in greater surface area and microporosity [4]. Basically, the processing variables such as temperature, particle size, applied pressure, particle packing, compositions and calcination atmosphere influence the microstructure that is produced at different calcination temperatures. Hence, the calcination temperature will give different pore size, the higher the calcination temperature, the smaller the pore size. Gaber et al. [8] mentioned that the pore size of the membranes decrease as the calcination temperature increase due to the external pressure during heating [8].

Therefore, in this paper, the silica ceramic membranes are synthesized by sol-gel dip-coating process at different calcination temperature. The synthesized silica ceramic membrane has been characterized by XRD, FESEM and FTIR to identify the physical and chemical properties of the membrane.

2. Materials and Methods

2.1 Membranes Fabrication. The ceramic support used was 10 inch Doulton OBE Ceramic with 32 mm internal diameter, 48 mm outer diameter while the support length is 200 mm. The water used throughout was distilled water. Tetraethyl orthosilicate (TEOS) was supplied by Sigma Aldrich and nitric acid by R&M Chemical. The ethanol also used was supplied by Systerm.

The silica sol will be applied to the porous ceramic supports of tubular configuration via sol-gel dip-coating method. In this process, TEOS, distilled water and ethyl alcohol (1:4.7:3.8 molar ratio) were mixed at 25 °C. After that, acid nitric added into the silica sol. Then, the ceramic support was dipped into this sol. The membrane was drying 24 hours in atmosphere overnight and continued with the calcination process for three hours. In this works, the calcination temperatures have varied to 400 °C, 500 °C and 600 °C respectively. The process of dipping the support in sol and calcination was repeated for second and third dipping number.

2.2 Membranes Characterization. The morphology of the membranes surface and support were determined using the field emission scanning electron microscope (FESEM) (JSM 6700F, JEOL). X-ray diffraction (XRD), was used to determine the element present of the fabricated membrane. The Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer System spectrum 100) was employed in determining the functional group of the membrane. By using FTIR, it can verify the presence of silica in ceramic membranes and provide the information on the structural bonding.

3. RESULTS AND DISCUSSION

Fig.1 demonstrated the XRD analysis of prepared silica ceramic membrane at different calcination temperatures, which are 400 °C, 500 °C and 600 °C. The XRD peak shows existence of silica hydrated (card number 71-6245) with highest peak 22.5°. Moreover, the peak intensity for ceramic membrane calcined at 500 °C and 600 °C are lower as compared when ceramic membrane calcined at 400 °C.

This explained that the silica grain growth has achieved optimum at 600 °C, indicated by the decrease in intensity of aluminum phosphate. The detected reflections were solely the expected reactions from ceramic
support (AlPO₄) and fabricated ceramic membrane (SiO₂), indicating that no other phase was present in the membrane.

Fig. 1 XRD pattern of fabricated silica ceramic membrane at different calcination temperature, (a) 400 °C, (b) 500 °C and (c) 600 °C

Fig. 2 FESEM images of fabricated silica ceramic membrane at different calcination temperature, (a) ceramic support; (b) 400 °C, (c) 500 °C and (d) 600 °C
Fig. 2 showed the FESEM micrographs of ceramic support and fabricated silica ceramic membranes at different calcination temperature of 400 °C, 500 °C and 600 °C. Besides that, the surface of raw ceramic support show highly porous structure (0.5 to 0.6 µm in diameter) while for the surface of fabricated silica ceramic membranes are more consolidated.

From the FESEM images, it was observed that there has a crack when calcined at 400 °C. Whereas, when calcined at 500 °C and 600 °C, the silica was consolidated on the surface structure of the membrane. This was a proof that the silica membrane has coated the ceramic support completely, thus covering all the pores on its surface. Next, it was also observed that the silica membrane more consolidated when calcined at 600 °C was noticeably lesser compared to the membrane calcined at 500 °C due to the deterioration of O-Si-O bond start at 565 °C at elevated temperature. This finding was also confirmed by Gaber et al. [7].

![Fig. 3 FTIR adsorption spectra of prepared ceramic membranes at different calcination temperature](image)

**Fig. 3 FTIR adsorption spectra of prepared ceramic membranes at different calcination temperature**

Fig. 3(a) shown the FTIR adsorption spectra of ceramic support while in Fig. 3(b) shows the FTIR adsorption spectra of the prepared ceramic membranes at different calcination temperature. Whereas in Fig. 3(b), it shown the highest peak intensity for membrane calcined at 600 °C which means the optimum temperature for silica grain growth. Based on this observation the lowest peak intensity presented for the membrane which calcined at 400 °C due to the deterioration of the O-Si-O bond as mentioned previously. The broad band in the region range between 1060 to 1090 cm⁻¹ correspond to the O-Si-O bond of mesoporous silica, altogether verify the existence of silica. IR adsorption at 791.4 cm⁻¹ shows the modification of Si-CH₃ group on the silica ceramic membrane surface as mentioned by Bowen et al. [9].

Based on XRD, FESEM and FTIR results, the fabrication of silica ceramic membrane are significantly affect physical and chemical at different calcination temperature at 400 °C, 500 °C and 600 °C. The result also revealed that the the silica ceramic membrane calcined at 500 °C can functionally reduce the present of crack and the surface ceramic membrane are more consolidated.
4. SUMMARY

As a conclusion, the silica ceramic membrane via sol-gel dip-coating method is successfully fabricated. The silica ceramic membranes have been calcined at different calcination temperatures 400 °C, 500 °C and 600 °C. The fabricated ceramic membrane is characterized physically and chemically. The silica ceramic membranes have been characterized by XRD, FESEM and FTIR. The XRD pattern showed the aluminum phosphate element for ceramic support and silicate hydrate element for prepared silica ceramic membrane. Under XRD analysis, the highest peak at 22.5° which refer to the presence of silica. FESEM micrographs showed consolidated SiO$_2$ on the surface of ceramic support when calcined at different temperatures. It was discovered that the pore size no longer visible when the silica ceramic membrane calcined at 600 °C which proved that the ceramic support was fully coated with silica membrane. Under FTIR analysis, the highest IR adsorption is between 1050 to 1090 cm$^{-1}$, which is refer the presence of O-Si-O functional group. In terms of calcination temperature, it shows that the optimum temperature was at 500 °C with less crack and more consolidated surface membrane.

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Effect of Calcination Temperature on Titanium Dioxide Synthesized by Sol-Gel Method

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ABSTRACT. In this paper, the effects of calcination temperatures on the sol-gel synthesized TiO2 powder were studied. TiO2 powder was prepared through sol-gel method and further heat treated by different calcination temperature of 400 °C, 500 °C, 600 °C and 700 °C. Thermal analysis of the dried TiO2 powder catalysts was carried out using DTA-DTG. While all treated powder were characterized by using XRD and SEM. Meanwhile the crystallite size of TiO2 samples increased as calcination temperature increased. The morphology of synthesized TiO2 also revealed the increment in particle size with increasing the calcinations temperature.

Keywords: Titanium dioxide, Photocatalyst, Sol-gel method, DTA-DTG, Phase transformation;

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1. INTRODUCTION

Since the discovery of photocatalytic properties of titanium dioxide (TiO2) by Fujishima and Honda, TiO2 had become one of the most popular and promising photocatalyst due to its strong oxidizing power of its holes, high photostability, redox selectivity and easy to prepare in the laboratory [1, 2]. This photocatalyst usually used in discovering application of materials, for example, shades, sunscreen salves, electrochemical terminals, capacitors, solar cells and even act as food colouring agent in toothpastes. There are various methods are available for the preparation of TiO2 powder. Among all methods, sol-gel are the most convenient due to the ability to control reaction at low temperature and able to design nanomaterial with demanded surface properties [3].

There are many studies have been carried out in the phase transition of TiO2 [4-6]. The phase transition of TiO2 from anatase phase to rutile phase, a symmetry change from I41/amd to P42/mnm due to low stability of low density solid phase of anatase. Kais and Misra studied that the conversion from anatase structure to rutile structure can be done by annealing at temperature 600 °C and completed at 1000 °C [7,8]. However, Su et al. [1], Papoulis et al. [9] and Wang et al. [10] found that small fraction of rutile mixed with anatase had shown excellent photocatalytic activities. The aim of this work was to investigate on the thermal composition and effect of calcination temperature on phase transformation of synthesized TiO2. Morphology of synthesized TiO2 powder were also revealed.

2. MATERIALS AND METHODS

In this study, TiO2 was synthesized by using sol-gel method with volume ratio Ti(OC3H7)4 :H2O:C6H5OH:CH3COOH is 1:2:1:0.53. First, 50 mL of deionized water was pre-heated up to 80 °C. Meanwhile,
13.25 ml of acetic acid was added into 25 ml of ethanol to form solution 1. After that, 25 ml of Ti(OC\(_3\)H\(_7\))\(_4\) was slowly added into solution 1 to form solution 2 and aged for 5 min at room temperature. Next, solution 2 was added slowly into the heated deionized water at 80 °C under magnetic stirring. The TiO\(_2\) sol was stirred vigorously for 30 min and then aged for 3 hours. It was then dried in hot oven at temperature of 110 °C for 24 hours to remove excess water content in the gel and form precursor powder. The synthesized TiO\(_2\) powders was calcined at different temperature. Powder 1(P-0) was the TiO\(_2\) precursor powders while powder 2 (P-400), powder 3 (P-500), powder 4 (P-600) and powder 5 (P-700) were prepared at calcination temperature of 400 °C, 500 °C, 600 °C and 700 °C, respectively. The calcination process was carried by using muffle furnace.

Thermal analysis of 10 g to 15 g TiO\(_2\) precursor powders were carried out using differential thermal analysis and thermogravimetric analysis (DTA/TGA) (Rigaku TG 8120) started at room temperature until 1400 °C with heating rate of 10 °C/min in air atmosphere. The crystal structure of calcined TiO\(_2\) powders were analyzed with X-ray diffractometer (XRD) (D/max-III, Rigaku using Cu-K\(_\alpha\) radiation). All XRD patterns were collected at room temperature in range of 2θ = 5-80° at a scan speed of 2 °/min while the diffraction signals were collected with step size of 0.02°. Rietveld refinement was performed by using XpertHighScore Plus software to quantify phase and refine the crystal structure. The crystallite size was measured using Williamson-Hall plot. The morphology of the samples were observed by using a scanning electron microscopy (SEM) from JEOL (Model: JSM 6460 LA).

3. RESULTS AND DISCUSSION

3.1 Thermal analysis of TiO\(_2\) precursor powder.

Differential thermal analysis and thermogravimetric analysis (DTA/TGA) curves recorded on the thermal behaviour of the TiO\(_2\) precursor powders from room temperature to 1400 °C as shown in Fig. 1. As can be seen in Fig. 1(a), the DTA curve has been segregated into four region with corresponding temperature interval, which was zone A (29-292 °C), B (292-385 °C), C (385-697 °C) and D (697-1400 °C) respectively. The initial state of precursor powder of TiO\(_2\) was a non-heat treated and stable xerogel formed. From zone A which shows the thermal data, there is a broad endothermic peak with minimum peak at temperature of 64.98 °C as shown in Fig. 1. Although the TiO\(_2\) precursor powder had been gone through drying process, there was still some content of solvent and water left which represented by the endothermic peak. After this peak onwards including in zone B, it had been transformed into amorphous TiO\(_2\) which exist in a range around 300 °C [11]. Next, the exothermic peak with maximum of 346.213 °C in zone B indicates to the crystallization of anatase. Meanwhile, the TiO\(_2\) would transform from amorphous into active anatase phase as the temperature keep increasing in zone C [12]. According to Pagacova and Huang [13,14], the crystallization of anatase to rutile phase was occur at a maxima exothermic peak. However, there was an almost non-detectable exothermic peak at temperature of 697.852 °C in this study and it was same as the observation of DTA results by Huang [14]. Moreover, in zone D, increased in temperature would lead to rutile phase crystallized and presented as the main phase of TiO\(_2\). The overall transformation shown as below:

\[
\text{Xerogel} \rightarrow \text{Amorphous} \rightarrow \text{Anatase} \rightarrow \text{Rutile}
\]

In Fig. 1(b), the TGA plot was labelled by stages which included stage I, II, III and IV which is located at temperature range of 29-87 °C, 87-292 °C, 292-383 °C and 383-697 °C, respectively. In TGA results, there are drastic drop of 6% in weight percentage in stage I. In this stage, weight loss indicate present of desorption of physisorbed water [6]. Next, there was a mass loss of 4% in stage II which indicated the degradation of the solvent including the isopropoxy group which still bonded with Ti after aging process [14]. While in stage III, there are a mass loss of 5% in weight percentage of organic compound such as carbonic species or carbon dioxide which may oxidized from the ethanol. Finally, there are slightly loss of 0.8% in weight percentage in
stage IV because it takes time for total removing the excess organic compound. After all the organic compound burnt of, TiO\textsubscript{2} rutile left in the alumina crucible was 84%.

3.2 Crystallography of calcined TiO\textsubscript{2}

As demonstrated in the Fig. 2, all samples contain TiO\textsubscript{2} anatase phase. However, only sample P-700 contain a small fraction of rutile phase. High intensity of rutile phase was diffracted at 27° corresponded to reflection from (110) crystal plane. In this study, there was no brookite phase present. According to Table 1, anatase phase and rutile phase have the same crystal system which was tetragonal but different in space group. During the conversion from space group I41/amd to P42/mnm, it can be said to be a phenomena of reconstructive polymorphism which caused by reassembly of atoms and extensive rearrangement of atomic bonds [7]. According to kais and Misra [7,8], anatase structure can be converted into rutile structure by annealing from 600 °C and completed at 1000 °C. Besides, this also can be proven by the DTA plot as discussed in section 3.1. The quantification of phases were tabulated in Table 4.1.
Table 1 Crystal structure and space group of TiO$_2$ under different calcination temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Symbol</th>
<th>Phase</th>
<th>wt.%</th>
<th>Crystal system</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-400</td>
<td>A</td>
<td>Anatase</td>
<td>100</td>
<td>Tetragonal</td>
<td>I41/amd</td>
</tr>
<tr>
<td>P-500</td>
<td>A</td>
<td>Anatase</td>
<td>100</td>
<td>Tetragonal</td>
<td>I41/amd</td>
</tr>
<tr>
<td>P-600</td>
<td>A</td>
<td>Anatase</td>
<td>100</td>
<td>Tetragonal</td>
<td>I41/amd</td>
</tr>
<tr>
<td>P-700</td>
<td>A</td>
<td>Anatase</td>
<td>88.1</td>
<td>Tetragonal</td>
<td>I41/amd</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>Rutile</td>
<td>11.9</td>
<td>Tetragonal</td>
<td>P42/mnm</td>
</tr>
</tbody>
</table>

Fig. 3 shows the XRD pattern for the main peak of TiO$_2$ anatase under different calcination temperature. The highest intensity peaks of anatase at (011) crystal plane were overlaid to be compared. The peak shifted to the low angles as the calcination temperature increased. At higher temperature, the lattice site was substituted by ion and thus increase in d spacing and shifted happen [15]. This also can be explained by lattice parameter as shown in Table 2. There was no significant change in lattice ‘a’ and ‘b’ unit cell but in ‘c’ unit cell. As the temperature increased, lattice ‘c’ unit cell was increased which indicated the elongation happen in the unit cell and thus leading to increase in d-spacing. Meanwhile, samples P-600 and P-700 have higher peaks as compare to sample P-400 and P-500 with 1055 and 1054 counts respectively. This indicates that they both have higher concentration of anatase phase or higher degree of crystallinity compound and larger grain size as compare to samples P-400 and P-500 [12,16].

In addition, the crystallite size, lattice strain and crystal density of TiO$_2$ under different calcination temperature was shown in Table 3. By using Williamson-Hall plot, all the phase was in nano range crystallite size. The crystallite size increased as the calcination temperature increased while the lattice strain tends to decrease. This indicate that heat treatment would enhanced the growth of anatase while rutile formed larger [12]. In addition, based on He’s study [17], the stronger and sharpen diffraction peaks as increased the calcination temperature indicate the formation of larger crystal size and higher crystal degree. While undergoing phase transition of sample P-700 resulted in increased densification and coarsening of TiO$_2$ particles as shown in SEM image Fig. 4 [7].

Table 2 Lattice parameter of TiO$_2$ under different calcination temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Symbol</th>
<th>Lattice parameter</th>
<th>Crystal volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>P-400</td>
<td>A</td>
<td>3.78665</td>
<td>3.78665</td>
</tr>
<tr>
<td>P-500</td>
<td>A</td>
<td>3.78672</td>
<td>3.78672</td>
</tr>
<tr>
<td>P-600</td>
<td>A</td>
<td>3.78444</td>
<td>3.78444</td>
</tr>
<tr>
<td>P-700</td>
<td>A</td>
<td>3.78455</td>
<td>3.78455</td>
</tr>
</tbody>
</table>
### Table 3 Structural parameter of TiO$_2$ under different calcination temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Symbol</th>
<th>wt.%</th>
<th>Crystallite size (nm)</th>
<th>Lattice strain (%)</th>
<th>Crystal density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-400</td>
<td>A</td>
<td>100</td>
<td>11.66</td>
<td>0.000</td>
<td>3.89</td>
</tr>
<tr>
<td>P-500</td>
<td>A</td>
<td>100</td>
<td>15.40</td>
<td>0.150</td>
<td>3.89</td>
</tr>
<tr>
<td>P-600</td>
<td>A</td>
<td>100</td>
<td>46.70</td>
<td>0.109</td>
<td>3.89</td>
</tr>
<tr>
<td>P-700</td>
<td>A</td>
<td>88.1</td>
<td>70.05</td>
<td>0.093</td>
<td>3.89</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>11.9</td>
<td>114.5</td>
<td>0.087</td>
<td>4.24</td>
</tr>
</tbody>
</table>

#### 3.3 Morphology of synthesized TiO$_2$ powders.

In this study, all powder samples are agglomerated and distributed randomly. The TiO$_2$ precursor powder, P-0 showed that the particles is in irregular shape, uneven surface and cubic like structure as shown in Fig. 4(a). While sample P-400 and P-500 were observed with an uneven surface and spherical in shaped but the particle size was increased as the temperature increased. For morphology of P-600, the shapes were elongated into irregular, sharpen in particle edges and changed into larger in particle size. At last, P-700 grew into larger particle size, possessed irregular and uneven surface with some sharp faced structure. From the morphologies observations, it shows that the higher the calcination temperature, the larger the particles size which has similar trend with what has been found by Wetchakun et al. [4]. This is due to the particles tend to stick together and agglomerated while crystal growth happen in higher calcination temperature.

![SEM morphology of TiO$_2$ powders with different calcination temperature](image)

**Fig. 4** SEM morphology of TiO$_2$ powders with different calcination temperature (a) P-0 (b) P-400 (c) P-500 (d) P-600 and (e) P-700 under magnification of 15 KX

#### 4. SUMMARY

In this study, TiO$_2$ has been synthesized by using the sol-gel method. From the DTG thermal analysis, TiO$_2$ was degraded in four stage. There was mass loss of 6%, 4%, 5% and 0.8% in temperature range of 29-87 °C, 87-292 °C, 292-383 °C and 383-697 °C respectively. The very first and major weight loss in stage I was due to desorption of physisorbed water. The degradation of solvent, organic compound and excess organic compound were happen in stage II, III and IV respectively. Besides, phase transformed from xerogel,
amorphous, anatase to rutile phase ascendingly with transformation of temperature of 65 °C, 346 °C and 697 °C are revealed in DTA and XRD analysis. From XRD analysis, it was found that single phase of anatase phase was obtained when calcined up to 600 °C and at 700 °C small amount of rutile started to crystallize. The crystallite size of the anatase phase also increased as a function of calcination temperature. The morphology of TiO₂ powder shows the higher the calcination temperature, the larger and sharpened the particles.

REFERENCES


Effect of Poling Parameter on Piezoelectric and Dielectric Properties of La and Sr Doped PZT

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**ABSTRACT.** La and Sr co-doped, modified lead zirconium titanate (PZT) ceramics, with composition \( \text{Pb}_{0.93}\text{La}_{0.02}\text{Sr}_{0.05}\text{(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_{3} \) was synthesized by dry-mixed planetary mill. The incorporation of La\textsuperscript{3+} and Sr\textsuperscript{2+} in the PZT lattice enhanced the tetragonality and suppressed grain growth thereby promoted piezoelectric and dielectric properties of the ceramics. The objective of this research is to determine the optimum poling parameters on La and Sr co-doped PZT (PLSZT) for better electrical properties. The optimum poling parameters (temperature, electric field and time) have been investigated via design of experiment (DOE) concept for the effective results. The results showed that when using the poling temperature at 140 °C with 4 kV/mm of electric field, the \( d_{33} \) and \( \varepsilon_{r} \) values were found to be highest at 327 pC/N and 1620, respectively. It revealed that poling temperature and applied electric field plays a dominant role in influencing electrical performance of PLSZT which may be suitable for possible device applications.

**Keywords:** PZT, Doped PZT, Poling, DOE, Piezoelectric;

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1. INTRODUCTION

Recent advances in ceramics have provided greater control over aspects of composition and microstructure that govern physical properties. Such control makes it possible to tailor ceramics with special chemical, thermal, mechanical, and electrical requirements \[1\]. Lead zirconate titanate (PZT) is one of the advance ceramics which has great technological interest due to their excellent piezoelectric and ferroelectric properties. It is also known as a ceramic perovskite material and it shows a marked piezoelectric effect widely used in the microelectronics industry. The piezoelectric material is the materials that can create electricity when subjected to a mechanical stress also known as direct piezoelectric effect. They will also work in reverse, which is generating a strain by the application of an electric field and is known as indirect piezoelectric effect \[2\]. Many base of PZT composition have been manufactured by chemical modification in order to satisfy the requirements and enhance the PZT properties especially in electrical properties.

In order to improve the electrical properties, many investigations have been done on altering the composition of the piezoelectric materials, which is by doping with other materials. Besides, the poling parameters also give the effect towards the electrical and mechanical properties of the system especially in dielectric and piezoelectric properties. The previous researchers had investigated La and Sr co-doped PZT to
improve the dielectric and piezoelectric properties [3]. Some researchers also have been study the poling effect of PZT ceramics but not many reports on doped PZT samples [4,5]. Based on Li et al. it is generally believed that the temperature plays an important role during the poling process because it leads to the best piezoelectric properties.

However, there were still remains a need for an efficient method that can achieve optimum poling parameters for doped PZT which is by using statistical design method. Therefore, this research came out with the objective to determine the optimum poling parameters on La and Sr co-doped PZT (PLSZT) based system using Design of Experiment (DOE) software. DOE is used because it is a design experiment which is a methodical way of intentionally changing a process and give the effective results [6].

2. MATERIALS AND METHODS

PbO, ZrO$_2$, TiO$_2$, La$_2$O$_3$ and SrCO$_3$ powders were used as starting materials to synthesize the La- and Sr-doped PZT. The mixture powders were prepared according to the stoichiometric ratios of Pb$_{0.93}$La$_{0.02}$Sr$_{0.05}$(Zr$_{0.52}$Ti$_{0.48}$)O$_3$, then the mixture was dry-mixed in a planetary mill for 40 hours. The milled powder was then pressed into pellets with 13 mm diameter with compaction pressure at 200 MPa and sintered at 1200 °C for 3 hours and then was undergo the characterization.

Phase formation of sintered samples were characterized using X-ray diffraction (XRD) technique. Meanwhile, the pellet samples were polished and thermally etched at 950 °C for microstructure analysis by using field emission scanning electron microscopy (FESEM) technique. For poling process, the pellet samples were polished and the both surface of samples were coated with silver paste. Then, the samples undergoes poling process by applying the surface sample in a contact with different electric fields (2, 3, and 4 kV/mm), temperature (100, 120 and 140 °C) and times (10, 15 and 20 min).

2.1 Design of Experiment (DOE)

DOE was used for La and Sr co-doped samples (PLSZT) after sintering. The effect of variables, such as temperature (X$_1$), electric field (X$_2$) and time (X$_3$) were studied using response surface methodology (RSM) based on central composite design (CCD). Factors used were 2$^3$ with 3 centre points and α value was 1.682. Table 1 shows the experimental conditions of this work.

**Table 1** Control factors and their levels in poling parameters using RSM

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Code</th>
<th>Level</th>
<th>Star point, α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low, -1</td>
<td>Medium, 0</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>X$_1$</td>
<td>100.0</td>
<td>120.0</td>
</tr>
<tr>
<td>Electric field (kV/mm)</td>
<td>X$_2$</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Time (min)</td>
<td>X$_3$</td>
<td>10.00</td>
<td>15.00</td>
</tr>
</tbody>
</table>

The sequence of poling parameters was carried out according to design of experiment (DOE) set by Minitab 16 Software (Response surface methodology by central composite design). Table 2 displays the sequence of poling parameters.
3. RESULTS AND DISCUSSION
3.1 Phase Analysis.

Fig. 1 shows the XRD patterns of sintered PZT and PLSZT samples. Both diffractograms can be fully-indexed to a single-phase tetragonal perovskite structure with a space group of P4mm. Besides, the peaks were shifted to the higher angle after addition of dopant materials due to the slight variation in lattice constant which indicates the substitution of La ion in the crystal lattice. When the peaks shifted to the higher angle, the lattice parameters contracted due to the difference in ionic radii between the Pb element (119 pm) and the La and Sr co-dopant ions (103 and 118 pm respectively) with creation of oxygen vacancy.

![XRD pattern of sintered pellet of pure PZT and PLSZT](image)

**Fig. 1** XRD pattern of sintered pellet of pure PZT and PLSZT

### Table 2 DOE of poling parameters using RSM

<table>
<thead>
<tr>
<th>Std. Order</th>
<th>Run Order</th>
<th>Temperature (°C)</th>
<th>Electric field (kV/mm)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1</td>
<td>120.0</td>
<td>4.7</td>
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</tr>
<tr>
<td>4</td>
<td>2</td>
<td>140.0</td>
<td>4.0</td>
<td>10.00</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>120.0</td>
<td>3.0</td>
<td>7.00</td>
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<tr>
<td>8</td>
<td>4</td>
<td>140.0</td>
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<td>20.00</td>
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<td>7</td>
<td>5</td>
<td>100.0</td>
<td>4.0</td>
<td>20.00</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>140.0</td>
<td>2.0</td>
<td>10.00</td>
</tr>
<tr>
<td>16</td>
<td>7</td>
<td>120.0</td>
<td>3.0</td>
<td>15.00</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>140.0</td>
<td>2.0</td>
<td>20.00</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>86.5</td>
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<td>15.00</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>100.0</td>
<td>2.0</td>
<td>10.00</td>
</tr>
<tr>
<td>15</td>
<td>11</td>
<td>120.0</td>
<td>3.0</td>
<td>15.00</td>
</tr>
<tr>
<td>17</td>
<td>12</td>
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<td>15.00</td>
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<td>10.00</td>
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<tr>
<td>11</td>
<td>16</td>
<td>120.0</td>
<td>1.3</td>
<td>15.00</td>
</tr>
<tr>
<td>10</td>
<td>17</td>
<td>153.5</td>
<td>3.0</td>
<td>15.00</td>
</tr>
</tbody>
</table>
The peaks shift to the higher angle as the doping La due to substitution of La$^{3+}$ (1.22 Å) and Sr$^{2+}$ (1.27 Å) to Pb$^{2+}$ (1.32 Å). Due to slight variation of atomic radius, strain will be generated in the matrix and cause the reduction in crystallite size in PLSZT. The peak intensity was also increased after adding the dopant due to the increasing of the number of oriented crystallite. Same observation also was made by Law et al. [7] which found that the increase of the peak intensities on XRD pattern was due to high number of domains oriented in the sample.

### 3.2 Microstructure Analysis.

Fig. 2 shows FESEM micrographs for undoped PZT and PLSZT samples. The micrographs show the grain sizes of PLSZT was homogeneously distributed throughout the sample with certain degree of porosity. The grain size was decreased with addition of dopants in PZT system (Fig. 2b). The reduction of grain size was due to the small substitution of La and Sr into Pb site and the others are precipitated on grain boundary and then suppressed the grain growth. This is because the crystal’s interior must be presented in lot of vacancy (dopedcations and oxygen) or there is no substitution has been occurred. Therefore, the deficiency of Pb led to increase vacancies at Pb and O sites, and subsequently, reducing the grain size. Bahanurddin et al. [3] also claimed that addition of La in PSZT shows the grain growth has been slowed down.

![Fig. 2 Surface view for (a) PZT and (b) PLSZT at 1000x magnification](image)

### 3.3 Piezoelectric coefficient.

Based on DOE result, the identifications of significant factor and interaction effect were made using analysis of variance (ANOVA). The quadratic model relationship was significant at $\alpha = 0.05$. In addition for lack of fit, $P > 0.05$ point out the model is in good fit. Table 3 tabulated the ANOVA for this work.

From the ANOVA results, a mathematical model in Eq. 1 can be expressed in order to predict piezoelectric effect in poling process with various poling parameter. This equation was formed based on the regression coefficient of piezoelectric coefficient. The standard deviation, $R^2$ and $R^2$ adjusted were 98.08% and 95.61% respectively. These indicate that the accuracy of model is 98.08%. This entire statistical test showed that the develop model was suitable for representing data and provide good relationship between variables and response.

\[
Y = 75.256 + 1.611X_1 + 68.861X_2 + 1.3X_3 - 0.004X_1^2 - 6.304X_2^2 - 0.04X_3^2 - 0.138X_1X_2 + 0.003X_1X_3 - 0.05X_2X_3
\]

\[
Y = d_{33}
\]

\[
X_1 = \text{Temperature}
\]

\[
X_2 = \text{Electric field}
\]
X₃=Time Factors of poling parameters point out positive values respectively. Increasing these factors will raise \( d_{33} \) value. In conjunction, the equation also indicates \( d_{33} \) more influence by electric field than temperature and time.

Fig. 3 shows piezoelectric coefficient (\( d_{33} \)) of PLSZT based on DOE run order. The value shows the increasing the temperature and electric field increased the \( d_{33} \) value (140 °C, 4 kV/mm and 20 min). However, there was not much different in \( d_{33} \) between others. Prewitt and Jones [5] also claimed by increasing of electric field and temperature increased the \( d_{33} \). This is because at an elevated temperature, higher degree of domain reorientation developed larger polarization in ceramic. Thus, it contributed to the higher the \( d_{33} \). At high electric field, the absolute extrinsic contribution due to irreversible displacement of domain walls increase in samples more highly poled.

**Table 3** Analysis of variance ANOVA for piezoelectric properties

<table>
<thead>
<tr>
<th>Source</th>
<th>Hypothesis, P</th>
<th>Regression coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>-</td>
<td>75.256</td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>0.001</td>
<td>1.611</td>
</tr>
<tr>
<td>Electric field</td>
<td>0.000</td>
<td>68.861</td>
</tr>
<tr>
<td>Time</td>
<td>0.177</td>
<td>1.300</td>
</tr>
<tr>
<td>Square</td>
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<td></td>
</tr>
<tr>
<td>Temp x Temp</td>
<td>0.105</td>
<td>-0.004</td>
</tr>
<tr>
<td>Electric field x Electric field</td>
<td>0.000</td>
<td>-6.304</td>
</tr>
<tr>
<td>Time x Time</td>
<td>0.311</td>
<td>-0.040</td>
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<tr>
<td>Interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temp x Electric field</td>
<td>0.039</td>
<td>-0.138</td>
</tr>
<tr>
<td>Temp x Time</td>
<td>0.825</td>
<td>0.003</td>
</tr>
<tr>
<td>Electric field x Time</td>
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</tr>
<tr>
<td>Lack of Fit</td>
<td>0.275</td>
<td></td>
</tr>
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</table>

**Fig. 3** \( d_{33} \) values of PLSZT samples corresponding to RSM
3.4 Dielectric permittivity.

Fig. 4 shows the dielectric permittivity ($\varepsilon_r$) of all the PLSZT samples at 1 MHz. Among all of the samples, the sample number 4 had the highest value of $\varepsilon_r$ (1620) while the sample number 16 exhibits lowest $\varepsilon_r$ (950). Sample 4 was poled at high temperature (140 °C) while sample 16 was poled at 120 °C. It shows the highest $\varepsilon_r$ was obtained at higher poling temperature because of the increasing in domain wall motion during poling process. Meanwhile, at low temperature the movement of the domain was slow and the dipole was not fully aligned and produced a low dielectric permittivity.

![Fig. 4 Dielectric permittivity of PLSZT samples at different poling parameter](image)

4. SUMMARY

La and Sr co-doped PZT ceramics were produced via high planetary mill. The perovskite structure was exists in PLSZT. The addition of dopants decreased the grain size of sample and increased the $d_{33}$ value. Meanwhile, the result of poling parameters based on DOE shows the highest value of $d_{33}$ (327 pC/N) and $\varepsilon_r$ (1620) at temperature (140 °C) and electric field (4 kV/mm).

ACKNOWLEDGEMENT

The author was very grateful to Universiti Sains Malaysia to support this research, under grant Fundamental Research Grant Scheme (FRGS)-6071282.

REFERENCES

Effect of Soaking Time to the Bending Strength of Porcelain with Palm Oil Fuel Ash

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ABSTRACT. Silica from a treated palm oil fuel ash (POFA) was used as a substitute material in producing an improved porcelain ceramics. POFA was grounded in a ball mill until the median particle size was reduced to about 50 μm. It was heated at 600 °C for 1.5 hours in an electric furnace. Then it was substituted quartz in porcelain composition from 5 wt.% up to 25 wt.%. The mixed powder was pressed into pellets at pressure of 91 MPa. All the pellets were sintered at 1100 °C for the soaking times of 1 hour, 2 hours and 3 hours, respectively. It clearly indicated that the bending strength of the samples increases with the increase in POFA substitution and the increase in soaking time. With a value of 45 MPa bending strength of the samples containing 15 wt.% of POFA and sintered at a soaking time of 2 hours is the highest. This could be attributed from the increase in mullite and sharp microstructural changes. Porcelain containing POFA has about 7% weight reduction compared to the standard porcelain.

Keywords: Bending strength, Bulk density, POFA, Porcelain, Quartz, Soaking time;

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1. INTRODUCTION

Porcelain ceramic is primarily composed of kaolin, feldspar and quartz, heat-treated to form a mixture of glass and crystalline phases (Na\textsubscript{2}O, K\textsubscript{2}O)–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} \cite{1}. Most of the reactions occurring during sintering are kinetically governed processes that do not reach thermodynamic equilibrium, since the industrial cycles are as short as 1 hour. Hence, it is very common for the finished product to contain crystals of quartz and feldspars that have not been entirely transformed. The plastic kaolin components, necessary to attain high green densities and advanced densification of the sintered product in a single fast sintering cycle, disappear completely to form mullite \cite{2}. From an economic perspective, porcelain stoneware accounts for 33% of the entire ceramic tiles market world-wide, at sales levels of 119.5 Mm\textsuperscript{2} in 1997 and 163.8 Mm\textsuperscript{2} in 1998. Moreover, in the last decade the global production, inclusive of porcelain ceramics, was oriented mainly towards large formats (less than 25 tiles per m\textsuperscript{2}), increasing from 42% in 1988 to 82% in 1998 \cite{3}. Despite the commercial interest in developing porcelain ceramic, very little research has been conducted in the field \cite{4}, leaving significant opportunities for investigation and study, particularly in the two topical areas of bending strength property and soaking time, which are the main topic of this paper. The objective of this
The paper is to study the bending strength of porcelain ceramics by substitution of quartz by palm oil fuel ash at different soaking times.

2. MATERIALS AND METHODS

The removal of excess carbon and other unburned organic materials contained in POFA is important to avoid their potential negative effect on finished product. The untreated POFA was dried in an oven at 100 °C for 24 hours and then grounded in a ball mill to reduce the particle size to improve reactivity. Then it was sieved using a set of sieves to remove the particles coarser than 50 µm. The milling time was approximately 1.5 hours at 200 rev/min. The calcination process of the untreated POFA was done at 600 °C for 1.5 hours in an electric furnace.

Porcelain powder was grounded separately in a ball mill. The treated POFA was gradually incorporated into the porcelain powder from 5 wt.% to 25 wt.% as shown in Table 1. The mixing process was done for 1.5 hours in a ball mill. The mixed powder was pressed into pellets at mould pressure of 91 MPa. All the pellets were sintered at 1100 °C for the soaking times of 1 hour, 2 hours and 3 hours, at a heating rate of 5 °C/min, respectively. The chemical composition of the raw materials were studied using X-ray fluorescence (XRF) machine while the amorphous structure of the samples were identified through XRD, and the microstructural features were studied by SEM. The bending strength was determined. The formula for the bending strength of a beam in three-point is as follows.

\[ S = \frac{3PL}{2bd^2} \text{ (MPa)} \]  

where, \( P \) is break load (N), \( L \) is outer (support) span (N), \( b \) is specimen width (cm) and \( d \) is specimen thickness (cm).

3. RESULTS AND DISCUSSION

XRF analysis is proficient in analyzing material contents inside POFA, hence the amount of \( \text{SiO}_2 \) can be observed. The presence of various compounds within porcelain and POFA sample can be seen in Table 2. This table shows the result of XRF analysis of porcelain and POFA. It is evident that \( \text{SiO}_2 \) is the major composition in all the raw materials viz: POFA, kaolin, feldspar and quartz with 66.91 wt.%, 69.30 wt.%, 72.70 wt.% and 99.40 wt.% respectively. Followed by alumina with 6.44 wt.%, 24.30 wt.%, 16.40 wt.% and 0.22 wt.% respectively.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The composition of quartz substitute by POFA (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MixNumber</td>
<td>Kaolin</td>
</tr>
<tr>
<td>AF1</td>
<td>50</td>
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<tr>
<td>AF2</td>
<td>50</td>
</tr>
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<td>AF3</td>
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</tr>
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<td>AF4</td>
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<td>50</td>
</tr>
<tr>
<td>AF6</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Chemical analysis of POFA and porcelain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Content (wt.%)</td>
</tr>
<tr>
<td>Composition</td>
<td>SiO\text{2}</td>
</tr>
<tr>
<td>POFA</td>
<td>66.91</td>
</tr>
<tr>
<td>Kaolin</td>
<td>69.30</td>
</tr>
</tbody>
</table>
Fig. 1 shows the graph of porosity versus POFA content, it can be seen from the graph that the least porosity was recorded with a value of 3.8%, 2.4% and 3.0% at a soaking time of 1 hour, 2 hours and 3 hours, respectively on 15 wt.% of POFA. As the substitution of quartz by POFA increases the porosity decreases until it reaches a minimum value and then increases again. Meanwhile the soaking time of 2 hours shows the least porosity at all composition of substituted POFA.

The sintering process is mainly dominated by surface diffusion at low soaking time and by volume diffusion at high soaking time [5-6]. According to Abadir et al. [7] the temperature coupled with the soaking time have a major role in increasing the diffusion coefficient. Therefore, an increase in soaking time can promote the densification process. In addition, the existence of oxides, such as CaO and K₂O in POFA were beneficial to the formation of low melting liquid. With the increase of soaking time, the low viscosity liquid flowed, filled the pore and consequently helped the densification process. The density of the sintered samples decreased with the high amount of iron content. However, porosity decreases as the substitution increases beyond 15 wt%, this is as result of bloating as confirmed by the SEM (Fig. 4). This result is in agreement with the result obtained by Yanyi [8] and Noh et al. [9].

The bending strength of porcelain tiles were measured as function of soaking time (Fig. 2). It is obvious that these changes in bending strength are related to porosity and bulk density developments in the bodies. The highest bending strength was achieved with value of 31 MPa, 36 MPa and 34 MPa for 1 hour, 2 hours and 3 hours on 15 wt.% of POFA, respectively. The bending strength increased with an increase in soaking time and substitution of POFA. However, after reaching the maximum soaking time at 2 hours, the bending strength begins to decrease due to the porosity development [10].

The bending strength is strongly dependent on the microstructure, especially on defects such as pores and cracks. The bending resistance of porcelain is strictly correlated with the material porosity. The prepared porcelain tile with a high bending resistance presents a very compact texture, a smooth surface with low porosity (Fig. 4(b)). The surface with a wide range of pore sizes, in particular coarse, shows lower mechanical performances. In a study carried out by Ece and Nakagawa [11] proposed that porosity may affect the mechanical properties of ceramic materials in two ways. First, it reduces the effective cross-sectional (load-bearing) area such that the mechanical property will be dependent on the minimum contact-solid area. The minimum solid (load-bearing) area is the actual sintered or the bond area between particles in the case of stacked particles, and it is case of stacked bubbles. Second, porosity leads to stress concentrations near the pores such that under mechanical loading, the true stress in the material is higher near the pores than at a far distance from them [9]. The surface of porcelain presents diverse micro structural elements, either intrinsic
features of the ceramic body (e.g. residual pores) or superficial defects created during the grinding process. This result is in line with bulk density results shown in Fig. 1.

Fig. 2 Effect of soaking time on the bending strength

Fig. 3 shows the XRD patterns of the porcelain body after sintering at 1100 ºC, between the soaking time of 1 hour and 3 hours. The peaks due to a given phase have been labelled. The main mineralogical phases of the sample are identifiable. They are: quartz (ICDD 046-1045), mullite (ICDD 089-2645) and cristobalite (ICDD 039-1425). The intensity of peaks resulting from quartz increases after sintering between the soaking time of 1 hour and 2 hours. Although the quartz is present at all sintering temperatures, the intensity of peaks decreases above the soaking time of 2 hours. Mullite and cristobalite phases, increases with increase in soaking time (Table 3). The reason for the increase in mullite is as result of reaction between $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ in the presence of temperature. While for cristobalite is as a result of quartz disillusion. This result is in agreement with the results obtained by Martín-Márquez et al. [12].

Fig. 3 The XRD curves of the samples containing 15 wt.% POFA

Table 3 XRD quantitative analysis of the body samples containing 15 wt.% POFA

<table>
<thead>
<tr>
<th>Soaking time (Hour)</th>
<th>Quartz (%)</th>
<th>Mullite (%)</th>
<th>Cristobalite (%)</th>
<th>Glassy phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39.2</td>
<td>18.5</td>
<td>20.0</td>
<td>22.3</td>
</tr>
<tr>
<td>2</td>
<td>38.0</td>
<td>31.2</td>
<td>23.7</td>
<td>7.1</td>
</tr>
<tr>
<td>3</td>
<td>32.5</td>
<td>15.1</td>
<td>10.4</td>
<td>58.0</td>
</tr>
</tbody>
</table>
Fig. 4 shows SEM images of the body mixes sintered at different soaking times. The samples sintered at 1100 ºC at a soaking time of 1 hour (Fig. 4a) shows a typical under sintering ceramic microstructure with high porosity. The general microstructure consists of quartz particles, kaolin-derived agglomerates, and a fine matrix of decomposed kaolin and feldspar.

![SEM images of the mixed samples](image)

**Fig. 4** SEM of the mixed samples containing 15 wt.% of POFA sintered at a soaking time of (a) 1 hour, (b) 2 hours and (c) 3 hours. All micrograph were taken with 1000X magnification

The microstructure of the sample sintered at a soaking time of 2 hours (Fig. 4b) is more compacted than that observed at lower soaking times because of the liquid phase formed from the fluxing agents and secondary mullite crystals. Although analysis allowed the quantification of 31.2% of mullite at the soaking time of 2 hours, its (mullite) formation is not visible by SEM, likely due to the small size of the first developed mullite crystals. At the soaking time of 3 hours (Fig. 4c) micro-cracks were developed this could be attributed to bloating due higher soaking time.

4. **SUMMARY**

The bending strength of porcelain body was found to increase with increase in substitution of quartz by POFA and soaking time. With a value of 36 MPa the highest bending strength was achieved at a soaking time of 2 hours on 15 wt.% substitution of quartz by POFA. Furthermore, the progressive substitution quartz by POFA in a porcelain body resulted in early vitrification of the mixtures. The bending strength result indicated that POFA has the potential to be used as a substitutive material and can improve the strength of the recycled aggregates porcelain.

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The authors would like to acknowledge the financial support of Universiti Tun Hussein Onn Malaysia. We would also like to thank the following Mr. Mohd Azrul Nizam bin Mustari, Mr. Fazlannuddin Hanur bin Harith, Mr. Shahrul Mahadi bin Samsudin, Mr. Mohd Tarmizi bin Nasir, Mr. Anuar bin Ismail, Mr. Ahmad Nasrull bin Mohamed, Norsidah Binti Harun, and Nooriskandar Sani for their assistance as laboratory staff.

**REFERENCES**


Effect of UV Irradiation on Apatite Deposition on Anodised TiO₂ Coating Formed Under Mixed Acid Solution

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ABSTRACT. Anodic oxidation method is used to produce thick TiO₂ coating layer in a mixture of acids electrolyte to modify the TiO₂ which is naturally formed on Ti with only few nanometers thick and inert. The TiO₂ coating is then underwent in vitro test to evaluate their bioactivity in simulation body fluid (SBF). In the present work, oxide coatings of TiO₂ were formed on Ti-Cp foil under potentials of 150V at current density of 100 mA.cm⁻² for 10 min. Multiple characterization techniques were used. X-ray diffraction (XRD) is used to obtain mineralogical phase. Scanning electron microscope (SEM) is used to obtain surface morphology. Chemical absorption of the apatite precipitation was tested by using Fourier transform infrared spectroscopy (FT-IR). Surface morphology from the results shows an increased porosity with smaller pore size for TiO₂ formed in mixed acids with higher molar concentration. According to in vitro results it was concluded that apatite precipitation was higher on TiO₂ coatings with increased Ti-O⁻ functional groups formed using UV.

Keywords: Titanium oxide, Anodic oxidation, UV, Simulation body fluid, Bioactivity;

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1. INTRODUCTION

TiO₂ has shown to exhibit strong physicochemical bonding between Ti implant and living bone because of its ability to induce bone-like apatite in body environment [1]. TiO₂ has three crystalline forms such as anatase, rutile and brookite [2] that may present both amorphous and crystalline structures, depending on process parameters. Crystalline oxides, that is, anatase and rutile present several distinctive features, such as photocatalytic behaviour, superhydrophilicity and biocompatible properties [3].

To improve Ti bioactivity, several surface-modifying techniques have been applied, such as chemical treatment, thermal treatment, electrochemical treatment and anodisation methods [4]. Anodic oxidation method is considered one of the most attractive methods for modifying Ti implant surface [3]. Anodic oxidation can form porous and relatively firm TiO₂ layer on Ti which is highly beneficial for the biological performance of the implant [5]. Anodic oxidation of Ti allows the controlled production of a protective oxide surface layer much thicker than that formed naturally. These coatings may be dense or porous, amorphous or crystalline, depending on the conditions, such as electrolyte type, solution concentration, and applied potential [6]. The electrolytes most commonly used to anodise Ti are sulphuric acid H₂SO₄ and phosphoric acid H₃PO₄ [7]. Those aqueous electrolytic solutions which contains modifying elements in the form of dissolved salts which is phosphorous (P) and/or sulfate (S) that incorporate into the resulting TiO₂ coating.

Further improvement of biocompatibility of Ti for orthopaedic and dental applications is endeavoured through the development of bone-likeapatite (hydroxyapatite HA) coating on TiO₂ interface [8]. It was found
that physico-chemical bonding between the metallic implant and living bones could be achieved by the formation of a HA in the body environment [9]. The bioactivity of a material can be predicted from the apatite formation in simulation body fluid (SBF), where the existence of phosphorous, calcium, and/or oxygen on anodised sample indicates that HA has grown on that material.

Recent studies have reported the enhanced of apatite formation ability using UV irradiation on TiO$_2$[10]. This is due to the photocatalytic ability of TiO$_2$ which can be excited with UV irradiation. During immersion in SBF the UV promotes cluster hydroxyapatite (HA) precipitation instead of homogenous HA thin film in the case of dark condition [11].

This work evaluates the formation of HA on TiO$_2$ formed by anodic oxidation. The impact of anodic oxidation parameters on the formation of HA on TiO$_2$ using SBF under UV will also be studied.

### 2. MATERIALS AND METHODS

#### 2.1 Sample Preparation.
Commercially-pure Ti (Cp-Ti) foils of dimensions 25 mm x 10 mm x 0.05 mm were wet hand-polished using 1200 grit (~1 μm) abrasive paper, followed by immersion in an ultrasonic bath with acetone, rinsing with distilled water, and dried in air.

#### 2.2 Anodic Oxidation.
Anodic oxidation was done in an electrochemical cell containing ~0.4 L of diluted mixed aqueous solutions; H$_3$PO$_4$ (Bendosen, 85 wt.%) and H$_2$SO$_4$ (Q-rec, 98 wt.%). The anode and cathode were Ti foil and the anodizing was done with a programmable power supply (Gen 750W/1500W, TDK-Lambda). The anodized foils were cleaned using autoclave and stored in distilled water. The associated experimental parameters are shown in Table1.

#### Table 1 Parameters used for anodic oxidation in H$_2$SO$_4$ and H$_3$PO$_4$ solutions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Electrolyte concentration (M)</td>
<td>0.1 M H$_2$SO$_4$</td>
</tr>
<tr>
<td></td>
<td>2.0 M H$_2$SO$_4$</td>
</tr>
<tr>
<td></td>
<td>0.1 M H$_3$PO$_4$</td>
</tr>
<tr>
<td></td>
<td>2.0 M H$_3$PO$_4$</td>
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<tr>
<td></td>
<td>0.1 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$</td>
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<tr>
<td></td>
<td>0.1 M H$_2$SO$_4$ + 2.0 M H$_3$PO$_4$</td>
</tr>
<tr>
<td></td>
<td>2.0 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$</td>
</tr>
<tr>
<td>DC Voltage (V)</td>
<td>150</td>
</tr>
<tr>
<td>Current Density (mA.cm$^{-2}$)</td>
<td>100</td>
</tr>
<tr>
<td>Duration (min)</td>
<td>10</td>
</tr>
</tbody>
</table>

#### 2.3 Apatite Formation Evaluation.
After anodic oxidation process, TiO$_2$ coating samples were subjected to in vitro test where they were immersed in SBF (1.5 M) at 36.5°C in a water bath under irradiation of UV mercury lamb (Cole-Parmer®, wavelength 365 nm, 9 W/cm$^2$) for 6 days. SBF were prepared according to Kokubo method [12]. The apatite formation was then evaluated using SEM, XRD, EDX and FTIR.

#### 2.4 Characterization.
The mineralogical phases of the coatings were determined using (1) X-ray diffraction (XRD, PANalytical X'Pert3 Powder), (2) the surface morphology were examined using a scanning electron microscope (SEM, Hitachi SUJ510) at accelerating voltage of 15 kV, (3) Elemental analyses were done using attached Energy dispersive spectrometer (EDS) (Horiba EmaxX-act®) and (4) the chemical absorption of the apatite precipitation were tested using Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Spectrum 100).
3. RESULTS AND DISCUSSION

Phase mineralogical analysis of TiO$_2$ coatings produced by individual and mixed acids solutions are shown in Figs. 1 and 2. Anatase (TiO$_2$, JCPDS card #00-021-1272) and rutile (TiO$_2$, JCPDS card #01-072-7374) crystalline can be observed. TiO$_2$ crystalline phases (anatase and rutile) can be observed on TiO$_2$ formed under H$_2$SO$_4$ solution, and mixture solution with higher H$_2$SO$_4$ concentration (Fig 1). While TiO$_2$ coatings formed under H$_3$PO$_4$ solution and mixture solution with higher H$_3$PO$_4$ concentration have observed amorphous structure (Fig. 2).

Fig. 1: Phase mineralogical analysis of TiO$_2$ anodised in 0.1 M H$_2$SO$_4$, 2.0 M H$_2$SO$_4$, 0.1 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$, and 2.0 M H$_2$SO$_4$ + Μ H$_3$PO$_4$ at current density 100 mA.cm$^{-2}$

Fig. 2: Phase mineralogical analysis of TiO$_2$ anodised in 0.1 M H$_3$PO$_4$, 2.0 M H$_3$PO$_4$, 0.1 M H$_2$SO$_4$, 0.1 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$, and 2.0 M H$_3$PO$_4$ + Μ H$_3$PO$_4$ at current density 100 mA.cm$^{-2}$

Fig. 3 Surface morphology of TiO$_2$ film surfaces obtained as follows: (a) 0.1 M H$_2$SO$_4$, (b) 0.1 M H$_3$PO$_4$, (c) 2.0 M H$_3$PO$_4$, (d) 2.0 M H$_3$PO$_4$, (e) 0.1 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$, (f) 2.0 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$, and (g) 2.0 M H$_3$PO$_4$ + 0.1 M H$_2$SO$_4$ at current density 100 mA.cm$^{-2}$

It can be noticed that the surface morphology at lower molarity (0.1 M Fig. 3 (a and b)) at both electrolytes has unorganized surface structure, where some areas has pores and others don't. While the structure at higher molarity and mixed acids have obtained organized surface porosity (Fig. 3 (c-g)). The
porosity at 2.0 M H$_2$SO$_4$ (Fig. 3 (c)) take donut-like shape while it take flat shaped pores at 2.0 M H$_3$PO$_4$ (Fig. 3 (d)) and its average pores size is lower than the average size of the pores at 2.0 M H$_2$SO$_4$. However, the porosity takes sponge-like shape at mixed electrolyte (2.0 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$) (Fig. 3 (f)), while it takes volcano-like shape at 0.1 M H$_2$SO$_4$ + 2.0 M H$_3$PO$_4$ (Fig. 3 (g)). In general, it can be noticed the average pore size of the coatings anodized in mixed electrolytes is lower than their corresponding at individual electrolytes.

According to in vitro results under UV irradiation in SBF the apatite precipitation on TiO$_2$ was obtained as shown in Fig. 4. It can be seen that apatite precipitation was in a form of clusters. This is due to the increased formation of Ti-O functional groups on TiO$_2$ surface that induce Ca$^{2+}$ ions which is believed to be caused by UV. This phenomenon has been explained by [13]. Apatite formation was highly obtained on Fig. 4 (a, b, f and g), which corresponds to apatite formed on TiO$_2$ anodised in low molar solutions and mixed solution with higher molarity.

Fig. 4 Surface morphology of TiO$_2$ surfaces immersed for 6 days in SBF under UV is obtained as follows: (a) 0.1 M H$_2$SO$_4$, (b) 0.1 M H$_3$PO$_4$, (c) 2.0 M H$_2$SO$_4$, (d) 2.0 M H$_3$PO$_4$, (e) 0.1 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$, (f) 2.0 M H$_2$SO$_4$ + 0.1 M H$_3$PO$_4$ and (g) 2.0 M H$_3$PO$_4$ + 0.1 M H$_2$SO$_4$ at current density 100 mA.cm$^{-2}$
However, these coatings have different mineral composition as seen in Figs. 1 and 2 and different surface morphology as obtained in Fig. 3. This can be related to the Ti-O functional groups formed using UV. Phase mineralogical analysis spectra has confirmed the formation of crystalline apatite (HA, JCPDS card #00-055-0592) on all TiO\textsubscript{2} coatings surface as shown in Figs. 7 and 8. Peaks oriented at (002) and (211) were higher on TiO\textsubscript{2} anodised in 0.1 M H\textsubscript{2}SO\textsubscript{4}, 0.1 M H\textsubscript{3}PO\textsubscript{4} and 2.0 M H\textsubscript{2}SO\textsubscript{4} + 0.1 H\textsubscript{3}PO\textsubscript{4}. These results are in a good agreement with the surface morphology results in Fig. 4. Which promote that higher apatite precipitation obtained higher HA crystalline.

Absorption spectra for TiO\textsubscript{2} as shown as Figs. 7 and 8 have a presence of sulfone (S=O) at band 1300-1350 cm\textsuperscript{-1} on TiO\textsubscript{2} anodised in H\textsubscript{2}SO\textsubscript{4} solution and phosphine (P-H) at band 950-1200 cm\textsuperscript{-1} was obtained on TiO\textsubscript{2} anodised in H\textsubscript{3}PO\textsubscript{4}. Both sulfone and phosphine were obtained on TiO\textsubscript{2} anodised in mixed solutions. Hydroxyl groups (OH) stretching region 3100-3400 cm\textsuperscript{-1} except for TiO\textsubscript{2} anodised in 2.0 M H\textsubscript{2}SO\textsubscript{4} and Ti-OH at band 3635, 3645, 3750 and 3840 cm\textsuperscript{-1} was also obtained on all the coatings. Water (H\textsubscript{2}O) at band 1860 cm\textsuperscript{-1} was also obtained on all the coatings, especially in coatings anodised in higher H\textsubscript{2}SO\textsubscript{4} concentration and in mixed solution with higher H\textsubscript{2}SO\textsubscript{4}, which obtained stronger water absorption band. This can be due to the water trapped inside the grooves on their complicated porous structure (Fig. 3).

Figs. 7 and 8 show absorption spectra for TiO\textsubscript{2} irradiated with UV for 12 hours. It can be seen that Ti-O functional group stretching has increased on all the coatings after exposed to UV. This has happened because TiO\textsubscript{2} (anatase) display photocatalytic activity under UV. Therefore, results in a formation of hydroxide groups [15]. Ti-OH groups then react with OH\textsuperscript{-} to form Ti-O\textsuperscript{2-} groups [14]. This could be related to the sharp stretching of Ti-OH at band 1100 cm\textsuperscript{-1} as seen in Fig. 9 for anatase crystalline TiO\textsubscript{2} coated anodised in 2.0 M H\textsubscript{2}SO\textsubscript{4} + 0.1 M H\textsubscript{3}PO\textsubscript{4}. It can be noticed that higher apatite formation has been resulted on coatings anodised in 0.1 M H\textsubscript{3}PO\textsubscript{4}, 0.1 M H\textsubscript{2}SO\textsubscript{4} and 2.0 M H\textsubscript{2}SO\textsubscript{4} + 0.1 M H\textsubscript{3}PO\textsubscript{4} as seen in Fig. 4 according to surface morphology. Along with higher HA crystallinity as resulted in Figs. 5 and 6 according to the phase mineralogy. This is can be related to larger Ti-O\textsuperscript{2-} stretching as obtained in coatings anodised in 0.1 M H\textsubscript{3}PO\textsubscript{4} and 2.0 M H\textsubscript{2}SO\textsubscript{4} + 0.1 M H\textsubscript{3}PO\textsubscript{4}. TiO\textsubscript{2} anodised in 0.1 M H\textsubscript{2}SO\textsubscript{4} has originally high Ti-O\textsuperscript{2-} stretching although it did not obtain significantly larger Ti-O\textsuperscript{2-} stretching after UV irradiation.
4. SUMMARY

The effect of UV irradiation on apatite deposition on anodised TiO$_2$ coating formed under mixed acid solution was successfully investigated. Based on in vitro results it was concluded that apatite precipitation was higher on TiO$_2$ coatings with increased Ti-O- functional groups formed using UV.

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Enhanced Visible Light Response of Phosphorus Incorporated TiO₂ Nanotube Arrays Photocatalyst

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ABSTRACT. Titanium dioxide (TiO₂) nanotubes incorporated with phosphorus (P) were synthesized via anodization of Ti in the electrolyte containing H₃PO₄ and ethylene glycol (EG) with 0.66 wt.% NH₄F. The morphology of the TiO₂ nanotubes can be tuned by changing the H₃PO₄ and EG contents. The TiO₂ nanotubes with 3.1 µm length and approximately 103 nm average diameter were as-anodized in 90 EG:10 H₃PO₄ at 30 V for 1 hour. The length and average diameter of the nanotubes increased with increasing voltage and water amount. The length of the nanotubes was 5.3 µm and the average diameter was 128 nm under optimized conditions (90 EG:10 H₃PO₄:1 H₂O at 60 V for 1 h). The as-anodized TiO₂ nanotubes were annealed under different atmospheres (argon and nitrogen) at 400 °C. XRD analysis revealed that the TiO₂ nanotubes were anatase. When the TiO₂ nanotubes were annealed in argon or nitrogen, a high photoluminescence (PL) intensity at 2.4 eV was observed in response to the 325nm light excitation. The high PL intensity is due to the increase in the number of defects upon reduction. According to photocatalytic degradation of methyl orange, the P doped TiO₂ nanotubes exhibited enhanced photocatalytic activity compared with carbon doped TiO₂ nanotubes, which might be a result of the P-incorporated induced band gap narrowing.

Keywords: TiO₂ Nanotubes, Anodization, Phosphorus doped, Dye Degradation;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Photocatalysis is not only an important industrial process in wastewater treatment but also in heavy metal remediation, sterilization and others. Recent work on titanium dioxide (TiO₂) has showed that it is widely used as photocatalyst for its efficiency, low cost and high stability [1]. However, it is activated only under UV light irradiation because of its large band gap (3.2 eV for anatase). As only 3% of the solar spectrum has wavelength shorter than 400 nm, it is very important to develop efficient visible light sensitive photocatalyst by the modification of TiO₂.

Recently, researchers [2,3] found that modification of TiO₂ by phosphorus seems to be a promising approach to enhance the photocatalytic activity. P-doped TiO₂ prepared by sol-gel method with NaH₂PO₃ as precursor showed an improved optical absorption in the visible light range [4]. Lv et al. [5] reported that P-doped TiO₂ showed higher photocatalytic degradation of RhB under solar light and UV light irradiation than pure TiO₂.

In this work, P incorporated TiO₂ NT prepared by anodization in ethylene glycol and phosphoric acid was demonstrated. The morphology, crystal structure and electronic structure of the samples formed at different applied voltage were characterized. In addition, the effect of annealing atmosphere on the chemical
composition was also studied. The effects of the surface properties on the photocatalytic activity were done by degradation of methyl orange (MO).

2. MATERIALS AND METHODS

A 1 x 5 cm² (Strem Chemicals, 0.27 mm thick) Ti foils were ultrasonically cleaned in acetone for 15 minutes followed by rinsed with deionized (DI) water and then air dried. Highly oriented P-TiO₂ NT arrays were fabricated by anodization in ethylene glycol (EG) and phosphoric acid (H₃PO₄) mixture electrolyte with 0.66 wt.% ammonium fluoride (NH₄F) using a Keithley Series 2611A potentiostate (60 V) and a conventional two-electrode configuration with platinum as cathode and Ti foil as anode. The anodization process was done for 1 hour. Afterward, the samples were cleaned in ultrasonic bath of acetone for 1 min, followed by rinsed with DI water and dried in a nitrogen stream. The obtained highly ordered CP-TiO₂ NT were annealed in an argon atmosphere at 400 °C for 4 hours with heating and cooling rate of 5 °C min⁻¹. The morphology of the CP-TiO₂ NT arrays was characterized using field emission scanning electron microscope (FESEM-EDX, Zeiss, Supra 35VP). X-ray diffraction (XRD, Phillip model PW 1729) were carried out to study the crystal structure of P-TiO₂ NT, while photoluminescence (PL, JovinBr). The photodegradation activities of CP-TiO₂ NT were evaluated by the degradation of methyl orange (MO). The initial concentration of MO was 30 ppm. The experiment was performed under sunlight for 5 hours. The concentration of MO was monitored by measuring the absorbance of samples at 465 nm using UV-Vis spectrophotometer (Perkin Elmer).

3. RESULTS AND DISCUSSION

FESEM images in Fig. 1 reveal that Ti anodized at 30V to 60V resulted in a formation of well aligned nanotubes. It is noticeable that the diameter and the length of the nanotubes increase with voltage. At higher anodization voltage, the electric field dissolution at the barrier layer occurs much higher resulting Ti-O bond undergoes polarization and become weakened promoting dissolution of the Ti⁴⁺. This will lead to greater driving force for ionic transport through the barrier layer at the bottom of the nanotubes favouring formation of [TiF₄]²⁻ complex that will eventually accelerate the pore growth. At the same time, the faster movement of the Ti/TiO₂ interface into the metal [6] resulted in the formation of long nanotubes. Based on the results, sample anodized at 60 V is selected for further investigation due to its higher length and larger diameter which are approximately ~5.3 µm and ~128 nm, respectively. The EDX result of the Ti anodized at 60 V shows that carbon and phosphorus content in the TiO₂ nanotubes are 10.92 At.% and 0.40 At.% respectively.

The XRD pattern of the CP-TiO₂ NT arrays anodized at different voltages are shown in Fig.2. The peaks for samples made in different voltages match well with anatase phase (PDF, No. 96-900-8214). However, the intensity of the anatase peak was different for sample anodized at different voltages. The intensity of anatase peak increases with increasing voltages. Such phenomenon could be related to the formation of more weakly crystalline CP-TiO₂ NT formed by anodic oxidation with increasing voltage. According to Habazaki et al [7], the formation of crystalline TiO₂ is possible when the formation is carried out at a certain threshold voltage where the amorphous to crystalline transformation is made possible. The said work referred 20 V as the voltage which allows this transformation to occur. The formation of the weakly crystalline oxide is believed not uniform throughout the oxide and is localized at certain region in a matrix of amorphous-like oxide. With annealing process, the weakly crystalline nanotubes transform to crystal structure corresponding to better crystallization of nanotube arrays.

The effects of annealing atmospheres were studied by annealing the CP-TiO₂ NT arrays in Ar and N₂. Both samples were anodized in optimized volume fraction of 90:10 (EG: H₃PO₄) with addition of 0.66 wt.% NH₄F at 60 V for 60 min prior to annealing process. The surface morphology of CP-TiO₂ NT annealed in Ar is shown in Fig.1(d) while CP-TiO₂ NT annealed in N₂ is shown in Fig.3. Annealing in argon atmosphere resulted in a formation of nanotubes with smoother and more uniform tubes whereas the sample annealed in nitrogen atmosphere is more rigid and less uniform. This may be due to the inert properties of argon gas which is less reactive compared to nitrogen gas.
Figure 1: FESEM images of CP-TiO$_2$ NT formed in 90:10 (EG:H$_3$PO$_4$) electrolyte containing 0.66 wt.% NH$_4$F for 60 min at (a) 30, (b) 40, (c) 50 and (d) 60 V. The inset shows the cross-section view of respective morphologies. (FESEM images taken after annealing at 400 °C for 4 hours in argon atmosphere)

Figure 2: XRD patterns of CP-TiO$_2$ NT prepared in 90:10 (EG:H$_3$PO$_4$) at (a) 30 V, (b) 40 V, (c) 50 and (d) 60 V for 60 min after annealed in argon atmosphere for 4 hours at 400 °C.
However, the dimensions of the tubes annealed in both atmospheres are almost similar; tube length, tube diameter and wall thickness approximately ~5.3 μm, ~150 nm and ~18 nm respectively. Besides that, the EDX show that the incorporation of C and P are 10.92 At.% and 0.40 At.% in Ar atmosphere whereas 5.03 At.% and 0.46 At.%, respectively.

![Fig.3 FESEM images of CP-TiO$_2$NT formed in 90:10 (EG: H$_3$PO$_4$) electrolyte containing 0.66 wt% NH$_4$F for 1 hr at 60 V and subsequent annealed at 400 °C for 4 hours in N$_2$. The inset shows the cross-section view of respective morphologies.](image3.png)

The PL results are shown in Fig.4. The room temperature PL spectra of CP-TiO$_2$ NT annealed in Ar and N$_2$ were obtained using the wavelength at the range of 325 nm to 800 nm. Based on Fig.4, the PL signals show there are two peaks at 400 nm and 525 nm appear for both samples. The band gap energy corresponds to peak at 400 nm 3.1 eV and for 525 nm 2.7 eV. This proves that there is an intermediate energy level in the TiO$_2$ energy band gap. It may be due to oxygen vacancies, defects, C and P dopants present in the TiO$_2$ NT.

![Fig.4 PL spectra and their Gaussian fit band of CP-TiO$_2$ NT formed in 90:10 (EG: H$_3$PO$_4$) electrolyte containing 0.66 wt% NH$_4$F for 1 hr at 60 V and subsequent annealed at 400 °C for 1 hours in (a) Ar and (b) N$_2$ atmosphere (excitation wavelength = 325 nm)](image4.png)
Fig. 5 shows the results of MO decolorization by C-TiO$_2$ NT formed in pure EG and CP-TiO$_2$ NT formed in EG:H$_3$PO$_4$ (90:10) under visible light irradiation. As seen from Fig. 5 C-TiO$_2$ NT formed in CP-TiO$_2$ NT formed in EG:H$_3$PO$_4$ (90:10) has high PC activity (29%) as compared to pure EG which has only 12% decolorization rate due to low AR of nanotubes obtained in C-TiO$_2$ NT.

**Fig. 5** Visible light decolorization of MO solution using CP-TiO$_2$ NT prepared in 90:10 (EG:H$_3$PO$_4$) electrolyte at 60 V for 60 min and pure EG containing 0.66 wt.% NH$_4$F.

**4. SUMMARY**

CP-TiO$_2$ NT can be successfully formed by anodization process in EG:H$_3$PO$_4$ (90:10) and 0.66 wt.% NH$_4$F at 60 V for 60 min with length of 5.4 μm, wall thickness of 32.2 nm and pore diameter of 128.64 nm. The rate of formation was 89.26 nm/min. This allows the effective photocatalytic degradation of MO with degradation rate of 29% compared to 12% using C-TiO$_2$ NT.

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**REFERENCES**


Enhancement of Double-Exchange Mechanism in Charge-Ordered Pr$_{0.75}$Na$_{0.25}$MnO$_3$ Ceramics by Cr Doped at Mn-Site

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ABSTRACT. Charge ordered Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ ($x = 0 - 0.04$) ceramics has been investigated to study the effect of Cr doping on structure and electrical transport properties as well as surface morphology which synthesized using the solid-state reaction method. X-ray diffraction (XRD) analysis revealed the crystalline phase of all samples consists of essentially single phase and crystallized in an orthorhombic structure. The Cr doping were influence the lattice parameters and the unit cell volume suggestively due to the different of ionic radius between Mn$^{3+}$ ions and Cr$^{3+}$ ions. DC electrical resistance measurement showed that, the $x = 0$ sample exhibited an insulating behaviour down to the lower temperature. Interestingly, the metal-insulator (MI) transition temperature for $x = 0.02$ and $x = 0.04$ samples were found to be around $T_{MI} \sim 120$ K and $T_{MI} \sim 122$ K respectively indicating the enhancement of double-exchange (DE) mechanism as a result of weakening the Jahn-Teller (JT) effect which caused the charge ordered (CO) state to be weakened. scanning electron microscope (SEM) images of Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ compound showed the morphology of the samples were quite uniform suggestively due to the good crystalline nature.

Keywords: Double-exchange mechanism, Charge ordering, Electrical properties;

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1. INTRODUCTION

Rare-earth manganites with perovskite structure of the general composition of type Re$_{1-x}$A$_x$MnO$_3$ where Re is a trivalent rare-earth ion such as La, Nd, Dy, Pr and A is a divalent alkaline-earth such as Ca, Sr or Ba has been received remarkable attention due to their unique physical properties as well as potential applications [1-6]. In addition, studies on these rare-earth manganites have revealed that colossal magnetoresistance (CMR) effect which is commonly attributed to the double-exchange (DE) mechanism is also suggested to be related to the Jahn-Teller (JT) effect and charge ordering (CO) [7]. Interestingly, the Pr$_{0.75}$Na$_{0.25}$MnO$_3$ has attracted interest due to the existence of CO transition at a higher temperature compared to anti-ferromagnetic (AFM) ordering ($T_{CO} \sim 260$ K, $T_N \sim 160$ K) [8,9].

Many reports showed that substitution directly at Mn-sites with a certain amount of transition metal element have influenced the physical properties of the material as well as charge-ordered (CO) state [7-11]. For instance, previous study on Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Fe$_x$O$_3$ [7] have shown the resistivity decreases with Fe content up to $x \leq 0.05$, and then increases subsequently with further Fe doping indicating a suppression of double exchange (DE) mechanism. Meanwhile, for Pr$_{0.6}$Na$_{0.2}$Mn$_{1.3}$Co$_{0.3}$ [10], the composition of $x = 0.04$...
showed metal-insulator (MI) transition connected with a ferromagnetic (FM) arrangement [10]. However, very few studies on effect of magnetic ion-doped at Mn-site are available in the literatures.

The Cr$^{3+}$ ion was suggested to be very effective element to suppress CO as well as induced the phase transition. In addition, Cr doping on the half-doped manganite also reveals a lot of anomalous electrical transport properties [11]. For example, in Nd$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ manganite, the electrical resistivity measurement for $x = 0$ sample showed a signal at 170 K indicates the signal on development of CO state. A MI transition at temperature 75 K was reported by $x = 0.03$ sample and increasing of Cr doped up to $x \leq 0.05$ was caused the MI transition to be disappeared suggestively due to reduction of DE mechanism [11]. Meanwhile, increasing of Cr doped up to $x = 0.07$ for La$_{0.9}$Ca$_{0.1}$Mn$_{1-x}$Cr$_x$O$_3$ compound caused a MI transition to shifted to lower temperature [12]. Thus, considering the entire study above, Cr doped at the Mn-site in Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ is expected to induce a MI transition as well as weakened the CO state as a result of weakening of the JT effect. However, to the best of our knowledge, such study on the Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ compound has not been previously reported.

In this paper, we report the effect of Cr doping on structure and electrical transport properties as well as surface morphology of charge ordered Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ ceramics. Cr doping has been chosen in this work due to the special nature where Cr$^{3+}$ ion which is iso-electronic in configuration with Mn$^{4+}$ ion. In addition, result of density and porosity are also presented and discussed.

2. MATERIALS AND METHODS

The Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ magnetic ceramics samples were synthesized using the solid state reaction method. A stoichiometric amount of Pr$_2$O$_3$, Na$_2$CO$_3$, MnO$_2$, and Cr$_2$O$_3$ powders with high purity ($\geq 99.9\%$) were carefully mixed and ground in an agate mortar with pestle for approximately 2 hours to ensure a homogenous mixture and fine powder was obtained. The mixture powder were then calcined in air at 1000 °C for 24 hours at the rate of 15 °C/min on heating in a Protherm Furnace Model PLF130/15 with several intermediate grinding followed by cooling at rate of 1 °C/min. The powder were then reground again for another a few hours and pressed into pellets in a 13 mm diameter and 2-3 mm thickness using Specac Dice Mole under a load of 6-7 tones using hydraulic pressure equipment. The pellets were then sintered at 1200 °C for 24 hours in air at the rate of 15 °C/min and slow cooled at room temperature at rate of 1 °C/min.

All the synthesized samples were ground again into fine powder and then characterized by X-ray diffraction (XRD) using Bruker D8 Advance model with a Cu$K_\alpha$ (1.544 Å) radiation at room temperature. The samples were scanned continuously in the range of $20^\circ \leq 2\theta \leq 80^\circ$ with scanning rate 2°/min. The result from XRD was analysed using X’Pert HighScore programme to confirm the crystalline phase of material. Resistivity of the samples was measured using the standard four probe method. The current leads and voltage leads were attached to the sample (typically, $\sim 10$ mm long, $\sim 3$ mm wide and $\sim 1$ mm thick) with silver paste and this characterization was performed in a Janis Cryostat Model CCS-350ST under zero magnetic fields. Microstructural characterization of the pellets sample was done using scanning electron microscope (SEM) by Hitachi SU1310 operating at 5 KV. Bulk density of the samples was determined by employing the Archimedes principle using acetone as the liquid buoyant.

3. RESULTS AND DISCUSSION

Fig. 1 shows the powder XRD patterns for all the Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ ($x = 0-0.04$) samples. XRD analysis revealed all the samples are essentially single phased and the peaks can be indexed to an orthorhombic structure with space group Pnma with no detectable impurity peaks and it is in line with the structure reported from the previous study [13,14]. Table 1 shows values of MI transition temperature ($T_{MI}$), lattice parameters, calculated unit cell volume ($V$), density ($D$) and porosity for all samples. It is interesting to see that the lattice parameters as well as calculated unit cell volume, $V$ decrease continuously with Cr content. In addition, the lack of existence of secondary phase from the XRD diffractogram and the decreasing of the $V$ of the samples with Cr content indicate some form of substitution involving of Cr$^{3+}$ ion taking place in the crystal
lattice which can be suggested to be due to the Cr$^{3+}$ ions has a smaller ionic radius (0.615 Å) continuously replaces the Mn$^{3+}$ ion with higher ionic radius (0.645 Å) [15,16]. A similar suggestion was also proposed for Nd$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Cr$_x$O$_3$ [15]. Apart from that, the substitution of Cr$^{3+}$ was also suggested to induce the lattice distortion and rearrangement of atom as a results of smaller cation in the B-site of the ABO$_3$ perovskite structure is responsible for the reduction in unit cell volume [17-19].

![Fig. 1 X-ray powder diffraction (XRD) pattern of Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ (0≤x≤0.04) samples](image)

Fig. 1 X-ray powder diffraction (XRD) pattern of Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ (0≤x≤0.04) samples

Fig. 2 shows the temperature dependence of the electrical resistivity for x = 0-0.04 samples. The x = 0 sample showed an insulating behavior in the temperature range of 80 K-300 K. Interestingly, a MI transition was observed at around $T_{MI} \approx 120$ K and $T_{MI} \approx 122$ K for the x = 0.02 and x = 0.04 samples respectively. The shifting of the MI transition to higher temperatures can be suggested to be due to the enhancement of double-exchange (DE) mechanism (Cr$^{3+}$-O-Mn$^{3+}$) as a result of weakening the Jahn-Teller (JT) effect indicating the CO state to be weakened. In fact, it is in line with a previous report [15]. The DE mechanism between Mn$^{3+}$ ion and Cr$^{3+}$ ion has been suggested to be possible occurs in this study due to the Cr$^{3+}$ ion may have a similar role with Mn$^{4+}$ where the Cr$^{3+}$($t_{2g}^{3}e_{g}^{0}$) ion have same electronic configuration with Mn$^{4+}$($t_{2g}^{3}e_{g}^{0}$) ion [15,20]. Apart from that, the increasing of Cr content also influenced the intensity of the resistivity where this can be suggested to be due to the increase of carrier concentration as result of enhancement of the DE mechanism [15].

![Fig. 2 Temperature dependence of the electrical resistivity of Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ (0≤x≤0.04)](image)

Fig. 2 Temperature dependence of the electrical resistivity of Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Cr$_x$O$_3$ (0≤x≤0.04)
Table 1 MI transition temperature ($T_{MI}$), lattice parameters, unit cell volume ($V$), density ($D$) and porosity of $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 0.04$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{MI}$ (K) ($\pm 0.1$)</th>
<th>Lattice parameter (Å) ($\pm 0.001$)</th>
<th>$V$ (Å³) ($\pm 0.1$)</th>
<th>$D$ (g/cm³) ($\pm 0.01$)</th>
<th>Porosity (%) ($\pm 0.1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.0$</td>
<td>-</td>
<td>a (Å) 5.446, b (Å) 7.696, c (Å) 5.445</td>
<td>228.2</td>
<td>5.71</td>
<td>11.0</td>
</tr>
<tr>
<td>$x = 0.02$</td>
<td>120.0</td>
<td>a (Å) 5.448, b (Å) 7.669, c (Å) 5.443</td>
<td>227.4</td>
<td>5.68</td>
<td>13.0</td>
</tr>
<tr>
<td>$x = 0.04$</td>
<td>122.0</td>
<td>a (Å) 5.449, b (Å) 7.659, c (Å) 5.444</td>
<td>227.2</td>
<td>5.51</td>
<td>14.0</td>
</tr>
</tbody>
</table>

On the other hand, the effect of Cr-doped on the surface morphology of the $x = 0-0.04$ samples are shown as in Fig. 3. The microstructure of the samples were discussed based on the images obtained from SEM. It can be seen that, all samples showed nearly spherical shape and the morphology of the samples were quite uniform suggestively due to the good crystalline nature of these sample [19]. Meanwhile, the values of porosity was observed to be increase with the increase of Cr doping in conjunction with the values of calculated unit cell for the samples which can be suggested to be due to difference of ionic radius between Cr$^{3+}$ ions and Mn$^{3+}$ ions.

![Fig. 3 SEM images for $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ samples (a) $x = 0.0$, (b) $x = 0.02$ and (c) $x = 0.04$](image)

4. SUMMARY

In conclusion, the influence of Cr doped in $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 0.04$) magnetic ceramics has been studied. It was found that, the calculated unit cell volume, $V$ decrease continuously with Cr content suggestively due to the Cr$^{3+}$ ion has a smaller ionic radius compare to Mn$^{3+}$ ion. Increasing of Cr doped induced a MI transition for $x = 0.02$ ($T_{MI} \approx 120$ K) and $x = 0.04$ ($T_{MI} \approx 122$ K) samples suggested to be due to the enhancement of double exchange (DE) mechanism as a result of a weakening of the JT effect. Apart from that, increasing of Cr content also caused a different surface morphology for the all samples indicating the Cr doped play an important role on influencing the properties of materials.

ACKNOWLEDGEMENT

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Fabrication and Characterization of Anorthite-Based Porcelain using Malaysian Mineral Resources

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ABSTRACT. The purpose of this study is to design a porcelain based on anorthite whose properties will fulfill the tableware market requirements such as high appearance quality and strength. To obtain the anorthite based porcelain, minerals such as ball clay, quartz, feldspar and dolomite were used as raw materials. The anorthite porcelain test pieces were fabricated by uniaxial pressing with 65 MPa and followed by sintering at 1100 °C, 1120 °C, 1150 °C, 1180 °C and 1200 °C for 1 hour soaking. The maximum flexural strength achieved was ~73 MPa when the dolomite used was less than 10 wt.% (TP2) and is comparable with that of the conventional porcelain.

Keywords: Anorthite-based ceramics, Porcelain, Ceramic table wares;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Bone china is a highly specialized product in terms of its appearance such as excellent whiteness and good translucency which make it the most premium type of tablewares in the world. Typical composition of bone china bodies are 50 wt.% bone ash, 25 wt.% china clay or kaolin and 25 wt.% feldspar. After sintering, the phases in the fired body usually consisted of 40 wt.% β-tricalcium phosphate (β-Ca₃(PO₄)₂), 30 wt.% anorthite (CaO.Al₂O₃.2SiO₂) and 30 wt.% calcium aluminosilicate glass [1]. Hence, bone china bodies are extremely crystalline which possessed good resistance to chipping and having high flexural strength of value about 100 MPa.

Unfortunately, bone china bodies require higher firing temperature to develop maturity in the sintered body. Typically, bone china was sintered at temperature above 1230 °C and then the glaze applied and fired on at the range of 1050 – 1100 °C. Usually, the bone ash used was produced from de-gelatinizing of cattle bones with steam to remove most of the organic matter and then calcined at about 1000 °C [2]. Undoubtedly, non-halal bones were used in production of the bone ash, especially in the major regions of the world. Thus, it had become a sensitive issue and as such it is not preferred by global Muslim consumers. Therefore, another source CaO was studied in the production of anorthite-based porcelain such as dolomite (CaCO₃. MgCO₃), limestone (CaCO₃), wollastonite (CaO.SiO₂) and calcite (CaCO₃).

Nowadays, dolomite was mainly used in the production of anorthite-based porcelain as a CaO source. In Malaysia, dolomite are abundant and cheaper than the other calcium containing minerals. In previous study, anorthite-based porcelain using dolomite as a source of CaO was sintered at low temperature which was less than 1200 °C [1]. This will reduce the cost of production of ceramic tableware products having good physical properties comparable to bone china and unequivocally guaranteed to be halal. In this work, anorthite-based porcelain were prepared using the Malaysian mineral resources namely clay, silica sand and dolomite.
Technological properties such as chemical composition, phase formed, sintering behaviour and flexural strength were investigated and reported in detail.

2. MATERIALS AND METHODS

The studied porcelain bodies were formulated using different combination of four starting raw materials viz. ball clay, feldspar, silica sand and dolomite. Composition of the raw materials are given in Table 1. Two new porcelain bodies (TP2 and TP3) have been designed and a commercial porcelain body (TP1) was used as a comparison. The TP1 was formulated with 30 wt.% ball clay, 40 wt.% feldspar and 30 wt.% quartz. Meanwhile, the TP2 and TP3 bodies were added with 9 wt.% and 23 wt.% dolomite (Table 2), respectively. The mixtures were uniaxial pressed at 65 MPa to produce cylindrical disks with 25 mm in diameter and 8 mm in height. The compacted powders were placed in alumina crucible and sintered at 1100 °C, 1120 °C, 1150 °C, 1180 °C and 1200 °C for 1 h soaking with similar heating rate of 3 °C/min.

### Table 1 Chemical composition of raw materials

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball clay</td>
<td>46.81</td>
<td>37.48</td>
<td>0.58</td>
<td>0.04</td>
<td>0.07</td>
<td>0.16</td>
<td>1.67</td>
<td>0.12</td>
<td>13.02</td>
</tr>
<tr>
<td>Silica sand</td>
<td>98.38</td>
<td>1.02</td>
<td>0.03</td>
<td>0.01</td>
<td>0.08</td>
<td>0.02</td>
<td>0.07</td>
<td>0.04</td>
<td>0.35</td>
</tr>
<tr>
<td>Feldspar</td>
<td>65.56</td>
<td>18.85</td>
<td>0.08</td>
<td>0.02</td>
<td>0.23</td>
<td>0.03</td>
<td>12.39</td>
<td>2.28</td>
<td>0.56</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.18</td>
<td>0.09</td>
<td>0.05</td>
<td>0.01</td>
<td>31.57</td>
<td>20.92</td>
<td>0.01</td>
<td>0.00</td>
<td>47.17</td>
</tr>
</tbody>
</table>

### Table 2 Composition of the investigated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ball clay (gm)</th>
<th>Silica sand (gm)</th>
<th>Feldspar (gm)</th>
<th>Dolomite (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1</td>
<td>30</td>
<td>30</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>TP2</td>
<td>30</td>
<td>30</td>
<td>40</td>
<td>10 (9 wt.%)</td>
</tr>
<tr>
<td>TP3</td>
<td>30</td>
<td>30</td>
<td>40</td>
<td>30 (23 wt.%)</td>
</tr>
</tbody>
</table>

The chemical composition of starting raw materials were determined using X-ray fluorescence (XRF, Shimadzu 1700, Japan). X-ray diffraction (XRD) was carried out to identify the phases present in the sintered bodies using Bruker equipment (Bruker AXS D8 Advance, Germany). The sintered bodies were further examined by measuring some of their physical properties such as linear shrinkage, water absorption, bulk density and flexural strength according to the standard methods as described in ASTM C373.

3. RESULTS AND DISCUSSION

The XRD pattern of samples subjected to the optimal sintering temperature are shown in Fig. 1. Noticeably, anorthite (CaO.Al$_2$O$_3$.2SiO$_2$) (ICDD: 00-018-1202) and quartz (ICDD: 00-046-1045) are the primary crystalline phases with smaller amount of diopside (CaMgSi$_2$O$_6$) (ICDD: 04-015-8345) were formed in TP2 and TP3 as shown in Fig.1, possibly due to the addition of dolomite. The mullite (3Al$_2$O$_3$.2SiO$_2$) (ICDD: 04-016-1586) having a higher density (2.80 g/cm$^3$) than anorthite (2.73 g/cm$^3$) was observed only in TP1 due to the absence of dolomite in the body mixture [3]. Therefore, TP1 exhibited highest bulk density (2.40
g/cm³) mainly due to formation of the mullite phase, and as such was denser than other porcelain bodies (Fig.4).

Fig. 2 and 3 shows the behaviour of the linear firing shrinkage and water absorption as a function of temperature. The linear firing shrinkage increases depending on the degree of sintering up to firing temperature reaching the optimum sintering temperature. It is noticeable that the linear shrinkage behaves differently below and above 1150 °C. The maximum linear shrinkage are 9.3% and 8.3% for TP2 and TP3, respectively, which corresponds fittingly to their volumetric densification [4]. The water absorption decreases with increase in sintering temperature due to reduction of the apparent porosity through the liquid phase sintering [1]. The TP1, TP2 and TP3 were observed to reach a value of water absorption 0.5% at sintering temperatures of 1200 °C, 1150 °C and 1180 °C, respectively.
Fig. 3 Water absorption of porcelain

Fig. 4 shows the variation in bulk density with sintering temperature. The bulk density values continue to increase and optimum values are achieved when the apparent porosity reached a minimum value (Fig. 5). Further sintering results to decrease of bulk density mainly due to expansion of the entrapped gases, commonly known as blisters and bloating [3,5]. The apparent porosity decreases with increasing sintering temperature due to the formation of a glassy phase that is mainly derived from the feldspar. Increased temperatures lead to increase in the amount of liquid phase and decreased viscosity of the liquid phase and filled the pores in the body. Therefore, the porosity in the body decreases [5].

Fig. 4 Bulk density of porcelain
Fig. 5 Apparent porosity of porcelain

Fig. 6 shows the flexural strength behaviour as a function of sintering temperature. The flexural strength of all samples increases with an increase in sintering temperature. On further sintering, the flexural strength values reach maximum values of 62.0 MPa for TP1, 72.4 MPa for TP2 and 71.6 MPa for TP3 and then decrease with a corresponding decrease in density [6]. The maximum flexural strength values for TP1, TP2 and TP3 fulfilled the commercial porcelain strength specification, usually in the range 40 - 80 MPa [3]. Generally, maximum flexural strength develop in a porcelain body when apparent porosity decrease to zero [1]. The similar result was observed in this study.

Fig. 6 Flexural strength of porcelain

4. SUMMARY
Anorthite-based porcelains were fabricated by using CaO source from dolomite. The addition of dolomite into the new formulated porcelain bodies has lowered the sintering temperatures. The samples containing dolomite can easily form substantial glassy phase due to the existence of magnesium element in the material used. The maximum flexural strength achieved was ~73 MPa when dolomite used was less than 10 wt.% (TP2). This meets the strength and appearance quality specifications of commercial porcelains that are available in the market.

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Fabrication of Bioactive Glass Powder Based on SiO₂-CaO-Na₂O-P₂O₅ System at Lower Melting Temperature

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ABSTRACT. In the present work, melt-derived method was deployed to fabricate new composition of bioactive glass (BG) from SiO₂-CaO-Na₂O-P₂O₅ system at lower melting temperature. Amorphous glass nature is discovered through X-ray diffraction (XRD) for all glass composition. Formation of silica network is established with the formation of functional groups Si-O-Si (bend), Si-O-Si (tetrahedral) and Si-O-Si (stretch) within all glass. The bioactivity of all BG composition is evaluated by incubation in Tris buffer solution for 7 days. Several crystalline peaks appeared in XRD after 7 days of incubation with characteristic of carbonate group (C-O) and P-O bands detected in FTIR on hydroxylcarbonate apatite (HCA) formation. Hence, the objective to develop new composition of BG fabricated at lower temperature was achieved with preservation of BG bioactivity.

Keywords: Melt-derived, Water quench, Bioactive glass powder, Bioactivity;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Bioactive glass (BG) is a well-known bioactive material that has the ability to develop hydroxylcarbonate apatite (HCA) layer on the surface which is essential for bond formation with tissue upon implantation in the body [1]. The classic bioactive glass was developed based on silicate network along with other oxides such as calcium oxide (CaO), sodium oxide (Na₂O) and phosphorus pentoxide (P₂O₅). The most widely researched bioactive glass is 45S5 composition and composed of 45SiO₂-24.5Na₂O-24.5CaO-6P₂O₅ in weight percentages (wt.%), also known as Bioglass®. It was reported that 45S5 was successfully used as bone filler in clinical treatment of periodontal diseases and in middle ear surgery [1,2]. The use of BG in such clinical treatment applications is due to the osteoproduction characteristics shown by BG. The prime character is obtained due to the rapid release reaction on BG surface which facilitate in releasing critical concentration of soluble silicon, calcium, sodium and phosphorus ions that induce the attachment, proliferation and differentiation of osteoblast (bone-forming cell) [3].

The capability of implant material to evoke hydroxyapatite (HA) layer on the surface upon immersion in simulated body fluids in vitro is often used as denotation of its bioactivity [4]. The rate of bioactivity of BG is dependent on the rate of ion release from the glass through its aqueous interface [5]. The bioactivity can be tailored and improved by several factors such as modification on the glass composition, pH of surrounding
environment, particle size and surface characteristic of BG [2,5]. Features such as low silica (SiO$_2$), high sodium and calcium oxides (Na$_2$O and CaO) content along with high ratio of calcium to phosphorus content [4,6,7] should be the factors in modification of glass composition. The concentration of phosphorus oxides (P$_2$O$_5$) in BG composition is also vital in stimulating optimum bioactivity of BG. It is reported that increase in P$_2$O$_5$ concentration resulted in faster apatite formation due to enhancement in glass reactivity [8]. A wide range of glass composition has been proposed to improve the biological, mechanical and processing of BG. However, the golden composition of 45S5 is still being used commercially and as subject of researches until today [7]. In addition, most of literature reported on higher melting temperature along with longer soaking time deployed during BG powder fabrication through melt-derived route [9-11].

Hence, the aim of the present work is to develop new composition of BG powder based on SiO$_2$-CaO-Na$_2$O-P$_2$O$_5$ glass network system that can be melted at lower melting temperature and to characterize the BG properties fabricated at different composition and melting temperature. The bioactivity of the BG is evaluated by immersion in Tris-buffer solution.

2. MATERIALS AND METHODS

2.1 Sample preparation. BG powder was produced using high purity and reagent grade silicon dioxide (SiO$_2$), sodium carbonate (Na$_2$CO$_3$), calcium carbonate (CaCO$_3$) and phosphorus pentoxide (P$_2$O$_5$). Briefly, two batches of BG composition were fabricated through melt-derived route. Table 1 presents the detailed on studied glass composition in mole percentages (mol.%). Bioglass (45S5®) composition was used as a control. The weight of each oxide powder was measured prior mixing using analytical balance. The correct amount of each oxide was mixed inside a polyethylene bottle for 24 hour on a horizontal roller at 125 rpm for homogeneity. The powder mixtures were then melted in a platinum crucible at 1400°C for 1 hour with rate of 10°C per minute an electrical furnace. The molten glass was quenched immediately into distilled water to obtain glass frit and dried overnight at 110°C inside an oven. Glass powder was obtained through dry milling using planetary mill, milled at 400 rpm for 1 hour. The glass powder was then sieved to obtain particle size less than 38 µm for material characterization. Similar methods were applied to melt glass with melting temperature defined based on previous work [12].

<table>
<thead>
<tr>
<th>Glass</th>
<th>SiO$_2$</th>
<th>CaCO$_3$</th>
<th>Na$_2$CO$_3$</th>
<th>P$_2$O$_5$</th>
<th>N$_c$</th>
<th>Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>45S5</td>
<td>46.13</td>
<td>26.91</td>
<td>24.35</td>
<td>2.60</td>
<td>2.12</td>
<td>1377</td>
</tr>
<tr>
<td>50S8P</td>
<td>51.89</td>
<td>24.47</td>
<td>20.12</td>
<td>3.51</td>
<td>2.69</td>
<td>1348</td>
</tr>
</tbody>
</table>

2.2 In vitro testing

The glass powder was immersed in Tris-buffer solution, pH 8 inside an incubator shaker with temperature set to 37°C at 100 rpm for 7 days. After immersion, the glass powder was filtered using filter paper and dried inside an oven for 1 hour at 70°C.

2.3 Sample characterization

The properties of glass powder were studied before and after immersion in Tris-buffer solution.

2.4 X-ray diffraction (XRD)
The phase composition of each glass composition was verified using X-ray diffraction (XRD) (Bruker D8 Advance) with copper anode (Cu Kα, λ = 1.5406 Å) where the patterns were recorded in a 2θ range from 10-70°.

2.5 Fourier transform infrared spectroscopy (FTIR)

The surface structural analysis of glass powders was identified using FTIR. The sample was analyzed with transmission technique using KBr pellets as a reference. The glass powder and KBr was mixed with ratio of 9 to 1 and pressed into pellet with diameter less than 5mm using handpressed machine. FTIR spectra for each glass composition were recorded between wavenumber 2000 and 400 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1 Characterization on BG powder before immersion in Tris-buffer solution

X-ray diffraction Analysis. Amorphous structure is observed for all glass composition with broad peaks between 30°-35° after glass melting without appearance of sharp Bragg peaks as shown in Fig. 1. This result indicated that the process step in forming glass via melt-derived is consistent although it was melted at different melting temperatures. The amorphous structure is obtained as glass melt is rapidly quenched in water in order to prevent phase separation [13].

![Fig. 1 X-ray diffraction of glass powder prior immersion in Tris-buffer solution](image)

3.2 Fourier transform infrared spectroscopy (FTIR). Characteristic of silica network is observed for all glass composition with peaks observed at 508 cm⁻¹ indicated the Si-O-Si bending mode, 751-768 cm⁻¹ assigned to Si-O-Si symmetric stretching mode of bridging oxygen atoms between tetrahedron, 902- 1082 cm⁻¹ corresponding to asymmetric stretching mode of Si-O-Si bonding, shown in Fig. 2 [14-16]. Existence of
residual carbonate group is observed at band located at 1459 cm\(^{-1}\) while presence of water adsorption at glass surface is notified at 1654 cm\(^{-1}\) [16].

![FTIR spectra of glass powder prior immersion in Tris-buffer solution](image)

**Fig.2** FTIR spectra of glass powder prior immersion in Tris-buffer solution

### 3.3 Characterization on BG powder after immersion in Tris-buffer solution

**X-ray diffraction (XRD).** Structural changes observed for all glass composition after 7 days immersion in Tris-buffer solution is shown in Fig. 3. However, lower intensity of crystalline peaks is observed for BG melted at lower melting temperature. The crystalline peak emerged at 26° observed for all glass composition is equivalent to the plane (002) in HA [16, 17]. This indicates process of ion leaching of glass occurred which initiates the formation of silica rich layer and calcium phosphate (CaO-P\(_2\)O\(_5\)) leading to the growth of apatite layer on glass surface [1].

![XRD pattern for 45S5 (a) and 50S8P (b) after immersion in Tris-buffer solution for 7 days](image)

**Fig.3** XRD pattern for 45S5 (a) and 50S8P (b) after immersion in Tris-buffer solution for 7 days
3.4 Fourier transform infrared spectroscope (FTIR). Formation of apatite is observed for all BG powder after 7 days immersion in Tris-buffer solution, shown in Fig. 4. Bands appeared at 803 cm\(^{-1}\) and 997 cm\(^{-1}\) indicating the formation of Si-O symmetric and O-Si-O asymmetric stretching vibration which highlights formation of Si-OH group due to ion exchange from solution after glass leaching leading to the growth of silica-gel layer on the glass surface [16, 18]. The present of split dual band at range of 550 to 600 cm\(^{-1}\) show characteristic of P-O (crystalline) in HA [16, 19]. Decomposition of original peak at 1459 cm\(^{-1}\) into split dual band at range of 1400 to 1500 cm\(^{-1}\) signify the characteristic of carbonate group (C-O) along with weak characterization of C-O at 875 cm\(^{-1}\). This finding suggests the growth of HA in the form of hydroxyl carbonate apatite (HCA).

Fig. 4 FTIR spectra for 45S5 (a) and 50S8P (b) after immersion in Tris-buffer solution for 7 days

4. SUMMARY

Melt-derived BG was successfully fabricated at lower melting temperature with formation of HCA observed on all BG samples after 7 days of immersion in Tris-buffer solution.

ACKNOWLEDGEMENT

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Improved Densification and Dielectric properties of ZBS-doped CaCu$_3$Ti$_4$O$_{12}$ Electroceramics

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ABSTRACT. Analysis and experimental was performed on ZBS-doped CaCu$_3$Ti$_4$O$_{12}$to investigate their electrical properties. The pellet samples were prepared via solid-state reaction method. Archimedes principle was used to examine the effect of glass dopant on the densification of CCTO. The density and dielectric properties of ZBS doped CCTO (0, 1, 3 and 7 mol%) sintered at 1040°C show a relative density of ~ 96%, a high dielectric constant of ~ 3000, and a dielectric loss of ~ 1.0.

Keywords: Solid state reaction, Electrical properties, Glass material;

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1. INTRODUCTION

Calcium Copper Titanate (CCTO) is a potential candidate used in microelectronic applications (capacitor, filters and resonator) due to its giant relative dielectric constant ($\varepsilon_r$ ~ 12 000 at 1 kHz) [1]. Higher $\varepsilon_r$ value means more charges can be stored and smaller devices can be fabricated. The relative dielectric constant of CCTO has been reported to be highly dependent on the processing conditions. The solid-state reaction technique is able to produce single phase CCTO but this process usually required a high sintering temperature (≥ 1100 °C) for tedious duration (> 12 hours) and dielectric loss (tan δ) obtained is too high for to be used in a commercial microelectronic applications [2]. Mu et al. [3] reported that the typical tan δ value for CCTO ceramics is about 0.1 at 1 kHz in room temperature. Besides, Rahman et al. [4] also stated that CCTO is suffering from a high dielectric loss (0.2-1.0) which prevents its potential applications to be commercialized.

The dielectric loss phenomena happen due to the rotation of the atoms in an alternating electric field. The rotation of a dipole in a material is like a small ball rotating in a viscous fluid. Under an external force which is produced by electric field, it tends to change from its original equilibrium state to a new equilibrium state. This process is generally referred to the relaxation process. Many researchers have proposed a ways to reduce dielectric loss and one of the solutions is by implied the possible doping to modify the CCTO compositions such as SiO$_2$-doped CCTO, Fe- and Nb-doped CCTO, Cr$_2$O$_3$-doped CCTO, CaTiO$_3$ doped CCTO, ZrO$_2$ doped CCTO.
However for this research, the goal is to produce CCTO ceramic with excellent dielectric properties include of high dielectric constant, high energy density and low dielectric loss. Therefore glass ceramic composite material has been proposed since glassyphases have high electrical resistance and low dielectric loss, so that the formation of this kind of phases, surrounding grains, could assist in the lowering of dielectric loss and in improving the overall dielectric properties of CCTO.

CCTO Glass ceramic materials are polycrystalline materials that can prepare by controlled the crystallization of glasses where it consist of crystal and glass phase. Glass ceramic was prepared by first obtaining a glass matrix by melt casting and then precipitating a crystal phase in the glass matrix during subsequent heat treatment [5]. High energy density capacitor fabricated by glass ceramic materials can store more than ten times energy per unit volume than the common capacitor.

The combination of high dielectric electroceramic materials and high breakdown strength of glass materials is hope can create high energy density capacitors. Based on our research review, there are some reports about the effect of addition of glass materials or glass formers into the CCTO [6], but there is no systematic study on the densification and dielectric properties with ZBS (ZnO-B2O3-SiO2) glass doped CCTO ceramics. Therefore, in this research ZBS glass were introduced not onlyto promote densification up to 96% but also increased the dielectric properties (high εr and low tanδ).

2. MATERIALS AND METHODS

The ZBS glass was prepared via wet-ball-mixing from high-purity starting materials. The mixture was dried in an oven and melted in alumina crucible using glass melting furnace (Lenton EHF 1800) at 1450 °C for 2 hours. The molten glass was manually poured into distilled water and the glass frits obtained were ball-milled to form a fine glass powders. Meanwhile, CCTO powder was prepared by solid-state reaction method using high purity starting raw materials of CaCO3, CuO and TiO2 powders. The mixture powders were wet-mixed with ethanol for 24 hours and dried-overnight in the oven. The dried-mixtures were calcined at 900 °C for 12 hours. Subsequently, the glass powder was mixed with CCTO’s calcined powder for different composition ratios as (x)ZBS + (1-x)CCTO, where x = 0, 0.01, 0.03 and 0.07 using zirconia balls media for 24 hours before pelletized. The samples were coded according to the ZBS doping concentration as Z0, Z1, Z3 and Z7, respectively. Then, green body was sintered at 1040 °C for 10 hours in air. The density of samples was determined using Archimedes principle method. The dielectric properties were measured using the Impedance Analyzer machine (RF Impedance/Material Analyzer 4291B Hewlett Packard) over a broad frequency range of 1 MHz to 1 GHz.

3. RESULTS AND DISCUSSION

Fig. 1 shows the relative density of the CCTO ceramics with different of ZBS addition. The Z1 sample was the densest with highest relative density (~96%) compared to pure CCTO (~94%). This result indicated that ZBS addition can help to improve the densification of the CCTO ceramics and enhance material transport rate during the sintering process. Z1 sample ceramics possesses superior wetting characteristic on the surface of CCTO ceramic and it helps to fill up the closed pores inside the ceramic body and improve the density of the sample. Hsiang et al. [7] had also stated that ZBS glass can improve the densification of BaTiO3 ceramic sample. However, Z7 sample did not result in high densification. This result may be explained by the formation of secondary phase through interaction between CCTO and glasses, which consumed large amount of glasses, added and resulted in the insufficient amount of liquid phase. Theoretical density value of CCTO is 5.07gcm-3, as reported by Moussa and Kennedy [8].
Fig. 1 Relative density of the CCTO ceramics with different ZBS addition

Fig. 2 shows the SEM micrograph of the ZBS-doped CCTO samples. The Z1 sample shows the average grain size of 5.43 μm. It can be stated that a small quantity of glass additive can reduce a grain size. Each of the samples shows almost the same grain size. This proves the presence of glassy phase can help in obtaining a homogenous microstructure. Increasing the glass content can reduce the average grain size with Z0(5.65 μm) > Z1(5.33 μm) > Z3(4.83 μm) > Z7(2.19 μm). The Z1 samples has less micro-pores compared to undoped CCTO (Z0), which can be attributed that the pores has been filled by the glass phase provided by the ZBS molten glass during sintering process. Previous researchers investigated that there is a fast grain growth at higher ZBS glass amount. A fast grain growth will reduce the average grain size, and then reduce the relative density. Too much ZBS glass content prevent an excessively of the grain growth [9]. This effect can be seen for the Z7 samples.

The effects of the glass additions on the dielectric constant of CCTO ceramics are shown in Fig. 3. The dielectric properties obviously depend on ZBS glass composition. The porosity and grain size played dominant roles in determining the magnitudes of dielectric behavior. The results shows that, the dielectric constant value for Z1 sample gives highest value up to ~ 3000 compared to other sample. The drastic changes in dielectric constant happen when grain boundaries at cooling stage re-oxide faster than the interior of the grains which prevents degradation of the enhanced conductivity of the bulk grains. Fast diffusion on grain boundary has made it become insulative leading to the formation of the higher dielectric constant.

The improvement in dielectric properties was also correlated to the relative density value of the pellets as shown in Fig. 1. In other words, higher densification may play a role in enhancing the value of dielectric constant. Besides, a higher density for a ceramic means there are more dipoles in a unit volume, so the sample with a higher density has a larger dielectric constant value. The improvements in densification are related to the step of nucleation theory where the reason for the development of discontinuous grain growth. Based on the theory, the discontinuous grain growth can occur by the step growth mechanism where the flat and faceted grain boundaries are expected to have singular structures which promoted abnormal grain growth.
Fig. 2 SEM micrographs of (a) Z0, (b) Z1, (c) Z3, (d) Z7

Fig. 3 Dielectric constant of ZBS doped CCTO samples. Dielectric loss investigations were carried out at different composition of ZBS glass as shown in Fig.4. The dielectric loss of CCTO can be reduced with the
addition of ZBS glass dopant. The Z1 sample exhibited the lowest dielectric loss, measured at a high frequency 1 MHz, where sample show 1.02 loss value. This value is much lower than the undoped CCTO sample (1.35). As mentioned above, ZBS glass dopant can be used to improve the densification of CCTO ceramics. Therefore, this indicates that ZBS glass doping can be used to lowering the dielectric loss value of CCTO.

**Fig. 4** Dielectric loss with different amount of ZBS glass

4. **SUMMARY**

The ZBS-doped CCTO ceramics samples were successfully prepared using solid state techniques. The densification and dielectric properties of CCTO ceramics are strongly depends on the content of ZBS glass and chemical reaction between the glass and CCTO. For the samples added with large amount of glasses composition, a secondary phase was formed, which resulted in the deterioration of densification and dielectric properties. The highest relative density of 96%, the maximum dielectric constant of 3000 and lowest dielectric loss of 1.02 was obtained from the sample added with 1 mol % ZBS glass.

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**REFERENCES**


Influence of Pentavalent Niobium on Microstructural and Mechanical Properties of ZTA Ceramic Composite via Cold Isostatic Pressing

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ABSTRACT. The influence of pentavalent niobium (Nb2O5) on microstructural and mechanical properties of ZTA ceramic composite via cold isostatic pressing (CIP) method was investigated. The microstructural analysis and phase transformation was determined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). XRD analysis revealed the presence of t-ZrO2, m-ZrO2 and Nb2Zr6O17 phase. The maximum value of hardness, fracture toughness and flexural strength was found at 1 wt.% of Nb2O5 addition with the value of 1840 HV, 8.6 MPa√m and 351 MPa, respectively. Thus, the addition of Nb2O5 results in an enhancement for the mechanical properties of ZTA ceramic.

Keywords: Hardness, Fracture toughness, Flexural strength, Cold isostatic pressing (CIP);

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Zirconia toughened alumina (ZTA) is a zirconia-alumina system where the toughness of alumina is enhanced by adding zirconia [1]. Zirconia undergo transformation toughening which lead to an improvement on mechanical properties of the composites [2]. Pentavalent niobium (Nb2O5) is found as one potential additive that can improve the mechanical properties of ceramics [3-5]. Previous work done by Hassan et al. [3] found that Nb2O5 improved the mechanical properties of ZTA ceramic by sol gel method using uniaxial press as compaction method. For this work, cold isostatic pressing (CIP) method was chosen as compaction method in producing the homogeneity of powder compact [6,7]. CIP can improved the mechanical properties through lowering the porosity of ceramic compared to uniaxial press method [8-10]. Therefore, this study focuses on the role of CIP as compaction method on the microstructural and mechanical properties such as hardness, fracture toughness and flexural strength behaviour for ZTA added Nb2O5 ceramics.

2. MATERIALS AND METHODS

For this work, 80 wt.% of Al2O3 (Alcoa, A16SG,99.0% purity) and 20 wt.% YSZ (Goodfellow, 94.6% purity) were used as starting materials. The amount of Nb2O5 (Merck, 99.5% purity) in weight percent was varied from 0 wt.% to 7 wt.% into the initial compositions by wet milling method. Then, the mixtures were dried to
100 °C and grinded to form powders. The mixed powders were compacted by uniaxial press at 15 MPa and followed by cold isostatic pressing (CIP) at 150 MPa for 2 min to form a cylindrical shapes with dimensions of 13 mm in diameter and 4 mm in height (for physical and microstructural characterization) and rectangular bars of dimensions of 40 × 10 × 10 mm (for mechanical evaluation). The green body was sintered in atmosphere at 1600 °C for 4 hours. The phase transformations of sintered body were analyzed by X-ray diffraction (XRD). Scanning electron microscopy (SEM) was used to observe the microstructure of each sample. The values of hardness and fracture toughness were measured by a Vickers indentation technique tester using a 30 kgf load. The fracture toughness values were calculated for all samples using the Palmqvist crack formula proposed by Niihara (1983)

\[ 3K_{ic} = 0.035 (H^* a^{1/2}) (3E/H)^{0.4} (c/a)^{0.5} \]  

(1)

\( K_{ic} \) is the fracture toughness, \( H \) is Vickers hardness, \( a \) is the half length of Vickers diagonal (μm), \( E \) is equal to the Young modulus of the samples and \( c \) is the length of the radial crack size (μm). Flexural strength was measured in a three-point bending test on a universal testing machine at a crosshead speed of 1 mm/min, and support distance of 20 mm.

3. RESULTS AND DISCUSSION

Table 1 shows the XRD analysis of the samples for different composition of Nb₂O₅ additions (0 - 7 wt.%). The phase existed in ZTA-Nb₂O₅ consist of alumina (Al₂O₃), tetragonal zirconia (t-ZrO₂), monoclinic zirconia (m-ZrO₂) and Nb₂Zr₆O₁₇ phase. Al₂O₃ are present as corundum matching ICSD pattern No. 98-005-7635 with hexagonal structure. Tetragonal zirconia and monoclinic zirconia was observed for all composition matching ICSD pattern No. 98-005-7635 and No. 98-007-1860. The XRD analysis also revealed the formation of secondary phase, Nb₂Zr₆O₁₇ (ICSD pattern No. 98-000-5068) starting at 3.0 wt.% Nb₂O₅ with orthorhombic structure. These identification phase's percentages correspond to the addition of Nb₂O₅. The lower addition of Nb₂O₅ (0 - 1 wt.%) related to the effect of t-ZrO₂ and m-ZrO₂ phase, which is attributed to the toughening mechanism (t → m). These mechanism are one of the factors to improve the toughness in ZTA-Nb₂O₅ composite [12]. Meanwhile, the higher Nb₂O₅ addition (3 - 7 wt.%) revealed the formation of Nb₂Zr₆O₁₇ phase. It was recorded that the highest formation of Nb₂Zr₆O₁₇ is 0.9 % at 7 wt.% Nb₂O₅ addition. This was proved by Energy dispersive X-ray analysis (EDX) in Fig. 2 with the presence of Nb element at YSZ grains.

<table>
<thead>
<tr>
<th>Nb₂O₅ addition (wt.%)</th>
<th>Phase Composition (%)</th>
<th>Al₂O₃</th>
<th>t-ZrO₂</th>
<th>m-ZrO₂</th>
<th>Nb₂Zr₆O₁₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80.4</td>
<td>18.4</td>
<td>1.1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>80.7</td>
<td>17.7</td>
<td>1.6</td>
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<td>6.3</td>
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<td>13.1</td>
<td>11.6</td>
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<tr>
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<td>68.6</td>
<td>13.9</td>
<td>17.5</td>
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<td></td>
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<tr>
<td>3</td>
<td>69.8</td>
<td>15.8</td>
<td>14.3</td>
<td>0.1</td>
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</tr>
<tr>
<td>5</td>
<td>77.2</td>
<td>16.9</td>
<td>5.1</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>78.5</td>
<td>17.5</td>
<td>3.0</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>
SEM micrographs for sintered samples of 0 wt.% and 7 wt.% of ZTA-Nb$_2$O$_5$ are shown in Fig. 1. Based on the microstructures, the grains for YSZ and Al$_2$O$_3$ are well distributed among each other. EDX analysis in Fig. 2 shows that the dark grains are Al$_2$O$_3$ and light grains are yttria stabilized zirconia (YSZ). The presence of Nb element was detected in YSZ grains, confirmed by the EDX analysis (Fig. 2). Meanwhile, Nb$_2$Zr$_6$O$_{17}$ phase found to be appeared at the YSZ grains when its amount exceeds the solubility limit.

![Fig. 1 SEM micrograph of ZTA- Nb$_2$O$_5$ composition (a) 0 wt.% and (b) 7.0 wt.%, at 3.0 K magnification](image)

**Fig. 1** SEM micrograph of ZTA- Nb$_2$O$_5$ composition (a) 0 wt.% and (b) 7.0 wt.%, at 3.0 K magnification

![Fig. 2 Microstructure and EDX analysis for ZTA with 7 wt.% of Nb$_2$O$_5$ addition](image)

**Fig. 2** Microstructure and EDX analysis for ZTA with 7 wt.% of Nb$_2$O$_5$ addition

Fig. 3 presents the results of hardness, fracture toughness and flexural strength of ZTA-Nb$_2$O$_5$ composites as a function of Nb$_2$O$_5$ content. As seen, the hardness, fracture toughness and flexural strength increased with increasing Nb$_2$O$_5$ content. The addition of 1 wt.% Nb$_2$O$_5$ gives the maximum value for hardness (1840 HV), fracture toughness (8.6 MPa.√m) and flexural strength (351 MPa). The dense compact through CIP enhanced the mechanical properties of this system, as the relative density achieved 97.4%-99.8% to the theoretical
density, where sample for 1 wt.% Nb₂O₅ gives the highest relative density (99.8%). CIP improved the particle packing and reorganized the microstructure, resulting in higher densification for sintered body [13]. Furthermore, the improvement of fracture toughness also can be related to the transformation toughening (t → m) due to crack deflection and crack bridging that occurs at the crack path after indentation. However, the properties gradually decreased when reached at 3 wt.% of Nb₂O₅ addition. This phenomenon was related with the presence of secondary phase, Nb₂Zr₆O₁₇. A secondary phase can promotes pore formation which might weaken the ceramics by reducing some of the mechanical properties. Pores were described as a discontinuity in the material, resulting in an undesirable effect [14]. This was confirmed by the results of porosity in Table 2, where the porosity found to increase at 3 wt.% of Nb₂O₅ addition.

**Fig. 3** Results of (a) hardness and (b) fracture toughness and flexural strength of ZTA-Nb₂O₅

Fig. 4 indicates the results of bulk density and theoretical density of ZTA samples with different addition of Nb₂O₅. The result of bulk density follows the pattern of theoretical density. This result clearly indicates that Nb₂O₅ enhances sinterability and the density of ceramics. However, at 3 wt.% the densities decreased due to excess of Nb₂O₅ beyond the solubility limit, which results in the presence of Nb₂Zr₆O₁₇ phase (Table 1). The results show that by increasing the Nb₂O₅ addition, the bulk density increased and the percentage of porosity decreased as illustrated in Table 2. Lower percentage of porosity enhances the mechanical properties of the ZTA ceramic. The highest density (4.6 g/cm³) with low percentage of porosity (0.08%), was found at 1 wt.% of Nb₂O₅ addition. Hassan et al. [3] stated that the ionic radius of Nb⁵⁺ (0.68 Å) is smaller compared to Zr⁴⁺ (0.79 Å) and Y³⁺ (1.019 Å). When Nb⁵⁺ enter into the Zr⁴⁺, it will caused a large amount of oxygen vacancies formed in the samples and accelerate the lattice diffusion, thus enhance the densification rate [15]. Furthermore, it also led to the formation of the observed new phase, confirmed by XRD result, which indicated in Table 1.
Fig. 4 Result of bulk density and theoretical density of ZTA-Nb₂O₅

Table 2 Result for porosity of ZTA-Nb₂O₅

<table>
<thead>
<tr>
<th>Nb₂O₅ addition (wt.%)</th>
<th>Porosity (%)</th>
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</thead>
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<tr>
<td>0</td>
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<td>0.1</td>
<td>0.23</td>
</tr>
<tr>
<td>0.3</td>
<td>0.24</td>
</tr>
<tr>
<td>0.5</td>
<td>0.24</td>
</tr>
<tr>
<td>0.7</td>
<td>0.09</td>
</tr>
<tr>
<td>1</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
</tr>
<tr>
<td>5</td>
<td>0.71</td>
</tr>
<tr>
<td>7</td>
<td>2.23</td>
</tr>
</tbody>
</table>

4. SUMMARY

The influence of pentavalent niobium (Nb₂O₅) on microstructural and mechanical properties of ZTA via CIP method was successfully investigated. The optimum composition are 1 wt.% Nb₂O₅ addition. The addition of Nb₂O₅ enhance the hardness, fracture toughness and flexural strength compared to ZTA without Nb₂O₅ addition. The enhancements reach a limit at 1 wt.% addition, which is attributed to the transformation of t → m phase. These proved that the toughening mechanism occurs for 1 wt.% addition. However, the effectiveness of these toughening mechanism deteriorate the mechanical properties with further additions (3 - 7 wt.%) which is corresponds to an existence of Nb₂Zr₆O₁₇ phase.
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The Effect of Boron Oxide on Concentration of Iron Ion Released from SiO\textsubscript{2}-B\textsubscript{2}O\textsubscript{3}-Na\textsubscript{2}CO\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3} Glass System

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ABSTRACT. Iron ion from borosilicate glass can be release in seawater depending on the immersion time by the corrosion process. The effect of boron oxide percentage in the quaternary system of glass was studied. The compositions of the glass system [wt.%: (55-x)% SiO\textsubscript{2}(15-x)% B\textsubscript{2}O\textsubscript{3}.25% Fe\textsubscript{2}O\textsubscript{3}.5% Na\textsubscript{2}CO\textsubscript{3}] where 15%<x<40% have been prepared with the different amount of B\textsubscript{2}O\textsubscript{3}(35-55 wt.%) and Fe\textsubscript{2}O\textsubscript{3} with Na\textsubscript{2}CO\textsubscript{3} were fixed. The glass was melting in the alumina crucible for 2 hours soaking time at 1300 °C and cooled to room temperature. The obtained glass was crushed and sieved with yielding a mean size of 2-4 mm. The glass samples in 50 mL synthetic seawater was tested under static condition in 16 weeks to determine the concentration of iron ion and weight loss of the glass samples. The concentration of iron ion was analyzed using UV-Vis Spectrophotometer. The scanning electron microscopy determined the morphology of the sample. From the dissolution studies, it was shown that the concentration of iron ion release was increased with the increasing percentage of B\textsubscript{2}O\textsubscript{3} content. However, the addition of silica oxide was increased the chemical durability of glass system. The percentage boron oxide at 55 wt.% of boron gives the optimum rate of iron ion released in seawater, which is 1.11ppm.

Keywords: Boron oxide, Ion released, Iron ion;

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1. INTRODUCTION

Pure borate glasses have a poor chemical durability when it comes to application and it is important in development of new materials such as oxides glass [1]. Bengisu in 2016 reported that, borate glass has high affinity to water but when it is combined with other oxide such as SiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}, the chemical durability can be improved by changing the structural [2]. The Controlled Release Glass (CRG) is a class of materials that completely dissolve in aqueous media. Their degradation of corrosion controlled process that follows zero order release over the life of the material, for example the release rate is constant and independent of time and concentration [3].

The glass structure is depends on two factors; network former and network modifier. Glass former or known as network formers consists of oxide such as SiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3}, which are indispensable in the formation of the glass. Meanwhile, network modifier acts as chemical additional in a glass system, which change the boron coordination from trigonal to tetrahedral [4] and also break the framework and produce non-bridging
The chemical durability, which is the resistance offered by a glass towards attack by aqueous solution and atmospheric agents, the releasing ion from the synthetic seawater will be affected whether slow or controlled release. It is very important for possible reaction between the glass surface and acid or aqueous medium [6].

Iron oxide (Fe$_2$O$_3$) was known as fertilizer, which is promoting the algae growth and also have a good effects of chemical durability in phosphate glass [6]. Previous studies show that transition metals such as Al$_2$O$_3$, ZrO$_2$, MnO$_2$ and TiO$_2$ have low softening point and tend to promote the chemical durability of the glass [7-13]. The presence of Fe$_2$O$_3$ will cause the Fe$^{3+}$ ion substituted at the silicon sites in the SiO$_2$-Na$_2$O-Al$_2$O$_3$-B$_2$O$_3$ glass system [14].

The aim of this work is to study the effect of B$_2$O$_3$ percentage on the iron ion released from the SiO$_2$-B$_2$O$_3$-Na$_2$CO$_3$-Fe$_2$O$_3$ glass system. Indeed, the SiO$_2$ percentage is added along the B$_2$O$_3$ percentage with the total is 70 wt.%. Therefore, glass dissolution test method was used to determine the concentration of iron ion with different percentage of boron oxide. Then, the morphology of glasses was evaluated from the scanning electron microscopy (SEM).

2. MATERIALS AND METHODS

2.1 Synthetic Seawater Preparation. 41.95 g of sea salt (Sigma-Aldrich) was weighed and mixed with 1 liter of deionized water using 1 L volumetric flask. Then, the solution was adjusted with 0.1 N HCl or NaOH to obtain pH 8.2

2.2 Glass Preparation. The chemicals compositions of glasses were shown in Table 1. The mixing reagent grade raw materials, such as SiO$_2$, B$_2$O$_3$, Na$_2$CO$_3$, and Fe$_2$O$_3$ were prepared for 100 g. The glass has been prepared by melting in the alumina crucible within 2 hours of soaking time at 1300 °C in the furnace and cooled to room temperature. The ion released and weight loss is determined through the immersion of the glass samples in 50 mL synthetic seawater for 16 weeks under the static condition. The morphology of sample were determined by the Scanning Electron Microscopy (SEM) (JOEL JDM-6360LA) was used in this study.

<table>
<thead>
<tr>
<th>Glass Coding</th>
<th>Compositions (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>30B</td>
<td>40</td>
</tr>
<tr>
<td>35B</td>
<td>35</td>
</tr>
<tr>
<td>40B</td>
<td>30</td>
</tr>
<tr>
<td>45B</td>
<td>25</td>
</tr>
<tr>
<td>50B</td>
<td>20</td>
</tr>
<tr>
<td>55B</td>
<td>15</td>
</tr>
</tbody>
</table>

2.3 Glass Dissolution. The chemical durability of glasses was determined by measuring the weight loss of the samples immersion. From the measurement, 1.0 g of glass samples were crushed in size of 2.0-4.0 mm was immersed in 50 ml of synthetic seawater under static condition for 16 weeks (112 days). The concentration of iron ion was analyzed using UV-Vis Spectrophotometer (UV 1800) with phenanthroline method [15] and weight loss of glasses was measured.
2.4 Weight loss % experiment. In 100 ml polyethylene bottles with covers, 1 g of glass grains (2.00-4.0 mm) was immersed in 50 ml of synthetic seawater for 16 weeks at room temperature. The weight loss (%) was calculated based on weight of sample before and after immersion.

3. RESULTS AND DISCUSSION

The effect of B₂O₃ on the iron ion release from the synthetic seawater was studied for six types of glass with different B₂O₃ content in a range of 30-55 wt.%. The iron ion released from synthetic seawater is illustrated in Fig. 1. It is show that the iron ion concentration increased linearly with the time but started to decrease at 12 weeks. This is due to the chemical durability of the glass in synthetic seawater [16]. Previous studies show that, normally B₂O₃ substituted for SiO₂ in network former sites in borosilicate glasses decreases the chemical durability of a glass and also increased the ion released [17].

![Graph](Image)

**Fig. 1** Concentrations of iron ion released from 0-16 weeks

The Fig. 1 shows the concentration of iron ion increased with increasing percentage of boron oxide content. From the results it can be seen that, the glass samples for 30B40Si, 35B35Si, 40B30Si and 45B25Si showed low concentration of iron ion. Since, the less of iron ion released, so that the pH of seawater tent to increased (alkaline solution) which is slow down the corrosion process [18]. Increase the amount of boron oxide and decrease the content of silica, the concentration iron ion increased. This is due to the solubility of the glass increased [19].

The iron ion released is depends on the glass composition. The boron anomaly in the borosilicate glass changed the coordination numbers from three to four and back to three depends on the addition of network modifier as alkalis or alkaline earth oxides. So that, when the glass is reacted in the acidic medium, the modifier cation can be exchanged with H⁺ in liquid medium (OH⁻).The ferrous ion was released when the content of the boron oxide increased [20].

SEM was conducted to further investigate on the surface morphology of glasses and also the size of pores. Fig. 2 show the SEM phase of 55B for (a) before and (b) after immersion for 16 weeks. The observation before
the immersion, there is less pores on the surface of glass. Meanwhile, after the immersion at 16 weeks, there is more pores appeared. This is owing to the iron ion was released out from the glass.

Fig. 2 SEM morphology for 55B glass (a) Before immersion and (b) After immersion for 16 weeks

The types of ions in a glass structure generally tend to release out of the glass surface when reacted in an aqueous solution. The ion released rate is depends on the glass composition and the state of the ions in the glass structure. From the Fig. 3, it is shown that the weight loss with different percentage of boron oxide content (wt.%). As percentage of boron oxide content increased, the weight loss of the glass also increased (0.13-0.47 g). The 50B20Si shows the highest value of weight loss, which is 0.471 g. This is due to the corrosion process when the glasses make contact with the aqueous medium [21] and the solubility of water increased [14].

Fig. 3 The weight loss of different contents of boron oxide (wt.%)

4. SUMMARY

In summary, this is clearly observed, the decreasing amounts of SiO₂ give the effect of chemical durability of the glass system, which is low and less stable. The concentration of iron ion was increased with the
increasing percentage of B₂O₃ content. The percentage boron oxide at 55 wt.% of boron gives the optimum rate of iron ion released in seawater, which the concentration is 1.11 ppm.

ACKNOWLEDGEMENT

The authors are grateful for the financial support from research grant FRGS 55095 and also thanks to Universiti Malaysia Terengganu for the facilities.

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Microstructure and Hardness of Zirconia Toughened Alumina (ZTA)
Ceramics by Hot Isostatic Press Sintering

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\textbf{ABSTRACT.} Mechanical properties of 8YSZ toughened alumina (ZTA) have been investigated. The compositions of 8YSZ as reinforce were varied from 0 wt.% to 25 wt.%. Both Al\textsubscript{2}O\textsubscript{3} and 8YSZ powders was mixed and sintered at 1600 \degree C for 1 hour using hot isostatic pressed sintering (HIP). The phases analysis were identified as corundum (Al\textsubscript{2}O\textsubscript{3}) and zirconium yttrium oxide (Zr\textsubscript{0.8}Y\textsubscript{0.12}O\textsubscript{1.94}). The hardness values for ZTA ceramics produced through HIP sintering found to improve the hardness of ZTA ceramics. The Vickers hardness results show that 15 wt.% of 8YSZ produced the optimum hardness which is the highest value of 1706.74 HV. In addition, the percentage of porosity appears to be diminished (~30%).

\textbf{Keywords:} Vickers hardness, Hot isostatic press (HIP), Porosity, Density;

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\section{INTRODUCTION}

The introduction of stabilize ZrO\textsubscript{2} into Al\textsubscript{2}O\textsubscript{3} as a sintering aid has been long practiced for densification of Al\textsubscript{2}O\textsubscript{3}\cite{1-5}. The best way to stabilize the cubic zirconia phase by using additives like Y\textsubscript{2}O\textsubscript{3}, CaO, MgO and CeO\textsubscript{2}\cite{6-8}. Amount of stabilizer plays an important role on size of tetragonal crystals which determines the critical stress required to activate the stress induced phase transformation. Increasing grain size yields a lower activation stress, which then leads to both larger transformed zones and act as shielding effects around a propagating crack\cite{6}.

However, while most of the researches have concentrated on toughening mechanism in order to improve the toughness of ZTA ceramics only but not to its hardness which is neglected their hardness properties. The approach under investigation here is the addition of intergranular phases of 8YSZ to limit grain growth as a first step and the application of external pressure from HIP as second step. 8YSZ is high temperature refractory ceramics composed of zirconium oxide stabilized with 8% yttrium oxide. Rahmawati et al.\cite{11} reported that 8YSZ show homogeneous morphology and without provides a line crack. Meanwhile, 8YSZ is a cubic form and has no phase transformation during heating from room temperature up to 2500\degree C and cooling\cite{12}. During heating, the methods of pressure sintering such hot isostatic pressing (HIP) are common examples. Although, HIP has the disadvantage of increased fabrication costs, but it is effective when a microstructure of high density and fine grain size must be guaranteed.
Therefore, the effectiveness of using combination of 8YSZ properties together with HIP sintering towards the microstructure and hardness of ZTA has been investigated. The porosity reduction by means of HIP has a significant beneficial effect on 8YSZ toughened alumina [13]. Thus, the influence of the combination process is believed to affect the microstructure by reducing the porosities and form densified ceramic.

2. MATERIALS AND METHODS

As starting powders, $\text{Al}_2\text{O}_3$ (99.0% purity) and commercially 8YSZ refer to 8 mol.% yttrium stabilized zirconia (94.6% purity) were used. The amount of 8YSZ was varied in different wt.% (0 to 25 wt.%) into the $\text{Al}_2\text{O}_3$ matrix by wet mixing method. The mixtures powders were uniaxial press at 10 MPa into cylindrical shapes mold with dimensions of $\Phi 13$ mm and 15 mm in height and the green body were HIP sintered at 1600 °C in argon gases with 150 MPa for 1 hour. Pressureless sintering technique have been carried out at 1600 °C for 4 hours soaking period as baseline samples for the purpose of improvement indicator. The density and porosity of sintered body were measured according to the ASTM C 830-00 test procedure. The phase identifications were analyzed by XRD, while microstructural investigation was performed using scanning electron microscopy (Hitachi TM3000 Tabletop SEM). The values of hardness were measured by a Vickers indention technique tester (Shimadzu HSV-20) using a 30 kgf load.

3. RESULTS AND DISCUSSION

The Vickers hardness of HIP and pressureless sintered ZTA ceramic sample is shown in Fig. 1. The hardness values for HIP samples, trend is gradually increased from 1632.7 HV (0 wt.% of 8YSZ) and reach the highest peak at 1706.74 HV (15 wt.% of 8YSZ). However, further additions (20 – 25 wt.%) show the gradually decrease in hardness due to exceeding solubility limits, because of excessive 8YSZ addition in the ZTA composition. Rejab et al. [14] stated that, an exceeded limits of added materials can result in deterioration of mechanical properties.

![Fig. 1 Vickers hardness values of HIP sintering as a function of 8YSZ content](image)

Table 1 shows XRD results of various 8YSZ added in $\text{Al}_2\text{O}_3$ matrix. Fig. 2 shows that overall peaks patterns were identified as corundum ($\alpha\text{-Al}_2\text{O}_3$) with ICSD file number 98-001-7443 and zirconium yttrium oxide ($\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$) ICSD file number 98-003-2793. Table 1 detailed the phase’s percentages for overall composition. These results proved that toughening mechanism provide by $\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$ phase reach a limit at 8.1% for 15 wt.% addition. Further increased of $\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$ phase deteriorate the hardness of ZTA ceramics. To further appreciate the role of the both phases as obtained by XRD analysis, the grains shape distribution of those phases in the microstructure were revealed by SEM analyses.
Fig. 2 XRD pattern of the Al$_2$O$_3$ added 8YSZ (a) 5 wt.%, (b) 10 wt.%, (c) 15 wt.%, (d) 20 wt.% and (e) 25 wt.%

Table 1 Phases percentages of various 8YSZ toughened Al$_2$O$_3$

<table>
<thead>
<tr>
<th>8YSZ</th>
<th>Phase Percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>5</td>
<td>99.6</td>
</tr>
<tr>
<td>10</td>
<td>97.7</td>
</tr>
<tr>
<td>15</td>
<td>91.9</td>
</tr>
<tr>
<td>20</td>
<td>86.0</td>
</tr>
<tr>
<td>25</td>
<td>83.3</td>
</tr>
</tbody>
</table>

Based on micrograph structure shown in Fig. 3, there are two distinct size and shade. ZrO$_2$ has lighter grains, smaller in size and discoidal shapes while Al$_2$O$_3$ refer to darker grains, larger in size and tabular shapes. The size of ZrO$_2$ is smaller in size because the material used is 8YSZ which is relatively smaller than Al$_2$O$_3$. The microstructures are more isotropic and homogenous. Smuk et al. [15] reported that HIP capable to eliminate large pores by diffusion and grain arrangement. Therefore, the sintered body fabricate by HIP capable to produce almost zero porosity bodies [16-20]. However, abnormal growth such as platelet grains occurs among ZrO$_2$ grains; they can be seen obviously in samples with 25 wt.% of 8YSZ addition. The deformation in
The grain shape of ZrO$_2$ could be due to exceeding solubility limits, because of excessive of 8YSZ addition in the Al$_2$O$_3$ matrix.

**Fig. 3** Scanning electron micrographs of Al$_2$O$_3$ ceramics with (a) 0 wt.% of 8YSZ, (b) 5 wt.% of 8YSZ, (c) 10 wt.% of 8YSZ, (d) 15 wt.% of 8YSZ, (e) 20 wt.% of 8YSZ and (f) 25 wt.% of 8YSZ, at 1K magnification. Light grains: zirconia; dark grains: alumina.
Based on Fig. 4, the bulk density values gradually increased as the amount of 8YSZ added increase until 15 wt.%. Naga et al. [21] stated that the improved density is very important for close the pore that networks prior to the HIP sintering. Based on the results, the addition of 5 wt.% of 8YSZ increase from 3.20 g/cm³ to 4.34 g/cm³ (10 wt.% of 8YSZ) and the density continues to increase until it reaches the value of 7.35 g/cm³ (15 wt.% of 8YSZ). However, the graph trend starts to decline to 5.04 g/cm³ (20 wt.% of 8YSZ). The density continues to gradually decrease until 3.29 g/cm³ (25 wt.% of 8YSZ). For the percentage of porosity, in the beginning at 5wt.% of 8YSZ the porosity is 19.48%. The porosity values decrease to 2.24% (10 wt.% of 8YSZ) and 1.94% (15 wt.% of 8YSZ). Then the porosity slightly increased to 4.4% (20 wt.% of 8YSZ) and react maximum to 15% (25 wt.% of 8YSZ). Therefore the effect of HIP sintering on the density of ZTA is proved, with a reduction of porosity. It shows that the optimum addition of 8YSZ is 15 wt.% which has the lowest porosity and highest densification.

Fig.4 Results of bulk density and percentage of porosity via HIP sintering technique

4. SUMMARY

Microstructure and hardness properties of 8YSZ added Al₂O₃ matrix via HIP have been investigated. An addition of 15 wt.% of 8YSZ provide the optimum properties of Vickers hardness 1706.74 HV. The change in shape of ZrO₂ grains are corresponding to exceeding solubility limits, because of excessive of 8YSZ addition in the Al₂O₃ matrix. Based on the presence work, HIP proved that external pressure sintering technique capable to obtain densified microstructure and improve the hardness of the Al₂O₃ ceramics through the reduction of porosity values.

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Microstructure and Strength Enhancement of Portland Composite Concrete using Polyvinyl Alcohol (PVA) and Silica Fume as Replacement Material

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ABSTRACT. Polyvinyl alcohol (PVA) and silica fume (SF) has been incorporated with Portland composite cement (PCC) to improve its’ properties. The first phase was to produce composite concrete with the addition of PVA at different level 0.5, 1.0, 1.5 and 2.0 percent. The second phase was to improve the early strength properties of PCC+PVA concrete by replacing cement with SF at different level 5, 10, 15 and 20 percent. The result shows that 0.5% addition of PVA gives a better result than control specimen in term of compressive strength. In fact, PCC+PVA+15%SF give the highest strength at 28 days. The EDX confirmed the increasing silica content in the concrete specimen when SF was added up to 20%. Furthermore, the morphology of specimens indicates hydration process occurs through the existence of Calcium Silicate Hydrate (C-S-H), Calcium Hydroxide (CH) and Ettringite needle at 56 days.

Keywords: Microstructure, EDX, Portland composite cement (PCC), Polyvinyl alcohol (PVA), Silica fume;

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1. INTRODUCTION

The construction of a concrete structure in last few decades has increased rapidly especially in the developing countries. This has burdened the cement manufacturer, and they have come out with composite cement called PCC. In Malaysia, a huge company such as YTL Cement Berhad has come out with this new product to reduce its operational cost. However, this PCC has a shortcoming where it delays the setting time of concrete when compared to normal concrete using the OPC [1].

This delay will affect the construction time where formwork cannot be removed after a few days when casting on site [2]. Therefore, another alternative material such as SF is needed to enhance the quality of concrete without affecting its strength or other characteristics.

The American Concrete Institute (ACI) defines silica fume as a “very fine noncrystalline silica produced in electric arc furnaces as a by-product of the production of elemental silicon or alloys containing silicon”. Silica fume is also known as micro silica, condensed silica fume, volatilized silica or silica dust. It is usually a grey
coloured powder, somewhat similar to Portland cement or some fly ashes. It can exhibit both pozzolanic and cementitious properties [3].

Replacement of 15% silica fume gives an optimum value for high early strength [4]. Pradhan (2013), studied the influence of silica fume on normal concrete and confirmed that the strength of concrete is increased and improve the pore structure at transition zone of concrete [5]. Then, silica fume addition in concrete mixture leads to improve concrete strength due to its ultra-fine particle size [6, 7].

The aim of this research is to determine the effect of PVA addition to the PCC+PVA concrete and to evaluate the effect of cement replacement with SF to the PCC+PVA+SF concrete microstructure and mechanical properties.

2. MATERIALS AND METHOD

The works have been divided into three phases. The first phase is to determine the optimum dosage of PVA addition. Portland Composite Cement (PCC) used in this study was supplied by YTL Cement Berhad, Kuala Lumpur Malaysia, complies with MS EN 197-1:2007 which content 20% fly ash (FA). The cement is in dry powder form with grey colour. The fine aggregate (sand) and coarse aggregate (granite) were supplied by the local quarry. Tap water from the domestic supply source available in the laboratory was used for concrete mixing.

The second phase is to improve the early strength properties of PCC+PVA concrete by replacing cement with SF at different level 5, 10, 15 and 20 percent but this time PVA was fixed at 0.5%. PVA value was determined after conducting the compressive strength test in the first phase.

The third phase is the testing of the sample according to standard. Hence, to observe how PVA and SF affect the concrete properties. For the microstructure, the test was perform using the scanning electron microscopy (SEM). In this study, field emission scanning electron microscope (FESEM SUPRA35) with high-resolution imaging was used to characterise the samples. The mechanical properties of concrete were determined such as compressive strength [8] and porosity [9]. Table 1 shows the mix proportion per cubic meter for PCC+PVA and PCC+PVA+SF. Figs. 1-3 show the samples being cured in the water tank, silica fume powder and PVA powder, respectively.

Table 1 Mix proportions for composite concrete – characteristic strength 30 N/mm² at 28 days

<table>
<thead>
<tr>
<th></th>
<th>Cement</th>
<th>Fine Aggregate</th>
<th>Coarse Aggregate</th>
<th>Water</th>
<th>PVA</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/m³</td>
<td>kg/m³</td>
<td>kg/m³</td>
<td>kg/m³</td>
<td>kg/m³</td>
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<tr>
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<td>882.5</td>
<td>782.5</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>PVAC 1 - 0.5% PVA</td>
<td>450</td>
<td>882.5</td>
<td>782.5</td>
<td>225</td>
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<td>0</td>
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<tr>
<td>PVAC 2 - 1.0% PVA</td>
<td>450</td>
<td>882.5</td>
<td>782.5</td>
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<tr>
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<td>882.5</td>
<td>782.5</td>
<td>225</td>
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<td>PVAC1 + 5% SF</td>
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<td>882.5</td>
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<td>PVAC1 + 10% SF</td>
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<td>882.5</td>
<td>782.5</td>
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</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

The increasing of strength can be observed from Table 2 where the compressive strength at 28 days dropped when adding PVA but increased after silica fume was added. Theoretically, the hydration process for ordinary Portland cement stop at 28 days. However, the strength of concrete was kept increasing up to 56 days due to the FA materials in the PCC [10] and also we can observe the influence of silica fume on the strength development on early stage was significant as referred to Table 2. Although the increment or difference is small, if we compare the capacity of load it can carry is significant for example PVAC 1 +15%SF can carry 55% higher than controlled specimen.

**Table 2** Compressive Strength for composite concrete

<table>
<thead>
<tr>
<th>Concrete Types</th>
<th>Compressive Strength N/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7 Day</td>
</tr>
<tr>
<td>Controlled – 0%PVA</td>
<td>25.50</td>
</tr>
<tr>
<td>PVAC 1 - 0.5%PVA</td>
<td>29.17</td>
</tr>
<tr>
<td>PVAC 2 - 1.0%PVA</td>
<td>27.60</td>
</tr>
<tr>
<td>PVAC 3 - 1.5%PVA</td>
<td>17.57</td>
</tr>
<tr>
<td>PVAC 4 - 2.0%PVA</td>
<td>18.07</td>
</tr>
<tr>
<td>PVAC 1 + 5%SF</td>
<td>31.00</td>
</tr>
<tr>
<td>PVAC 1 + 10%SF</td>
<td>34.17</td>
</tr>
<tr>
<td>PVAC 1 + 15%SF</td>
<td>40.50</td>
</tr>
<tr>
<td>PVAC 1 + 20%SF</td>
<td>37.00</td>
</tr>
</tbody>
</table>

Fig. 4 shows the EDX result of composite concrete at 56 days for all the samples. Fig. 4(a-d) shows an increment of element carbon (C) due to the increasing of PVA from 0.5% to 2.0%. PVA is a water-soluble synthetic polymer, and when we add to the composite concrete, it will blend homogeneously without creating any cohesive mass during the mixing process plus it reduces the porosity and this help to increase the strength.

Fig. 4(e-h) shows the EDX results of Si element amount which is silica that increase as the result of silica fume addition to the composite concrete. The microstructure has no particular pattern (unstructured...
Also, there are a few visible void and micro crack that can be seen such as Fig. 4e. The crack is due to the shrinkage effect as the hydration took place in the concrete sample. The length of crack however is very small around 5 µm and the width of crack is less than 2 µm. This result can be considered as insignificant when compare to the standard of major crack in normal construction practice which is around 3 mm in width.
Izwan Johari et al., 2018

Fig. 4 EDX result of PCC+PVA at 56 days (a-d) and PCC+PVA+SF at 56 days (e-h), calcium silicate hydrate (C-S-H), calcium hydroxide (CH)

4. SUMMARY

PVA as addition to composite concrete using Portland composite cement was increasing the late strength of composite concrete at 56 days. To improve the early strength of hardened concrete, the usage of silica fume is highly recommended. The micro structure of PCC+PVA concrete shows a good bonding between aggregate, PVA and PCC. The results indicate that 15% SF give the best result and the increment of load capacity is more than 50% than the controlled specimen.

ACKNOWLEDGMENT

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REFERENCES

Performance of POFA-Based Alkali-Activated Mortar Exposed to Elevated Temperatures

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ABSTRACT. This research work was conducted to investigate the residual strength performance of POFA alkali-activated mortar when subjected to different levels of elevated temperature. 100% POFA, sand and (Na₂SiO₃(aq)/NaOH(aq)) ratios of 2.5, 2, 1 and 0.5 were used in the preparation of POFA alkali-activated mortar mixtures. 50 mm x 50 mm x 50 mm cube specimens were tested after 60±5 °C heat curing to study the effect of exposure to 3 levels of elevated temperature; 300, 600 and 900 °C. The performance metrics used to assess the impact of exposure to elevated temperatures were the residual compressive strength, weight loss and visual appearance. The alkaline activator ratio and the elevated temperature have induced specific impact on the residual compressive strength of the POFA alkali-activated mortar specimens. For all alkaline-activator ratios, increased strength was recorded for the specimens exposed to 600 °C temperature, however for mortar specimens exposed to 300 °C and 900 °C temperatures strength reduction was recorded. Microstructural changes of the POFA-alkali activated binder was investigated using scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS) as a result of the elevated temperature exposure. Superior performance of the 600 °C specimens was also revealed as a result of the post-heating solidification of molten POFA alkali-activated binder.

Keywords: Palm oil fuel ash (POFA), Alkali-activated binder, Elevated temperature;

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1. INTRODUCTION

Alkali-activated binder, an environmentally sustainable material, recently attained the status of accepted engineering binding material. It is an engineering or scientific term used to describe inorganic polymers that are based on aluminosilicates produced from the synthetic interaction between pozzolanic materials or compounds (geopolymeric precursor) with alkaline solution [1]. Materials coming from solid wastes and by-products endowed with silica and/or alumina such as fly ash qualifies as a pozzolanic component of geopolymerization [2]. Generally, geopolymers are known to be energy efficient and good in resisting fire
because of very close semblance of their properties to ceramics. They harden at ambient temperatures, yet are sufficiently durable and stable at high temperatures. Hence, the concrete produced through the process of geopolymerization might possess higher resistance against fire compared to the ordinary portland cement (OPC) concrete [1,3]. These properties allow for their use in buildings, especially in cases of insulation against fire. When compared to conventional organic polymers, glass, ceramic, or cement, geopolymers are non-combustible, heat-resistant, formed at low temperatures, and fire/acid resistant [3]. Previous works have studied the responses of geopolymer when subjected to elevated temperature using materials such as metakaolin [4,5], fly ash [6,7], and granulated blast furnace slag [3] etc.

For this study, geopolymer mortar was produced using palm oil fuel ash (POFA), an agricultural ash residue of palm oil mill, obtained from the burning of palm fibres and palm kernel shells at temperature of about 800 - 1000 °C to produce steam for electricity generation in biomass thermal power plants. This geopolymer mortar was achieved by mixing the POFA with alkaline activated solution (NaOH\textsubscript{aq} and Na\textsubscript{2}SiO\textsubscript{3aq}) in the presence of sand to form mortar and actively transforms into hardened geopolymer. This was subsequently subjected to elevated temperature. Researchers have always used residual compressive strength as a mechanism to study the response of geopolymer concrete under elevated temperature. Mohammad et al. [8] studied the residual compressive strength of concrete produced from 20% replacement of cement by weight with POFA. The prepared samples were exposed to elevated temperatures of 100, 300, 500 and 800 °C and were cooled after by two systems – room temperature by natural breeze and water spray. It was found out that the POFA concrete performed better with higher residual strength than normal concrete. In addition, the high temperature and cooling systems affected greatly the mass, color and patterns of crack of the concrete containing POFA.

Compressive strength and microstructure of geopolymer mortar containing POFA subjected to elevated temperature were also studied by Ranjbar et al. [6]. POFA replaced fly ash in succession of 25% until the 100% POFA content and subjected to four levels of elevated temperatures 300, 500, 800 and 1000 °C. The study revealed that all specimens lost their strength when exposed to temperature above 500 °C. The high POFA specimens deformed when subjected to temperature above 800 °C while the FA specimens maintained thermal stability. In previous studies, geopolymer with partial replacement of portland cement, fly ash, metakaolin or granulated blast furnace slag by POFA have been used to study elevated temperature effects on the produced concrete or mortar. However, in this present study, the developed geopolymer mortar was synthesized from 100% POFA.

The objective of this study is to investigate experimentally, the performances of POFA-based geopolymer mortar and their response to three elevated temperatures at 300 °C, 600 °C and 900 °C. Room temperature was used as reference to investigate the compressive strength and microstructural characteristics of the POFA-based geopolymer mortar.

2. MATERIALS AND METHODS

2.1 Palm Oil Fuel Ash (POFA). Untreated raw POFA was collected from local palm oil mill. The raw POFA was dried in an oven at 100 ± 5 °C for 24 hours to remove its moisture and then sieved using a set of sieves (600 µm, and 300 µm) to remove unburnt materials coarser than 300 µm. The ash obtained after sieving was ground in a mechanical ball mill with capacity of 150 balls of different sizes (6 mm to 32 mm) and a rotating speed of 180 rpm, to reduce its particle size and improve its reactivity. To remove unburned carbon and prevent glassy phase crystallization, in addition to agglomeration of particles, POFA was calcined using low heat treatment (550 °C for 90 min). To further improve the surface area, the calcined POFA underwent another round of grinding in the ball mill. The loss on ignition (LOI) values before and after heat treatment is 21.60 and 2.3%, respectively. The reduction in the LOI value is compensated for, by the increase in mass percentages of other oxide components. With total oxides of silicon, aluminium and iron of 78.07%, it complies with the specification of ASTM C618 class F. The particle size distribution of the final stage of preparation of POFA was determined using Turbotrac S360 particle size analyser (PSA). The surface areas
were determined using Micromeritics ASAP2020 BET using nitrogen gas adsorption. Specific surface area of POFA after treatment was 1.5 m$^2$g$^{-1}$ with average particle size of 2.97 μm. Table 1 shows the oxide compositions of POFA, which were determined using x-ray fluorescence (XRF) technique.

### 2.2 Aggregates
Fine aggregate (FA) used in the study is dune sand of fineness modulus of 1.85 and specific gravity in the saturated and surface dry (SSD) condition is 2.62.

<table>
<thead>
<tr>
<th>Chemical composition (mass%)</th>
<th>POFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide (SiO$_2$)</td>
<td>66.91</td>
</tr>
<tr>
<td>Aluminum oxide (Al$_2$O$_3$)</td>
<td>6.44</td>
</tr>
<tr>
<td>Ferric oxide (Fe$_2$O$_3$)</td>
<td>5.72</td>
</tr>
<tr>
<td>Calcium oxide (CaO)</td>
<td>5.56</td>
</tr>
<tr>
<td>Magnesium oxide (MgO)</td>
<td>3.13</td>
</tr>
<tr>
<td>Sodium oxide (Na$_2$O)</td>
<td>0.19</td>
</tr>
<tr>
<td>Potassium oxide (K$_2$O)</td>
<td>5.20</td>
</tr>
<tr>
<td>Sulfur oxide (SO$_3$)</td>
<td>0.33</td>
</tr>
<tr>
<td>LOI</td>
<td>2.3</td>
</tr>
</tbody>
</table>

### Table 1 Chemical composition and physical properties of POFA

2.3 Synthesis of alkali-activators (AA). Commercially available Na$_2$SiO$_3$(aq) of initial silica modulus (Ms = SiO$_2$/Na$_2$O) of 3.3 and NaOH$_{(aq)}$ of 10M concentration were used as alkali-activators (AA). The constituent percentage of Na$_2$SiO$_3$ (aq) are as follows: H$_2$O:62.11%, SiO$_2$:29.13% and Na$_2$O:8.76% and constituent percentage of 10 M NaOH$_{(aq)}$ is as shown in Eq 1.

\[
(30.80\%) 10M \text{NaOH}_{\text{pellets}} \text{ + (68.28\%)} H_2O_{\text{dist}} \rightarrow (24.01\%) 5\text{Na}_2\text{O} \text{ + (6.79\%)} 5\text{H}_2\text{O}_{\text{bonded}} \text{ + (68.28\%)} H_2O_{\text{dist}}
\]

All the available water was from added free water and water contained in the AA. The distilled water and NaOH pellets of 99% purity were used in the preparation of the 10M NaOH$_{(aq)}$. The mass of solids (pellets) used is 399.98 g in 1 L of solution.

2.4 Superplasticizer. A commercially available superplasticizer satisfying the ASTM C494 Type F requirements was used to achieve adequate rheological properties in the fresh mortar as POFA is highly hydrophobic.
2.5 Mixture design. The AA to binder ratio was kept at 0.5 for all the mixtures. The total silica modulus (Ms = SiO$_2$/Na$_2$O) was obtained from activator’s relative proportion – (Na$_2$SiO$_3$$_{(aq)}$/10M NaOH$_{(aq)}$) such as 71.43/28.57 with an equivalent ratio of 2.5:1. The proportion of the mixtures are given in Table 2.

<table>
<thead>
<tr>
<th>Specimen Designation</th>
<th>POFA (kg/m$^3$)</th>
<th>Sand (kg/m$^3$)</th>
<th>Free water (kg/m$^3$)</th>
<th>Alkaline to POFA ratio</th>
<th>Total alkaline liquid (kg/m$^3$)</th>
<th>10M NaOH$_{aq}$ (kg/m$^3$)</th>
<th>Na$_2$SiO$<em>3$$</em>{aq}$ (Ms = 3.3) (kg/m$^3$)</th>
<th>SP (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP$<em>{0.5}$H$</em>{10}$S$_{2.5}$</td>
<td>676.5</td>
<td>1217.6</td>
<td>67.647</td>
<td>0.5</td>
<td>338.235</td>
<td>96.634</td>
<td>241.601</td>
<td>67.647</td>
</tr>
<tr>
<td>AP$<em>{0.5}$H$</em>{10}$S$_{2.0}$</td>
<td>676.5</td>
<td>1217.6</td>
<td>67.647</td>
<td>0.5</td>
<td>338.235</td>
<td>113.884</td>
<td>224.351</td>
<td>67.647</td>
</tr>
<tr>
<td>AP$<em>{0.5}$H$</em>{10}$S$_{1.0}$</td>
<td>676.5</td>
<td>1217.6</td>
<td>67.647</td>
<td>0.5</td>
<td>338.235</td>
<td>169.118</td>
<td>169.117</td>
<td>67.647</td>
</tr>
<tr>
<td>AP$<em>{0.5}$H$</em>{10}$S$_{0.5}$</td>
<td>676.5</td>
<td>1217.6</td>
<td>67.647</td>
<td>0.5</td>
<td>338.235</td>
<td>225.501</td>
<td>112.734</td>
<td>67.647</td>
</tr>
</tbody>
</table>

2.6 Specimen preparations. To remove air pockets, which might affect the properties of the mixture, the POFA and the sand were thoroughly mixed together. AA (mixture of Na$_2$SiO$_3$$_{(aq)}$ and NaOH$_{(aq)}$) was added subsequently, allowed to mix for five mins and then followed by the water and superplasticizer, which was left to mix for another 4-5 min. The overall mixing time was approximately 12 min and the flowability of the fresh mortar was examined using the flow table test. The mixtures were cast in two equal layers into 50 x 50 x 50 mm oil-smeared cube molds and vibrated for 15 s. The samples were demolded after 12 hours in the laboratory covered in vinyl bags to prevent moisture loss. The demolded samples were placed in sealed vinyl bags undisturbed and subjected to 60±5 °C curing for 24 hours. After cooling down from curing, the physical properties like weights and densities were recorded. The control specimens were tested for compressive strength after 7 days of casting and oven curing. The compressive strength test was done using the MATEST crushing test machine of model C-99 at the loading rate of 0.9 kN/s. The other specimens were subjected to elevated temperature at 300, 600 and 900 °C, thereafter tested for residual compressive strength.

2.7 Curing regime and elevated temperature. The specimens were left to harden after casting, covered in polythene bags for 24 hours at 25 °C before subjecting to heat curing at 60±5 °C for a another 24 hours. After that, the specimens were demolded and physical properties were observed and recorded. The hardened specimens apart from the control specimens were exposed to selected elevated temperatures of 300 °C, 600 °C and 900 °C at an incremental rate of 4.4 °C/min using a 1200 °C-capacity electrically operated furnace. These temperatures were sustained for 2 hours before the specimens were allowed to cool down naturally in the furnace in order to prevent the specimen from thermal shock. The specimens were visually observed for any physical change, weighed and their residual compressive strength measured as discussed earlier.

2.8 Microstructural Investigation. To better understand the behaviour of the specimens after subjecting to elevated temperature, microstructural study of the developed POFA alkaline-activated mortar was conducted. Scanning electron microscopy (SEM) imaging equipped with energy dispersive spectrometry (EDS) was performed to understand the microstructural changes in the specimens at different exposure temperature. The phase composition and the crystalline content of the alkaline-activated mortar were also investigated using x-ray diffraction (XRD) test. In addition, thermogravimetric analysis (TGA/DSC) was performed on the treated POFA to assess its stability under thermal stress.

3. RESULTS AND DISCUSSIONS

3.1 Thermal analysis of POFA. The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves for POFA are shown in Fig. 1. From the figure, the TG curve illustrates a very slow decrease in mass until it reached 727 °C. This indicates a highly thermally stable material whose mass loss stabilizes after 1100
The thermal performance of POFA as base material in POFA alkali-activated binder is important in order to ascertain its stability when subjected to elevated temperature. A low thermal degradation of POFA especially up to 700 °C at 3% weight loss is an important finding as the exothermic peak temperature of OPC was reported [9] to be between 100 °C - 170 °C, a value far lower than that of POFA.

3.2 Compressive strength of POFA alkali-activated mortar. The compressive strength of hardened POFA alkali-activated mortar specimens before and after exposure to 300, 600 and 900 °C-elevated temperature are shown in Fig. 2. A clear dependence of the specimen's compressive strength on the alkaline activator (AA) ratio was established in the plot where strength increases with the increase in the AA ratio for all unexposed (control) specimens. This is because of increased generation of SiO$_2$ species as the alkaline ratio increases, which not only increase the SiO$_2$/Al$_2$O$_3$ ratio but also increases the Si-O-Si bonds. A relatively low strength recorded with the POFA alkali-activated mortar specimens was as a result of its low alumina content. This limits the amount of aluminate bridges between the silicate species that can be achieved in order to form a good strength aluminosilicate gel. A closer look at Fig. 2 revealed a decrease in strength of the 300 °C and 900 °C specimens in comparison with the control specimens. In the case of 300 °C mortar specimens, the low residual strength was due to loss of chemically bound fluid from the matrix of the POFA alkali-activated mortar due to heat. However, the heat was inadequate for the matrix to proceed into the molten phase, hence resulting in the non-homogenous appearance of the matrix. As shown in the SEM micrograph, there is a clear interphase between the solid and some of the partially formed molten phases. This brought to the matrix some weaknesses, and as a result, there was loss of strength in the POFA alkali-activated mortar specimens.

As for the 900 °C mortar specimens, there was a huge decomposition of the molten phases formed at 600 °C elevated temperatures, leading to microstructural coarsening of the POFA alkali-activated mortar matrix. This
destruction of the POFA alkali-activated products leads to higher microstructural particle grains, hence, highest loss in residual compressive strength.

![Graph showing compressive strength of POFA alkali-activated mortar at 300, 600 and 900 °C specimens](image)

**Fig. 2** Compressive strength of POFA alkali-activated mortar at 300, 600 and 900 °C specimens

![SEM micrographs of specimens](image)

**Fig. 3** SEM micrographs of specimens (a) Unexposed, (b) 300 °C, (c) 600 °C and (d) 900 °C

**4. SUMMARY**

The following conclusions were drawn from the study on the response of POFA alkali-activated mortar to elevated temperature. The POFA alkali-activated mortar specimens responded differently to the different levels of elevated temperature. At 300 °C elevated temperature, there was a loss in compressive strength of the POFA alkali-activated mortar specimens due to loss of chemically bound water to heat leaving behind empty pores. This led to shrinkage and cracks within the matrix framework. There was an increase in compressive strength at 600 °C for the POFA alkali-activated mortar specimens in all AA ratios. This is due to the microstructural strengthening by the molten phase formation at that temperature, which hardens after cooling and gives some strength to the matrix. There was a huge loss in compressive strength for the POFA alkali-activated mortar specimens exposed to 900 °C due to decomposition of the molten phases formed at 600 °C elevated temperatures leading to the weakening of the matrix of the mortar specimens.
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REFERENCES

Preliminary study on Preparation and Characterization of Ceramic Membrane for Water and Wastewater Filtration

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ABSTRACT. Ceramic membranes are widely used in filtration as it was high chemical resistant, able to withstand high temperature and pressure, and has long life span. In this study, multilayer ceramic membrane (MLCM) was produced in three layers using titanium dioxide (TiO₂), alumina and porous porcelain as top, intermediate and support layer, respectively. The thickness of top layer was vary by using different concentration/amount of TiO₂ ranging from 6 to 12 wt.%. Interlayer of MLCM was observed by using SEM while density and porosity was measured using Archimedes principle. Physical observation on samples shows a good formation of multilayer membrane without formation of cracks. SEM micrograph revealed that higher concentration of TiO₂ produce thicker top layer which is decrease in pore sizes. Density was increased while porosity was decrease with increment of TiO₂ concentration. As a conclusion, multilayer ceramic membrane without any cracks was successfully produced and greatly potential to be used for water and wastewater filtration.

Keywords: Ceramic membrane, Multilayer, Titanium dioxide, Filtration;

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DOI: 10.30967/ijcrset.1.S1.2018.154-159

Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Water pollution was an increasing problem over the last few years. This is because of increasing in human population and increasing industrial activities. The progress of textiles, leather, surface treatment, mining, automotive and general chemical process industries lead to increase the concentration of colorant and dangerous ions of heavy metals not only in the wastewaters but even in drinking ones [1]. It can be quickly passed along the food chain and can cause various problems. Meanwhile, dyeing wastewater from the textile industry contains large amounts of dyestuff together with significant amounts of suspended solids, salts and trace metals. This dyeing wastewater can cause serious environmental problems due to its high color, large amount of suspended solids and high chemical oxygen demand. The best ways to solve this problem is by using the materials such as membrane filtration that can separate waste and water, and be reused for other benefits. Ceramic membrane can be designed in single or multilayers structure.

In multilayer ceramic membrane (MLCM), alumina normally used as support due to excellence mechanical and chemical properties. Ceramic membranes normally have an asymmetrical structure composed of at least two, mostly three, different porosity levels [2]. In order to reduce the surface roughness, a mesoporous has been applied first before applying the active micro porous top layer. The macro porous support ensures the mechanical resistance of the nano filtration process. These elements are grouped together in housings and these membrane modules can withstand high temperatures, extreme acidity or alkalinity and high operating
pressures that will make it suitable for many applications where polymeric and other inorganic membranes cannot be used. The development of such multilayer configuration includes, shaping of an appropriate support material, formation of mesoporous interlayers, and microporous top layer. Alumina, titania, zirconia or silica are considered as the main ceramic materials for the formation of the multi-layer structures [3]. Ceramic membrane permeability depends primarily on its porosity, pore tortuosity and morphology.

The effectiveness of the membrane is influenced by its structural properties for separation during the filtration process and it can be controlled during the fabrication of the membrane. The function of MLCM can be enhance by incorporating TiO₂ as top layer. TiO₂ layer will act as organic pollution degradation by photocatalytic action in presence of light and give advantage over conventional filtration membrane. The aim of this research was to prepare and characterize the multi-layer ceramic membrane for water and wastewater filtration by using of TiO₂ as top layer. The effect of different concentration of TiO₂ toward physical and morphological structure of MLCM will be investigated in this study.

2. MATERIALS AND METHODS

2.1 Support layer

Commercial ready mixed porcelain cake which is supply by Abbe Bay Sdn. Bhd. was used in this research. Porcelain cake was grind into powder and added with appropriate amount of water to form dough and shape to tubular form by using the extrusion method. The sample then dried at room temperature for 24 hours to ensure homogenous drying before heated in oven for 70 °C for another 24 hours. Samples were sintered at 900 °C for 2 hours holding time to produce tubular alumina support.

2.2 Interlayer Membrane

An intermediate layer was coated on the support layer in order to increase filtration ability. The powder suspension technique was being used to prepare the alumina (Al₂O₃) intermediate layer. A deflocculated suspension of alumina can be obtained by mixing the alumina powder, binder and dispersing agent (aqueous solution). The ratio of the alumina powder to water containing binder and dispersing agent is 30:70 wt.%. The sample was being prepared by using dip coating method. After the sample was dried at room temperature for one day, the sample was heated in oven for 70 °C to make sure the sample was totally dried before sintered at 1000 °C.

2.3 Top Layer

The preparation of top layer has being prepared by using pouring method with different concentration of TiO₂ (6-12 wt.%) in 100 ml of solution containing binder and dispersant. The thickness of the layer is control by pouring for 1 min on the top of intermediate layer, the remaining solution was discarded. Sample then dry at room temperature for 24 hours and in oven for 70 °C for another 24 hours before sintered at 1000 °C as 2 hours holding time. The MLCM then characterized for density and porosity using Archimedes principle and morphological observation using SEM.

3. RESULTS AND DISCUSSION

A good multilayer ceramic membrane was obtained without cracks for samples, example of sample produce at 6 and 12 wt.% of TiO₂ are shown in Fig 1. It is clearly seen a good bonding between support, intermediate and top layers.

Density and porosity of MLCM was determined using Archimedes principle. It was found that The density of MLCM was increased from 1.75 to 1.85 g/cm³ with increasing concentration of TiO₂ from 6 wt.% to 12 wt.%, as shown in Fig. 2(a). This is due increment in amount of TiO₂ which contributed to mass and better packing arrangement of particle in at higher concentration of TiO₂ [4]. As the density increase, the amount of porosity of MLCM was decreased from 35% to 25% as shown in Fig. 2(b).
The amount of porosity in MLCM will influence the filtration of the membrane. For better filtration, the pore size distribution of the multi-layer ceramic membrane must be larger and this makes the volume of water more collected at the highest porosity [5].

Fig. 1 Example of MLCM produces at (a) 6 wt.% and (b) 12 wt.% of TiO$_2$.  

Fig. 2 (a) Density and (b) Porosity of MLCM at different concentration of TiO$_2$.

Fig. 3 shows the morphology of fracture surface of MLCM. It can be seen the good bonding between layers was obtained without cracks. The thickness of the top layer was found increase with increasing concentration of TiO$_2$. At 6 wt.% TiO$_2$ the thickness of top layer was around 20.6-20.7 μm, compared to 41.0-56.2 μm for 12 wt.% TiO$_2$. The required thickness for membrane are normally between 1-50 μm [6]. The thickness of the
layer can be controlled by the percentage of the powder added to the suspension and the coating time. The pore size of MLCM with 6 wt.% was larger (20-200 μm) compared to 12 wt.% TiO$_2$ which is around 30-70 μm. As previously describe, higher concentration of TiO$_2$ produce better particle packing and also reduce the pore sizes and pore volume.

![Fig. 3 Morphology of MLCM (a) 6 wt.% TiO$_2$ and (b) 12 wt.% TiO$_2$](image)

4. SUMMARY

MLCM was successfully produced without any crack between its interlayer. Increasing the concentration of TiO$_2$ give better particles packing and increase the density of MLCM. 12 wt.% TiO$_2$ produce smaller pore size and amount of porosity which is suitable for filtration under high pressure in the future study.

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Rheological Behaviour and Fired Properties of Malaysia Clay from Mersing(Johor) In Application to Manufacturing of Ceramic Tile

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ABSTRACT. The aim of this research work was to evaluate the rheological behaviour and firing properties of Mersing clay from the state of Johor, Malaysia. The knowledge of this study is crucial to evaluate the potential of the clay as a raw material in application to ceramic tiles. Rheological behaviour was identified by deflocculant demand, thixotropy, zeta potential and cation exchange capacity (CEC). Fired properties were determined by linear fired shrinkage, water absorption, bulk density, apparent porosity and fired colour. It is found that the clay is suitable to be used for wet milling process in manufacturing of tiles with low in CEC value (16 meq/100g) and high in zeta potential between -40 to -45 mV from pH of 6 to 12. The fired properties of the clay are greatly influenced by its mineralogical and chemical composition, especially fluxing oxides of K₂O from illite, which promotes formation of liquid phase. Therefore, the Mersing clay demonstrates that it is most appropriate to be used as a raw material for the production of ceramic tiles.

Keywords: Clay, Deflocculant demand, Zeta potential, Thixotropy, CEC;

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1. INTRODUCTION

Clay is widely used as the main raw materials in the manufacturer of ceramic tiles. In Malaysia, clay can be easily found in the state of Johor especially in the Mersing District [1]. The land in Johor is mostly utilized for agriculture, mainly oil palm and rubber plantations [2]. For geological survey, Johor has six main geological formations underlying the soil, namely Quaternary, Tertiary, Cretaceous-Jurassic, Triassic, Permian, Intermediate Intrusive, Acid Intrusive and Devonian. The soils of Johor can be classified into three groups, namely sedimentary, alluvial and miscellaneous soils where these soils have been differentiated into soil series and associations. The distribution pattern of these soil series and associations reveals a close relation with those of different geological lithologies within the state [2]. However, very little research works were conducted on the clay in Mersing as most researchers is focusing on research work related to advanced ceramic materials.

Rheological properties of slurries during wet milling process and fired properties are important measurement to ceramic tile manufacturer. The dispersion of clay by wet milling process is a fundamental step to obtain homogeneous and stable system, which is characterized by rheological properties [3]. The viscosity of clay suspension can be reduced by introducing suitable deflocculant with minimum concentration, where it can be measured by deflocculant demand. Furthermore, clay undergoes changes
during firing process as a result of physical, chemical and mineralogical modification [4]. In terms of clay mineral, kaolinite-illite mixture is widely used in ceramic tile industry, where alkaline fluxes (such as K₂O and Na₂O) in reaction with silica and alumina promote liquid phase formations that facilitate densification [4]. Rheological and fired properties of clay will depend on the composition and the homogeneity of the mixture mainly on the clay minerals [5]. Therefore, the aim of this research work is to evaluate the rheological behaviour of Mersing clay together with their fired properties viz. linear fired shrinkage, water absorption, bulk density, apparent porosity and fired colour. The knowledge derived from this study is crucial for evaluating the potential applications of Mersing clay in designing the ceramic tiles body formulation.

2. MATERIALS AND METHODS

2.1 Sample Preparation. Raw clay from Mersing (Johor) supplied by KBB Minerals Industries SdnBhd was collected for this research work. For sample preparation, the clay was dried at 110 °C for 24 hours and grounded to fine particles by using agate mortar. Later, the clay was homogenised by coning and quartering technique to collect representative samples. The sample was wet milled according to common industrial ceramic tiles procedures and dried at 110 °C for 24 hours. Milled powder was moisturized to moisture content of about 6% [6] and follow by crushing and sieving operations through 500 µm sieve to ensure break down of agglomerates. Later, the sample was aged for 2 hours in enclosed environment to ensure homogeneity of moisture across the powder particles. The humid samples were pressed to button of 50 mm in diameter (powder of 24 g) with pressing pressure of 27 MPa and dried at 110 °C for 24 hours. Dried buttons were fired using Nabertherm N60/14 furnace with firing temperature of 1000 to 1250 °C with holding time of 30 min.

2.2 Characterization. The thermal behaviour, mineralogical and chemical composition (Table 1) of the studied clays were described elsewhere [7], where Mersing clay has reported containing high illite and quartz. The studied clay was characterized by deflocculant demand, thixotropy, zeta potential and Cation Exchange Capacity (CEC). Deflocculant demand and thixotropy were obtained by using Torsion Viscometer (Gallenkamp type) with fluidity and over swing as measurement for rheological behaviour. Three types of deflocculant were used, namely sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP) and sodium metasilicate (SMS). Zeta potential was measured by using Brookhaven Zeta plus zeta meter [8]. CEC was measured and by using ammonium acetate method and expressed as mili-equivalents (meq) of cation adsorbed per 100g of clay [9]. For fired properties, linear fired shrinkage was measured from the variation of the length between the dried and fired samples. The water absorption was determined from weights differences between the as-fired and water saturated (immersed in boiling water for 2 hours and follow by cooled water for 4 hours) samples. Bulk density and apparent porosity of fired samples were determined by Archimedes principle by using distilled water. The fired colour of fired samples were analysed in terms of L*, a* and b* values by using Hunter Lab Mini Scan EZ.

<table>
<thead>
<tr>
<th>Table 1 Chemical analysis of Mersing clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>68.14</td>
</tr>
</tbody>
</table>

* Loss on Ignition

3. RESULTS AND DISCUSSION

3.1 Deflocculant Demand and Thixotropy. Fig. 1 shows the rheological behaviour of Mersing clay with various deflocculant with concentration of 10% of solid content of deflocculant. Deflocculant is used during wet milling process to disperse slip. Fig. 1a shows that both STPP and SHMP shows low in deflocculant
demand with Mersing clay of about 0.06% of deflocculant added as compare with SMS of 0.18%deflocculant added to achieved maximum fluidity, which indicates that SMS is not the preferable options to be used in processing of Mersing clay through wet milling process. Similar observation was observed for thixotropy of Mersing clay after 1 min at rest (Fig. 1b).

3.2 Zeta Potential and CEC. Fig. 2 shows the zeta potential of Mersing clay. For pH range of 2 - 12, the zeta potential of Mersing clay is negative and indicate that the clay particles consists of net negatively charge over the whole range of pH [8,14,15]. An increase in the pH of clay suspension is resulted in drastic increase of the negatively charge until pH of 6 (acidic region). The zeta potential of Mersing clay was saturated between -40 to -45 mV from pH of 6 to 12 (alkaline region). The main contribution to the negatively potential is the structural or permanent negative charges located on the basal face of the clay particles formed by isomorphic substitution of Al and Si ions in the crystal lattice with lower valence metal ions. Therefore, the basal face is permanently net negatively even with very low pH [16-18]. At low pH (acidic region), it was observed that the negative zeta potential becomes smaller in magnitude, which was due to the permanent surface charges formed isomorphic substitution of lower valence metal ions in the clay crystal structure being progressively neutralised by the pH - dependent positive edge charges that become more important with decreasing pH. These positive charges are not sufficient to completely neutralise all the permanent negative charges even at low pH [15-17].

CEC value of Mersing clay is 16 meq/100 g. The extent of clay’s ability to adsorb cations indicates the extent of disorder in its structure by CEC measurement. Typical CEC value of well - ordered kaolinite, disordered kaolinite and illite are 3 - 6 meq/100g, 15 - 40 meq/100g and 10 - 40 meq/100g, respectively [10-13]. Generally, the CEC reading of Mersing clay is considered low and coincided within the range of CEC value
mentioned above. It gives guide to likely physical characteristics and indication of amount of electrolyte required to be added to achieve flocculation or deflocculation [12]. For tile manufacturer with wet milling process, it is always desired to select clay with low CEC value, which will promote low in viscosity of ceramic body suspension (such as clay) after milling process.

Both CEC and zeta potential characterised the surface property of Mersing clay’s particles in suspension, where the magnitude of these parameters is often used to measure the strength of the repulsive interaction between particles [15]. Stable colloidal suspension can be achieved by increasing the negatively charged of clay particles [19]. If zeta potential of ceramic suspension has not achieved sufficient negatively charged of clay particles to counter positive ions in medium, low repulsion force between particles occurred and particles will approach each other by attractive Van der Waals force and hence agglomeration will occur, which is not desired by tile manufacturer by wet milling process. It is always desired to select clay with low CEC and higher zeta potential in negative values in processing of tile body formulation by wet milling operation.

3.3 Fired Properties. Fig. 3 (a) shows the linear fired shrinkage and water absorption of Mersing clay. Fired linear shrinkage increased (from about 1% to 11%) and water absorption (from 18% to 0%) decreased from firing temperature of 1000 to 1200 °C. Water absorption was saturated above firing temperature of 1200 °C, while fired linear shrinkage shows small reduction trend which is due to forced expulsion of the entrapped gases resulting in blisters and bloat at firing temperature of 1250 °C [20]. Fig. 3 (b) shows the bulk density and apparent porosity of Mersing clay, which provide information of densification behaviour. Bulk density increased and apparent porosity decreased from firing temperature of 1000 to 1200 °C. Water absorption is closely related to porosity and densification of clay after firing operation, where increasing firing temperature leads to liquid phase formation due to present of fluxing oxides especially K2O [7] from illites [7]. The liquid phase formation will penetrate the pores, decreases the porosity and water absorption and increase the bulk density, where it has greatly contributed to densification processes after firing operation [21]. The liquid surface tension and capillarity of liquid phase will help to bring pores close together and reduce porosity [4, 21, 22].

Water absorption is determining parameters to define the category of ceramic tiles. According to ISO 13006 (1998) [23], ceramic tile has divided into four categories on the basis of water absorption: ≤ 0.5% (Group Bla), 0.5 - 3.0% (Group Blb), 3 - 6% (Group Bll), 6 - 10% (Group Bli) and >10% (Group BlIII). Mersing clay is considered suitable to be used by tile manufacturer for wide ranges of application.
Table 2 shows the fired colour of Mersing clay in $L^*$, $a^*$ and $b^*$ values. $L^*$ value indicates the lightness scale with 0 is black and 100 is white. The $L^*$ value decreased with increasing firing temperature from 1000 to 1200 °C, which later maintain at $L^*$ value of 62 to 63 from firing temperature of 1200 to 1250 °C. The $a^*$ value shows saturated trend from firing temperature of 1000 to 1150 °C and reducing trend after firing temperature of 1150 °C. The $b^*$ values shows overall increasing trend from firing temperature of 1000 to 1150 °C and decreasing trend from firing temperature of 1150 to 1250 °C, where increasing $b^*$ values will increase the intensity of yellowish colour. The fired colour of Mersing clay is affected by the present of TiO$_2$ and Fe$_2$O$_3$.

**Table 2** Fired colour of Mersing clay

<table>
<thead>
<tr>
<th>Firing Temperature, °C</th>
<th>Fired colour, $L^*$ value</th>
<th>Fired colour, $a^*$ value</th>
<th>Fired colour, $b^*$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>83.88</td>
<td>5.03</td>
<td>10.33</td>
</tr>
<tr>
<td>1050</td>
<td>84.17</td>
<td>4.43</td>
<td>9.64</td>
</tr>
<tr>
<td>1100</td>
<td>80.48</td>
<td>4.68</td>
<td>11.77</td>
</tr>
<tr>
<td>1150</td>
<td>71.31</td>
<td>5.05</td>
<td>14.44</td>
</tr>
<tr>
<td>1200</td>
<td>62.33</td>
<td>3.01</td>
<td>11.28</td>
</tr>
<tr>
<td>1250</td>
<td>63.61</td>
<td>2.29</td>
<td>10.65</td>
</tr>
</tbody>
</table>

**Fig. 4** Physical appearance of fired buttons of Mersing clay

4. **SUMMARY**

Mersing clay from Johor, Malaysia was investigated and characterised by rheological and fired properties. For rheological properties, Mersing clay shows low in CEC and high in zeta potential in negative value without flocculation and thixotropy issue. Mersing clay is considered suitable to be used in wet milling process for manufacturing of ceramic tiles. The fired properties of Mersing clay is greatly influenced by its mineralogical and chemical composition. The densification, water absorption and fired colour of Mersing clay is influenced by fluxing oxides of K$_2$O from illite, which promotes formation of liquid phase. At low firing temperature, Mersing clay is considered suitable for production of wall tiles with good in fired colour. At high firing temperature, Mersing clay is suitable for production of floor and porcelain tiles with darker tone in fired colour. In general, Mersing clay is suitable to be used for all ranges of ceramic tiles. It is expected that the present investigation work will also help to expand the application of Mersing clay to other ceramic industries such as bricks, sanitary wares, refractories, decorative wares and etc.

**ACKNOWLEDGEMENT**

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The Effect of Sintering Temperature of 8YSZ Powder to Densification and Crystal Structure

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ABSTRACT. In this paper, effect of sintering temperature on the microstructure and phase transformation in 8 mol% of yttria stabilized zirconia (8YSZ) has been studied. 8YSZ ceramic materials sintered at 1550 °C to 1700 °C were investigated. The fraction of tetragonal to monoclinic transformation increase with the increment in sintering temperature as grain size increase. Major fraction of monoclinic zirconia phase was found in 8YSZ matrix after increase sintering temperature. The fraction of cubic zirconia phase was also found increase slightly with the increase in sintering temperature. Empirical results from XRD, SEM and density clearly indicate that the highest densification and dominant phase obtained. Granulated 8YSZ presented that no significant on sintering temperature.

Keywords: Yttria stabilized zirconia, Densification, Rietveld refinement, X-ray diffraction;

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1. INTRODUCTION

Granulation is an agglomeration method that obtains granules with desired characteristics and functionality [1]. Gardner et al. [2] stated that granulated powder are good in flow ability and filling performance during compaction, thus can produce dense ceramic. Granulated powders provide rapid uniform fill to minimize part to part variations. Besides, granulated powder allows rapid and continuous release of entrapped air during compaction to avoid the formation of defects like delamination that might occur due to channelling of escaping air that to occur in non-granulated ceramics. Granulated 8 mol% of yttria stabilized zirconia (8YSZ) is one of the most common electrolytes materials used in solid oxide fuel cell (SOFC), with many advantages such as low thermal expansion coefficient (10.7 × 10⁻⁶ K⁻¹), low thermal conductivity (2.1 Wm⁻¹ K⁻¹) at 1000 °C, high thermal shock resistance [3]. In order to produce dense 8YSZ ceramic, the effect of temperature needs to be systematically studied. Wang et al. [4] pointed out that sintering process induces particles to bonded together by diffusion, mass transport from the regions with the high chemical potential to lower chemical potential and neck growth between particles. After sintering, residual porosity occurred due to presence of free gaps between particles. Consequently, Ali et al. [5] had reported that sample tends to increase the bonding strength between particles as well as lower the modulus of elasticity for some ceramic. Therefore, the present research was conducted to investigate the effect of sintering temperature on the microstructure and phase stability of 8YSZ ceramic. The structure and phase stability was studied by using X-ray diffraction (XRD) while scanning electron microscope (SEM) was used to elucidate the microstructure.
2. MATERIALS AND METHODS

The work described in this paper was conducted with the same material used in a previous paper [6, 7]. Powders of 8 mol% yttria-stabilized zirconia (8YSZ) with average particle size less than 160 µm were purchased from Maju Saintifik. The particle size distribution was determined with a laser diffraction analyser (Mastersizer S, Malvern, Worcestershire, United Kingdom). Phase composition of 8YSZ powder comprised of 3.8% of monoclinic crystal structure. A sample of 3.5 g of 8YSZ and approximately 3 to 4 drops binder polyvinyl alcohol (PVA) were mixed and press into cylindrical sample (diameter = 20 mm and height = 2.4 mm) with pressure 220 MPa by using Automatic hydraulic press (3890.4NE000). Compact green body pellets were undergoes different sintering temperature 1550 °C, 1600 °C, 1650 °C and 1700 °C and hold for 4 hours, respectively. Density of the sintered ceramics were measured based on Archimedes principle, while phase composition were analyzed with X-ray diffractometer. All XRD patterns were collected at room temperature in range of 2θ = 5° to 90°. The diffraction signals were collected with step size of 0.02°. Rietveld refinement method using Xpert HighScore Plus software to quantify phase and refine the crystal structure. The crystallite size (D) was estimated from line broadening of the (111) peak. D was calculated from Scherrer equation: D = 0.9λ/βcosθ; where λ is the wavelength of the X-rays, β is the corrected full width at half-maximum of the peak and θ is the diffraction angle. Besides, the surface of the sintered specimens observed by HITACHI TM3000 Tabletop Microscope.

3. RESULTS AND DISCUSSION

Fig. 1 (a) shows that typical spectra of XRD for (ZrO$_2$)$_{0.92}$(Y$_2$O$_3$)$_{0.08}$ ceramics sample prepared at varying sintering temperatures (1550 °C, 1600 °C, 1650 °C and 1700 °C for 4 hours). The phase composition of 8YSZ ceramic only consists of tetragonal zirconia (ICSD 98-002-0789) with space group P42/nmc, cubic zirconia (ICSD 98-003-2797) with space group Fm3m and monoclinic zirconia (ICSD 98-010-8439) with space group P121/c1. The main phase composition including cubic ZrO$_2$ and tetragonal ZrO$_2$, followed by monoclinic ZrO$_2$.

The XRD patterns reveal the absence of extra reflections corresponding to any secondary phase of impurity in the ceramics because solid solutions involving there elements have formed through inter-diffusion and the solid solubility is below than the corresponding limit. Reflections at 30°, 35° and 50° were observed in all sintered 8YSZ ceramic samples attribute to the overlapping of cubic and tetragonal phases. It was obviously display that the particular peaks involves the combination of both cubic and tetragonal phases. It is hard to single out that particular peak is refer to what phases. Thus, crystal structure refinement by using Rietveld method was used to identify the polymorphs present for each sample as display in Table 1. Moreover, it is visibly that cubic zirconia generated high intensity at sintering temperature 1550 °C. Major monoclinic phases was detected at hkl, (11$ar{1}$) at 28° and (111) at 31.3°. The 8YSZ sintered at different temperature have same phase structures (cubic, tetragonal and monoclinic). Colomer et al. [8] stated that the highest intensity peaks corresponding to 8YSZ solid solution can be observed at (111), together with defined peaks corresponding to a cubic zirconia phase. It is well known that in cubic zirconia the coordination of Zr$^{4+}$ ion is formed by 8 oxygen neighbors place at equal distances. The diffraction peaks with Miller indices (111) cubic phase show a shift to higher d-values (2.992) at 1600 °C whereas the peak shifted to a lower d-value (2.973) at 1550 °C. The peaks that correspond to the cubic phase are further shifted towards lower d-values.

Sintering temperature has exerted a significant influence on the typical diffraction peak positions and lattice parameters of 8YSZ [9]. From the results of qualitative phase analysis in Fig. 3(a), the intensity of diffraction pattern was not clearly revealed. When focusing at position 30° in Fig. 3(b), the intensity of diffraction pattern is the highest at 1550 °C, followed by 1650 °C, 1700 °C and 1600 °C. Correspondingly, an obvious variation in the unit cell parameters of both phases has occurred with the change in sintering temperature in ceramic. The position of the (111) diffraction peak of 8YSZ has moved to low angle region.
with the increasing of sintering temperature, demonstrating the reduction of unit cell parameter of 8YSZ. It can be supported by the quantitative results as tabulated in Table 1. As presented in the Table 1, demonstrates the percentages of tetragonal (T), monoclinic (M) and cubic (C) phases of various sintering temperature (1550 °C to 1700 °C) that obtained by XRD analysis. The tetragonal phase decreasing with increment in sintering temperature. This is due to the lattice parameter started to undergo expansion when temperature arise. The cubic phase content increase from 31.3 % to 36.8 % at sintering temperature from 1550 °C to 1600 °C. This explained that the decomposition Y³⁺ ion of tetragonal 8YSZ diffused to cubic phase at high temperature [3]. A significant growth in cubic lattice parameter ascertain oxygen vacancy with increased sintering temperature. Monoclinic phase content was increasing as an increment in sintering temperature. It displays about 9.1% appears after sintered at 1550 °C and increase up to 18.5% at 1700 °C. Thus, Liu et al. [10] states high sintering temperature 1700 °C promotes phase transformation (tetragonal to monoclinic) due to volume changes in the phase stability of 8YSZ.

![Fig. 1](a) XRD pattern of the 8YSZ ceramics with various sintering temperature (1500 °C, 1600 °C, 1650 °C and 1700 °C) sintered for 4 hours in air and (b) comparison of dissimilar sintering temperature at position of 30°

### Table 1 Percentage of phases in each sample

<table>
<thead>
<tr>
<th>Sintering Temperature, °C</th>
<th>Tetragonal</th>
<th>Cubic</th>
<th>Monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1550</td>
<td>59.7</td>
<td>31.3</td>
<td>9.1</td>
</tr>
<tr>
<td>1600</td>
<td>50.8</td>
<td>36.8</td>
<td>12.4</td>
</tr>
<tr>
<td>1650</td>
<td>53.0</td>
<td>34.5</td>
<td>12.5</td>
</tr>
<tr>
<td>1700</td>
<td>47.3</td>
<td>34.2</td>
<td>18.5</td>
</tr>
</tbody>
</table>

The lattice parameters of tetragonal started to deform where c-axis undergo contraction and a-axis elongation when calcination temperatures higher than 1000 °C. Such deformation change tendency of lattice parameters as Y ion incorporate into the lattice of zirconia to form a substitution solid solution [11]. Besides that, Y ion has larger ionic radius than of Zr ion; when it incorporates into the lattice, the unit cell of zirconia expand. At temperature below 900 °C, most of the Y ion are only mixed and not a substitution of Zr atoms in the structure. It was concluded that increasing the sintering temperature suppress the grain growth. Thus, the transformation from monoclinic to tetragonal also increasing. The crystalline size for the tetragonal to
The cubic phase transformation is ~6 nm from 1550 °C to 1650 °C. The crystallite size may become larger if the crystallite suffers higher lattice strain due to high sintering temperature at 1700 °C. Thus, higher the sintering temperature can lead to rapid decomposition of tetragonal 8YSZ. As a result, the effect of sintering temperature on granulated 8YSZ presented low densification (62%-67%), low percentages of cubic phase (31% - 36.8%) and eventually contributed to low ionic conductivity.

SEM morphologies of 8YSZ ceramics sintered at 1550 °C to 1700 °C for 4 hours are presented Fig. 2. The densification of the specimens was measured at different sintering temperature. The morphology shows that sample was not fully densified. Table 2 indicated that the densification of 8YSZ samples sintered at 1550 °C was about ~67.40% while the rest is only approximately ~ 62%. This variation was parallel with the SEM results depicted in Fig. 3. But then in previous research, Patil et al. [12] and Zhang et al. [13] stated that sintering temperature at 1550 °C of 8YSZ can achieve densification almost ~98%. Grain growth in Y2O3 stabilized zirconia will distribution of Y3+ ions plays a significant role in densification process. According to segregation of Y3+ ions on grain boundaries for 8 mol% Y2O3 stabilized zirconia suppresses the grain growth by a mechanism of solute drag, while the relatively uniform distribution of Y3+ ions for 8YSZ has a weak effect of solute drag resulting in higher grain growth rate [14]. Grain growth of 8YSZ was not achieved throughout sintering process, which Wang [4] pointed out that sintering process induces particles to bonded together by diffusion, mass transport from the regions with the high chemical potential to lower chemical potential and neck growth forms between particles. Finally, Ali et al. [5] had reported that sample tends to increase the bonding strength between particles during sintering process.

Table 2 Result of densification of 8YSZ at various sintering temperature

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Bulk density (g/cm³)</th>
<th>Densification (%)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1550</td>
<td>3.805</td>
<td>67.40</td>
<td>32.60</td>
</tr>
<tr>
<td>1600</td>
<td>3.585</td>
<td>62.26</td>
<td>37.74</td>
</tr>
<tr>
<td>1650</td>
<td>3.626</td>
<td>62.48</td>
<td>37.52</td>
</tr>
<tr>
<td>1700</td>
<td>3.598</td>
<td>62.44</td>
<td>37.56</td>
</tr>
</tbody>
</table>
In general, surface diffusion is a matter redistribution where particles transport through the pores surface, the concentration of adsorbed particles, i.e. surface coverage is a function of complex nature of the interaction between the adsorbed particles and the surface atoms [15]. Surface diffusion is important phenomena for a sample to densify. Fig. 3 clearly shows that overall 8YSZ granulated sample was not undergo any surface diffusion between particles which cause porosity to be occurred. When surface diffusion not happen between particles, consequently lattice diffusion from the surface will not take place. It followed by grain boundary diffusion and lattice diffusion from grain boundary difficult to form between particles. Therefore, empirical results from Table 2 shown that the studied samples densified less than 95% was ascribe to huge particles size different (16-160 μm) between one another. It was demonstrated that the surface diffusion undergoes long distance transport of particles and hard to diffuse among particles.

Fig. 3 Morphology of 8YSZ sintered at 1700 °C, at magnification 1000x

4. SUMMARY

Several factors such as grain size, porosity, sintering temperature and stress are responsible for densification in 8YSZ sintered samples. Although many studies on 8YSZ or ZrO$_2$ based material can be densified when sintered at 1550 °C, but in present study even sintered up to 1700 °C still not densified. It did not revealed that the sintering temperature is an important factor affecting the densification of granulated 8YSZ. The results showed that the granule 8YSZ strongly independent on the sintering temperature. Sintering temperature at 1550 °C to 1700 °C was lead to low densification was about 62% to 67% only. It had proven that sintering temperature does not affect significantly on 8YSZ granule particles. Further experiment will be investigated on the densification of the granule 8ysz.

REFERENCES


The Effect of Surfactants on the Stability of TiO$_2$ Aqueous Suspension

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ABSTRACT. To produce TiO$_2$ nanoparticles suspension for coating applications, it is vital that the nanoparticles are well dispersed in liquid media and remain stable without sedimentation for a certain time. In this study, TiO$_2$ suspensions were dispersed in aqueous media using ultra-sonication in the presence of various types of surfactants; Sodium dodecyl sulfate (SDS), Hexa-decyltrimethylammonium bromide (CTAB) and Pluronic F-127 (PF-127). Three parameters were investigated; amount of surfactant, time-dependent stability and effect of charges (ions) on the TiO$_2$ dispersion and the suspension stability behavior. The addition of surfactant produced more dispersed and stable TiO$_2$ in aqueous suspension. 2.5 wt.% of all type surfactant was found to produce the most stable suspension with high turbidity and measurable particle size. CTAB was found to provide more stable TiO$_2$ suspension than SDS and PF-127 attributed from electro-steric stabilization.

Keywords: TiO$_2$, Stability, Surfactant, Turbidity, Zeta potential;

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1. INTRODUCTION

Titanium dioxide (TiO$_2$) can be used in various industries, such as for environment and health-care. For environment, it is widely used as self-cleaning coating [1], water treatment [2] and materials for air purification [3]. In health-care, it is used as antibacterial [4] and anti-cancer [5]. These two applications require TiO$_2$ nanoparticles (NPs) to be dispersed in aqueous environment and enter the aquatic ecosystem. The outcomes of TiO$_2$-NPs in aqueous environment depend on their physical and chemical properties such as surface characteristics and sizes and other chemical species in water. To prepare the TiO$_2$ dispersion it requires deagglomeration of NPs clusters to represent individual particles with size as smallest as possible and stabilizing these NPs in the suspension for a certain time. The main problem with TiO$_2$-NPs is they typically insoluble in aqueous medium, hence obstructing its utilization as colloidal dispersion or stable suspension. The NPs have strong tendency to agglomerate due to large surface area as compared to submicron particles. Generally, the agglomeration is caused by Van der Waals attraction forces between particles. In the case of TiO$_2$-NPs, the surface is hydrophobic in nature, while the electrostatic interaction between NPs in aqueous medium resulting accumulation and agglomeration of TiO$_2$ to size larger than 3 μm [6].
The aggregation of TiO$_2$ NPs plays a key role in their fate in aqueous environment. It is explained why the commercial TiO$_2$-NPs are often shipped as dry powders; for easy handling because storage these NPs in dispersed water could not be kept in nanoscale range. In coating industries especially for photoactive and UV-blocking, the uniform and transparent coating is essential which relies on the ability of TiO$_2$-NPs to have minimum degree of agglomeration and the NPs can be distributed homogeneously or in desired patterns [7]. While in medicine, the agglomeration can lead to misleading interpretation of the toxicology and the uptakes of NPs into the biological system [8]. There are several methods to suppress the agglomeration or to deagglomerate the NPs in colloidal state such as by counterbalanced of electrostatic and steric stabilization [9-13]. Stability of NPs in aqueous environment is determined by the pH of solution and surface charges of the NPs in water [10]. Deagglomeration proceeds through the break-up of bonds between single NPs crystallites in the aggregates. These can be achieved by creating an electrical double layer at the solid-liquid interface or by adsorbing polymers or surfactants on the NPs surfaces [14]. A stable colloid solution needs some type of inter-particle repulsion to overcome the nature of van der Waals attraction. Electrostatic stabilization is achieved by addition of charge (ion) to NPs so that they can repel each other and this is often occurs under influence of pH. Steric stabilization is achieved by adsorption of polymer to the surface of NPs forming a thin layer which prevents the NPs from agglomeration [15]. Addition of polyelectrolyte into a NPs suspension will generate a combination of electrostatic and steric stabilization termed as electro-steric [16,17]. Steric stabilization or polymer-induced interactions arise from the adsorbed polymer chain of the surfactant that protrude into the solvent and provide protective layer on the NPs surfaces [15]. There are three main factors brought to the efficient stabilization; the adsorbed layer should be thick enough to avoid the van der Waals attraction, the adsorbed molecules should be adsorbed strongly to the entire NPs surfaces and the chains that protrude into solvent should be in good solvent conditions [18].

To disperse TiO$_2$-NPs in aqueous medium, an external force is needed to overcome the van der Waals attractions. Sonication is commonly used to break up agglomerated NPs in a solvent because the oscillation of liquid cause nucleation and collapse of solvent bubbles; bubble formation and collapse at the surface of solids can be very effective in chopping solids [19]. In this work three types of surfactants with various functional groups were used as stabilizing agent to stabilize the TiO$_2$ aqueous suspension. The aim is to study the behaviour of TiO$_2$-NPs when dispersed in aqueous medium in the mean of turbidity, zeta potential and particle size. The main objective is to determine the most suitable surfactant to stabilize TiO$_2$ in aqueous media.

2. MATERIALS AND METHODS

The readily synthesized anatase TiO$_2$ particles were prepared as described by previous study [20]. To prepare the TiO$_2$ suspension, 0.025 g of TiO$_2$ NPs was dispersed in 50 mL of distilled water using ultrasonic homogenizer equipped with temperature controller (Ultrasonic Elma, E15H) for 30 min. Three types of surfactants were used; Sodium Dodecyl Sulfate (SDS) molecular weight (Mw) of 288.372 gmol$^{-1}$, Hexadecyltrimethylammonium bromide (CTAB) Mw of 364.45 gmol$^{-1}$ and PluronicF-127 (PF-127) Mw of 12 600 gmol$^{-1}$. The required amount of dispersant from 0 to 3 wt.% was added into the TiO$_2$ suspension followed by further sonication for 30 min. The suspensions were then aged overnight at room temperature. Prior to characterization, the suspensions were re-dispersed using the same homogenizer for 3 min. The suspensions were characterized using UV-Visible spectrometer (Lambda 35, Perkin Elmer) to measure the turbidity of the suspension over time (1 to 4 hours). Turbidity is relative to the ability of the TiO$_2$-NPs to remain dispersed in the suspension. Zeta potential analyser (Zeta Plus, Brookhaven Instruments) was used to measure the zeta potential which indicates the surface charge of the NPs in the suspension. Particle size was measured using Nanophox (Sympatec).
3. RESULTS AND DISCUSSION

To demonstrate the stability of TiO$_2$ NPs in aqueous solution, time dependent % transmittance (%T) was measured by UV/Vis spectrometer. The %T was converted to turbidity value using Beer Lambert Law equation as stated in Eq. 1:

$$\text{Turbidity} = 100 - \%T$$ (1)

3.1 Effect of surfactant concentration. The % transmittance data was recorded after 1 hour from the re-dispersion time (after overnight aging). Fig. 1 shows the trend of the turbidity as a function of surfactant concentration for all type of surfactants. In this study, turbidity value is used to determine the ability of the TiO$_2$-NPs to remain dispersed in the suspension. High turbidity reflects the dispersion of NPs in suspension while low turbidity means most NPs are sediment to the bottom of suspension. Among all, CTAB shows highest turbidity while PF-127 is the lowest. CTAB has higher turbidity in all concentration range compared to control sample. In contrast, SDS and PF-127 show lower turbidity than control sample at surfactant < 2.5 wt.%. All TiO$_2$-NPs suspensions show that 2.5 wt.% of surfactant concentration has the highest turbidity which is about 40–50. Turbidity starts to decrease at 3.0 wt.% for CTAB and SDS but slightly increase for PF-127.

![Fig. 1 Turbidity of TiO$_2$ suspensions as a function of surfactant concentration](image)

3.2 Effect of sediment time. The stability of the TiO$_2$ NPs to remain disperses in aqueous media with and without surfactant was monitored with time. Turbidity was measured at 1, 2, 3 and 4 hours from re-dispersion time to get a complete time dependent measurement, respectively. Fig. 2 depicts the turbidity of all TiO$_2$ suspensions as a function of time to show the degree of stability of NPs. It shows that at 2.5 wt.% of surfactant, turbidity of all suspensions is in the range of 35 to 45 at 1 hour measurement. These suspensions are more turbid compared to control sample (TiO$_2$ suspension without surfactant) and surfactant solution. This means that in the presence of surfactant most NPs are remain stable to disperse in aqueous media but without surfactant NPs are easily sediment to the bottom. After 2 hours, the turbidity decreases to about 10 to 20 for SDS and CTAB and about 10 to 15 for PF-127. These values remain unchanged for the third and fourth hour. This indicates most NPs are settled to the bottom of suspension after 2 hours, leaving the surfactant-stabilized NPs to remain disperse in the suspension.
3.3 Effect of surfactant type. The stability of TiO\(_2\) suspensions was further characterized with measurement of zeta potential (ZP). Zeta potential represents the potential stability of the suspension and indicates the degree of repulsion between adjacent, similarly charged particles in the suspension. It is a function of the surface charge of the particles [17]. In dispersions where value of the ZP is close to zero (isoelectric point), particles tend to agglomerate. The higher the magnitude of ZP, the more stable of the suspensions can be [9]. At highly negative or positive values of ZP (more than 30 mV or less than -30 mV [21]) particles in dispersions tend to repel each other, thus no agglomeration occurs. Fig. 3 shows the chemical structure of the SDS, CTAB and PF-127. The chemical structure helps to understand how surfactant can contribute to the potential stability of TiO\(_2\) suspension.

![Fig. 2 Turbidity of TiO\(_2\) suspensions containing different surfactants as a function of time](image)

![Fig. 3 Chemical structure of three different surfactants; SDS, CTAB and PF-127](image)

Table 1 shows the ZP and particle size range of all suspensions as a function of surfactant concentration. TiO\(_2\) suspension without surfactant shows low ZP and the particle size is out of range of measurement. This can be explained by the agglomeration of TiO\(_2\) NPs which caused the suspension to easily sediment to the bottom. The addition of surfactants to TiO\(_2\) suspensions leads to higher ZP and attainable particle size attributed to more stable TiO\(_2\) NPs in aqueous solution. Among all surfactants, PF-127 shows the lowest ZP.
which stands the reason for low turbidity. As a zwitterionic surfactant, PF-127 has less positive charges compared to CTAB. It is also a long carbon chains polymer that can adsorb onto the TiO$_2$ surfaces and bond them with each other causing flocculation of NPs that result in destabilization of the suspensions [22].

The presence of CTAB in TiO$_2$ suspensions leads to the change of magnitude of ZP from negative to positive, indicating possible electrostatic interaction between cationic CTAB and TiO$_2$. The electrostatic interaction could occur between the OH groups of TiO$_2$ with the cetrimonium (hexadecyltrimethylammonium) cations of CTAB. At 2.5 wt.% surfactant, suspension with CTAB has the highest ZP (48.74 mV) which explained why it has the highest turbidity and particle size is in the range of 1 nm to 2 μm. At 3 wt.% CTAB, the ZP is slightly decreases which indicating the excess amount of CTAB weaken the stability of suspension, probably due to the adsorption of polymer chain to the NPs surfaces that may lead to flocculation [22]. This is agreed with the decreasing of turbidity and increasing of particle size up to 6 μm. Suspension containing SDS although show higher ZP than CTAB but seems to have lower turbidity probably because it has insufficient repulsive forces to overcome the van der walls attractions between TiO$_2$ NPs [15]. This is also supported by the larger particle size for TiO$_2$ added with SDS than CTAB. SDS is an anionic surfactant with sulfate groups as the active site for interactions. Since there is no electrostatic interaction between SDS and TiO$_2$, the stabilization might come from the strong adsorption of this surfactant to TiO$_2$ surface due to the multiplicity of sulfate groups in the whole polymer [23]. Thus, this study suggests TiO$_2$-NPs suspension is stabilized better by the repulsive forces from excess cationic attributed from electrostatic interaction between TiO$_2$ and CTAB and also from steric repulsion of CTAB. These results are in agreement with previous studies done by Naeini et al. [24] that reported the TiO$_2$ suspension added with NH$_3$ was stabilized up to 360 min attributed from the OH- which has larger space size than H$^+$ groups. The suggested that the TiO$_2$ suspension added with NH$_3$ was stable due to the repulsive forces between similar charges and an extra steric repulsion from the NH$_3$.

<table>
<thead>
<tr>
<th>Surfactant (wt.%)</th>
<th>Zeta potential (mV)</th>
<th>Particle size range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SDS</td>
<td>CTAB</td>
</tr>
<tr>
<td>0.0</td>
<td>-10.19</td>
<td>-10.19</td>
</tr>
<tr>
<td>1.0</td>
<td>-64.04</td>
<td>38.09</td>
</tr>
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<td>-58.12</td>
<td>51.94</td>
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<td>2.5</td>
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</tr>
<tr>
<td>3.0</td>
<td>-47.64</td>
<td>44.33</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Nil</td>
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</tr>
</tbody>
</table>

4. **SUMMARY**

This study demonstrates that colloidal suspension of TiO$_2$-NPs was stabilized at high turbidity up to 1 hour, sufficient for observation of particles aggregation and surface charge studies. CTAB shows better dispersion and stability of TiO$_2$-NPs than SDS and PF-127.

REFERENCES


[21] Information on http://www.malvern.co.uk


Thermal Assessment of Kpata Fireclay for Refractory Applications

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ABSTRACT. This study focused on the thermal properties of the Kpata fireclay in order to look into its refactororiness. Thermogravimetry (TGA), differential thermal analysis (DTA) and thermal conductivity tests were carried out to analyse the fireclay's thermal properties. The fireclay was also compacted and fired at various firing temperatures. The TGA result indicated that there was material weight loss at 0.26 mg, 0.56 mg and 1.74 mg at temperatures of 90.53 °C, 425.12 °C and 578.87 °C respectively. The DTA revealed that there were exothermic and endothermic material reactions. The Kpata fireclay also had a thermal conductivity of 0.33 K (W/m.k). Apparent porosity of fired fireclay showed that the porosity was reduced as firing temperature increased. These conditions indicated that Kpata fireclay has the possibility in refractory and insulating applications.

Keywords: Thermal property, Fireclay, Refractory;

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1. INTRODUCTION

The rapidly witnessed request for an efficient and effective thermal insulation system through the use of earths naturally endowed clays used as fireclay refractories can never be over emphasized thermal industries. Fireclay refractories are insulating materials used as thermal barriers to store heat and conserve energy [1].

Furnaces as a thermal system are used for heat generation, melting, heat treatment that required extreme conservation in order to reduce heat losses for efficient and maximum heat efficiencies [2]. This will promote the least consumption of fuel as well as maximum production as an effort to maintaining maximum working temperatures [3]. Energy cost has increased and more importantly because of the role played by refractories in ceramic, glass and metallurgical industry cannot be over emphasized [4].

In recent time cost of energy has become high and the emergence of a new wide range of refractory materials with high temperature insulation technology that are proficient to restrain the leakage of heat at a higher temperature [5]. Fireclay refractory brick are materials that can withstand heat above 538 ° contained Al2O3, SiO2, H2O as alunino-silicate. It is frequently used as thermal storage materials in form of bricks for furnace lining [6]. The insulating materials used today includes; ceramic coating, ceramic fiber glass, calcium silicate, insulating castables [7]. Very lately, refractory materials with porosity up to 10-30 % [8] are used as refractory bricks with high thermal conductivity suitable for the outer layers of furnace as refractory linings [9]. Refractory materials with 70-80 % of porosity [8] are used as insulating materials with a low thermal conductivity and suitable for the inner walls of furnaces [10]. The knowledge of thermal conductivity, energy
absorption and heat capacity of these refractory materials is very necessary and critical to solving heat losses challenge. Thermal conductivity is the amount of heat conducted in a unit time through a unit area normal to the direction of heat flow \([11]\). Heat flow through solids is due to elastic vibration of atoms or due to transfer of energy by free electrons \([12]\). Heat capacity is the quantity of heat (energy) necessary to raise a major quantity of a material \(C_P\) and is measured in J/g°C \([13]\). Thermal conductivities depend entirely on the lattice vibration of atoms and molecules \([14]\). There exists a relationship between the thermal conductivity of refractory insulating materials with other thermal analysis methods in order to have total comprehensive understanding of the materials thermal behaviour through the techniques of thermogravimetry analysis (TGA) and the differential thermal analysis (DTA)\([15]\). The formal deals with material weight losses while the later deals with material reaction in the thermal environment that can result to either exothermic or endothermic and may involve both reactions depending on the type and nature of the refractory material \([16]\). Clay of aluminosilicate group can be a better preference as specified in this study. It can replace the glass fiber that usually posed a health challenge to the producers and end users.

Nigerian clays are not only abundant but health friendly, cheaper and of unlimited advantage in resolving the problems highlighted. The motivation for this study therefore, was to investigate the measurement and analysis of thermal conductivity of the Kpata clay for its suitability as refractory and insulating materials.

2. MATERIALS AND METHODS

The collection of the clay sample was from Kpata clay deposit in Kogi state of the North central geo-political zone of Nigeria. The packaging and handling of the clay sample was performed according to the standard method of collection and transportation of soil \([17]\).

2.1 Test samples preparation. The Kpata clay was crushed using the ball-mill. The sieve shaking machine was vibrated for 10 min. The amplitude was 0.5 maximum with the arrangement for 50 µm was obtained according to these order of sieves, 63µm, 50 µm followed by pan at the bottom. The sieve analysis was conducted according to ASTM E11-500 \([18]\).

2.2 Thermal analysis. The sample Kpata clay of 60 g was measured as required quantity and poured into the alumina crucible and then situated inside the sample chamber. The thermogravimetry thermal analysis (TGA) and the differential thermal analysis (DTA) test were performed simultaneously using the technique of simultaneous thermal analysis (STA) thermal-balance apparatus (Linseis STA).

2.3 Thermal conductivity. The determination of thermal conductivity of Kpata clay was by hot guided plate steady state technique as presented in Fig. 1.

The test sample was prepared into a circular size of 4 mm thick with diameter of 25 mm. It was positioned in the thermal apparatus for thermal conductivity measurement at room temperature. The clay sample was located in between two iron rods on the hot guided plate apparatus. Thermocouple sensors was inserted below and above the surfaces of the sample was viewed and observed the temperature at the upper and the lower surfaces respectively as the heat flows through the sample clay. The thermocouple was connected to the data logger; it records temperature with respect to time. The thermal conductivity measurement was accomplished according to \([19]\).

\[
q = -KA \frac{dt}{dx}
\]  

Where \(q\) is steady state flow, \(k\) is thermal conductivity, \(A\) is the cross sectional area of the clay material, and \(dt/dx\) represents the temperature gradient.

2.4 Firing process. The powder specimen was compacted using a mould into pallets by use of the hydraulic press caver machine. The application of force of 5 kN was administer with a holding tim of 60 seconds. The sampleKpataclay was fired varied Firing temperature of 900 °C, 1000 °C, 1100 °C and 1200 °C with a heating rate of 2.5 °C /min. and a soaking time of 2 hours.

2.5 Apparent porosity. The fired clay sample was weighed using digital balance and documented as dried weight \(D\) (g). The sample was positioned in the triple stand basket and immersed in water, then weight
taken and documented as suspended weight $S$ (g). The soaked sample removed from water and weighed and documented as soaked weight $W$ (g). Apparent porosity test was determined according to [20].

$$AP = \frac{W - D}{W - S} \times 100 \%$$  \hspace{1cm} (2)

3. RESULTS AND DISCUSSION

3.1 Simultaneous ThermalAnalysis (STA). The TGA of Kpata clay as presented graphically in Fig. 2 displayed at temperature of 90.53°C the sample clay encountered material weight loss of 0.26mg signifying 0.43%. This suggested the water being evaporated from the material clay. At temperature of 425.12°C the material clay sample demonstrated further weight loss of 0.56mg signifying 0.5%. This disclosed that the molecular structure of the clay sample was influenced by the temperatures above 300°C – 350°C and carbonaceous material in the sample clay had decomposed and consequently caused material weight loss. At temperature of 578.87°C there was another weight loss of 1.74 mg which signified 1.97%. The influence of TGA was seen to have caused weight loss in the clay. The dehydroxylation of the minerals in the sample clay as ensued at these temperatures. It implied the beginning of the initial phase in the oxidative degradation of the sample clay material. Flux compounds like $P_2O_5$, $CaO$ and $K_2O$ exhibited reaction from 900 °C which suggested the beginning of the Firing process, material crystallization and phase change [21,22].
The differential thermal analysis (DTA) as presented graphically in Fig.3 showed an indication that the clay specimen experienced exothermic reactions at temperatures of 517.4 °C and 1150 °C respectively. This means the clay material absorbed energy at these temperatures. Another reaction of endothermic was exhibited by the clay at the temperature of 989.9 °C which signified the clay released energy at that particular temperature. The DTA caused exothermic reaction in the clay sample as energy being absorbed and the endothermic reaction in signifying energy being released [21,22].

Fig. 2. TGA curve for Kpata fireclay brick

3.2 Apparent porosity. The highest apparent porosity value of the sample was 43.76 % at the least firing temperature of 900 °C as compared with lowest porosity value of 21.58 % attained at the highest firing temperature of 1200 °C. The porosity of the sample fell within the standard values of 20-30 % for refractory fireclay bricks [8]. It was revealed in Fig.4 that when the Firing temperature was increased, the volume of sample clay open pores decreased. This showed that the Firing temperatures have influenced the apparent porosity of the sample.

3.3 Thermal conductivity. The thermal conductivity of Kpata clay sample exhibited the value of 0.33 K (W/m.k) and fell within the standard values of 0.01 to 1.1 K (W/m.k) for refractory fireclay bricks [12-14]. Thermal conductivity of the clay sample was attained as a caused through the atomic and lattice vibration which is impeded via structural disorder by the heating. Consequently, thermal conductivity dropped with the increasing temperature. Temperature gradient determines the direction of heat flow.

Fig. 3. DTA graph of Kpata fireclay brick

Fig. 4 Apparent porosity of Kpata fireclay brick at varied firing temperatures
4. SUMMARY

The results of the Kpata fireclay refractoriness were found to be within the standard values for refractory fireclay bricks. The thermal properties of the fireclay brick as investigated through thermal methods of TGA, DTA and thermal conductivity concluded that the Kpata fireclay brick was found to be potential candidate for refractory applications.

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REFERENCES


Dynamic Mechanical and Roughness Analyses of Polypropylene/Kaolin Nanocomposite

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ABSTRACT. The topography and dynamic mechanical properties of polypropylene (PP) incorporated with kaolin were studied to appraise their true engineering functions. Atomic force microscopy (AFM) and dynamic mechanical analysis (DMA) were accomplished to investigate the effects of different kaolin loadings on the topography and dynamic mechanical properties of the PP/kaolin nanocomposite. The PP was discovered to be inside the interparticle space of the kaolin as revealed by AFM. The PP/kaolin nanocomposite demonstrated a fine and smooth surface roughness (Ra) of the matrix with increase kaolin loading by maximum of 87.68% and hence displayed improved adhesion properties within matrix and the kaolin; that was accountable for the enhancement of the tribological properties of the nanocomposites. Increase in kaolin loading can significantly enhance the storage modulus and reinforcing effect of PP/kaolin nanocomposite.

Keywords: Polypropylene, Kaolin, Roughness, Dynamic mechanical analysis;

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1. INTRODUCTION

Polymer nanocomposites involve developing area of contemporary research and have established considerable devotion from industries and academia. Nanocomposites reveal unforeseen hybrid properties. Several features of these composites are discovered by numerous scientists. The nanocomposites produced from clays as fillers have been progressively innovated and explored by many researchers. They have shown extraordinary upgraded properties, including superior barrier property, thermal stability, enhanced mechanical properties and reduced flammability [1]. Specifically, PP is an essential class of polymer material due to its remarkable features and distinct applications. The development of nanocomposites require intercalation of clay layers into organic compounds, causing a stretched and organophilic layered structure [2]. Melt intercalation and in situ polymerization are common techniques by which organoclays are incorporated into the polymer matrix. The advances in substantial enhancements of mechanical properties
are offered by these methods through dispersal of the clay in the polymer matrix [3,4]. The desired materials of high-technology instruments and applications are therefore obtained from these novel nanocomposite materials.

The role of PP/clay composites is motivated as a result of their potential uses in the automotive industry. Little investigation on PP/clay nanocomposites are conducted by Toyota group researchers and shows that dynamic storage moduli of the Polypropylene (PP) clay hybrids (PPCHs) remained greater than those of PP lesser at approximately 150 °C [3]. Dynamic mechanical properties of PP composites and dispersion rate were reported after synthetizing PPCH via bare melt-blending of three constituents; PP, maleic anhydride improved polypropylene oligomers (PP-MA), and clays which are incorporated into stearyl ammonium [3]. The reports done by Wang et al., [5] investigated the impacts of using different loading of three fillers silica (SiO₂), calcium carbonate (CaCO₃) and phenolic microsphere (PFM) in producing PP composites. They found that the PP composites displayed 1.4 times greater impact strength property than the pristine PP.

However, earlier studies of PP/clay nanocomposites on dynamic mechanical properties have been frequently dedicated to montmorillonite, and only few studies were established using kaolin. Kaolin is the utmost common 1:1 (two layer sheet) natural clay mineral with its fundamental unit containing tetrahedral sheet of SiO₂, siloxane units and an octahedral sheet of alumina (AlO₂(OH)₄) [6]. When modified, kaolin particles can become uniformly dispersed in the polymer matrix and be used as a functional filler for polymers due to its light colour, distinct stratified configuration, and obtainability [7,8]. In this work, studies on enhancement of dynamic mechanical properties as a result of PP/kaolin nanocomposites produced by melt intercalation of PP, kaolin and PP-MA as compatibiliser at different loadings of kaolin were established. AFM studies were conducted to ascertain the surface morphology and roughness of the PP/kaolin nanocomposite.

2. MATERIALS AND METHODS

2.1 Materials. Polypropylene (PP) copolymer of Titanpro SM-240 resin grade used in the present research, was provided by Lotte Chemical Titan (M) Sdn. Bhd. The SM-240 was in pellet shape with density of 0.894 g/cm³, and melt flow index (MFI) of 230 °C/2.16 kg as measured according to ASTM D1238. The coupling agent, Polypropylene grafted maleic anhydride (PP-g-MA) was supplied by Sigma Aldrich. Whereas kaolin was acquired from Kaolin (Malaysia) Sdn. Bhd. The distinct kaolin samples were sieved to particle size of 45 µm. The kaolin particles exhibit chemical composition in wt. % as: SiO₂ 57.633, Al₂O₃ 37.766, Fe₂O₃ 0.86, MgO 0.596, CaO 0.346, K₂O 1.801, TiO₂ 0.605 and P₂O₅ 0.311. Lastly, the di-amine carbide powder (urea) was obtained from Bendosen Chemical Company, China.

2.2 Sample Preparation. Method of Valaskova et al. [9] and Suzi et al. [10] were used to conduct the surface treatment of kaolin. Planetary milling of 250 g of kaolin with 165 g of urea was homogeneously carried out for 15 min using a planetary mill (Fritsch Pulverisette 6). Prolonged heating of regulated mixture was carried out at 95 °C in a laboratory oven (MummertLinn High Therm) for 48 hours to accomplish intercalation of urea into kaolin interlayer. Ultrasonic bath (Elmasonic E30H) was applied for 5 hours long at low temperature and delamination of kaolin was achieved. The separation of urea from the mixture was carried out by mixing 50 g of treated kaolin with 1.5 L of distilled water in a beaker and stirred. Sedimentation was used to detach the liquid portion from solid portion and subsequently dried at 60 °C for 24 hours in an oven.

2.3 Preparation of PP/K Nanocomposite. The nanocomposites were produced by melt intercalation method with heated two-roll mill model PW 3000 for 20 min, with speed of 10 rpm. The temperature rolls are 190° and 177 °C for front and back respectively. The coupling agent used was PP-g-MA. The nanocomposites consists of 1, 3, 5 and 7 wt.% of kaolin as filler.

2.4 Methods. Samples were analysed using dynamic mechanical test (TA instruments DMA Q800) at temperature of 25 °C - 170 °C, heating rate 5 °C/min and vibration frequency of 1 Hz. The verification of surface roughness and topography of samples were carried out by Atomic force
microscopy (AFM) of SPM microscope (XE-100 Park Systems) on a contact mode.

3. RESULTS AND DISCUSSION

3.1 Dynamic Mechanical Analysis (DMA). DMA was used in this work to determine the effect of loading kaolin nanoparticle on dynamic mechanical operation of PP/K nanocomposites. Diez-Pascual et al. [11] reported that viscoelastic properties of the polymers are affected when polymer matrix are incorporated with dispersed inorganic fillers. Fig.1 displays the temperature dependence on the loss tangent (tan δ), storage modulus (E’), and loss modulus. PP and its nanocomposites consisting of different kaolin concentration are extremely advantageous in determining the operation of samples under stress and temperature.

**Fig. 1** DMA spectra of pristine PP and PP/K nanocomposites (a) Storage modulus, (b) Tan δ and (c) Loss modulus.

The ability of a material to store input mechanical energy and elasticity is usually illustrated by storage modulus [12]. The storage modulus of the nanocomposite is greater than that of the pristine polymer as
illustrated by DMA. The storage modulus obtained with pristine PP was 1200 GPa at 40 °C, and it reduces over the whole temperature range. Relaxation of the amorphous region is related to the plateau region detected at range of temperatures of 100 to 110 °C. The more kaolin loading, the higher the storage modulus at various temperature range. Upon loading different wt % of kaolin, the storage modulus at 43 °C rise to 12,200, 12,500, 12550 and 12,600 GPa for nanocomposites compositions of 1, 3, 5 and 7 wt.% kaolin respectively, which is virtually 9.5% boost of storage modulus compared to that of pristine PP crystals. Hence, PP/K nanocomposites display greater storage modulus through the evaluated temperature range. The result is in agreement with Cabedo et al. [13]. Identification in the percent of crystallinity is usually due to the rise in the storage modulus. Thus, the rise in the storage modulus might be ascribed to the reinforcing effect of kaolin complemented by the homogeneous dispersion (lacking of agglomerates) of kaolin within the polymer matrix.

Measurements of the energy dissipation (damping) capacity of the material can be investigated by tan δ curve, which exhibits peak at 105 °C and additional broad peak around 149 °C for pristine PP. The glass transition temperature (Tg) is correlated to the initial peak at 105 °C and damping within the crystalline lamellae occurs in subsequent peak at 149 °C. At about 170 °C an intense fall occurs in the storage modulus and a rapid rise in tan δ owing to the onset of melting of PP crystals.

Fig. 1c displays the deviation of the temperature as a function of loss modulus E″. The loss modulus E″, expresses the sticky feature of the constituent together with ability of the material to dissipate energy. Conforming to Fig. 1c, pristine PP has lower loss modulus compared to PP/K nanocomposites. PP nanocomposite reformation with modified nanoclay affected rise of E″ at low temperature zone. Loss modulus decreases at higher temperature region. Similar result was obtained by Benmesli and Riahi [14].

**Fig. 2** AFM topographic images of (a) PP, (b) PP/K 3%, and (c) PP/K 5 %

### 3.2 Atomic Force Microscopy

Fig. 2 illustrates the surface roughness properties of pristine PP and PP/K nanocomposites consisting 3% and 5% nanoclay particles in 2d and 3d topography with uniform dispersal of kaolin in PP matrix. The PP/K nanocomposite shows higher surface roughness (Fig. 1c) compared to pristine PP which exhibit smoother surface (see Fig. 1a). In order to amend surface and bulk properties of functioning materials, inorganic additives are constantly incorporated in polymer matrix [13-15]. Typically, owing to
numerous reasons such as size, mobility, end group functionalities, relative composition and molecular structure; organic additives are capable to move to the surface of polymers. Significant higher roughness of PP nanocomposite surface occurs by the increase in kaolin loading as filler, hence increase roughness to about 86.7%. This result is confirmed by reports of improvement in mechanical properties through DMA studies above. These findings are in agreement with Parvinzadeh et al. [16] & Hajiraissi and Parvinzadeh [17].

4. SUMMARY

The study highlighted the role of kaolin in PP nanocomposite in enhancing dynamic mechanical properties and increasing surface roughness to about 86.7%. The integration of kaolin into PP matrix with increase kaolin loading can highly upgrade the storage modulus. It has proven the exhibit of a laudable reinforcing effect to PP/K nanocomposite for the benefit of technological developments.

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Effect of Banana Peel Fiber as Reinforcement in Low Density Polyethylene/Durian Seed Starch Blends

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ABSTRACT. The effects of banana peel fiber (BPF) as reinforcement in low density polyethylene (LDPE)/durian seed starch (DSS) blends were studied. The LDPE/TPS ratio was fixed at 90/10 wt.% and reinforced with different content of BPF (from 0 to 40 wt.%). These mixtures were melt compounded using internal mixer and compression molded using hot press machine. After that, the mechanical behavior, physical properties and biodegradation rate of the obtained molded sheets were investigated. From the analysis, the optimum blend ratio of LDPE/TPS is achieved at 10 wt.% BPF with maximum tensile strength of 6.058 MPa. This has been evidenced by scanning electron microscope (SEM), in which the fibers are seem to be embedded within the matrix, thus indicating strong interfacial adhesion between fiber and matrix. In fact, the compatibility between LDPE/TPS blends and BPF has been proved by the formation of hydrogen bond in FTIR results. Furthermore, the samples have also demonstrating biodegradability whereby some surface discoloration and erosion can be clearly seen after being buried in soil for 14 days.

Keywords: Thermoplastic starch, Banana peel fiber, Low density polyethylene;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Low Density Polyethylene (LDPE) is one of the common polymers that has been used for many applications such as toys, food packaging, etc. Disposal of used plastic products made from petroleum has become a public concern due to their non-degradability and their potentially hazardous to the environment. One of the solution for non-degradable plastic is to fill the polymer with biodegradable materials such as starch. Starch can be extracted from various botanical sources and it is renewable, abundant and inexpensive natural biopolymer. There are few types botanical sources can be used as starch such as banana and sago. However, it seems that the utilization of durian seed as a source of starch is rarely reported. Durian seed contains 50 - 70% carbohydrate and 20.8% amylose [1] which can be considered high since in general amylose make up 20% of the granule and amylpectin, the remainder. Thus, this study is focused on the utilization of durian seed as a source of starch. By adding starch into synthetic plastic, biodegradable plastic can be achieved.

Normally, interfacial adhesion between LDPE and starch is poor because LDPE is hydrophobic meanwhile starch is hydrophilic and it can reduce the mechanical properties and increase water absorption [2]. One of the possible solution to improve the properties is to add natural fiber in LDPE and durian seed starch blends. Natural fibers as reinforcement for polymeric matrices have been studied during decades due to many
advantages presented by these fibers are abundance and therefore low cost, biodegradability, flexibility during processing, low density, relatively high tensile and flexural modulus and non-toxic. The studies from Naidu et al. [3] did show that, by loading banana peel into polymer matrix composites did increase tensile strength. By adding banana peel fiber into the composites, it is expected that, the eco-friendly and better properties of biodegradable composite can be developed. Thus, this study exploring the effect of banana peel fiber as reinforcement for LDPE/durian seed starch blend.

2. MATERIALS AND METHODS

2.1 Preparation of LDPE/TPS reinforced BPF composite sheet. The seeds for starch were sliced into small pieces (2-2.5 mm). After that, the seeds were put into an oven for 24 hours at 60 °C followed by grinding the seeds by using a grinder and sieved to size of 100 μm. 5 g of durian seeds flour were added into 100 ml of distilled water and soaked and stirred constantly between 6 hours to 8 hours at room temperature. After that, the slurry was filtered and precipitated overnight at 4 °C. Next starch cake was dried for 24 hours in the oven at 40 °C. Finally, the starch was sieved. DSS powder needs was vacuum dried by heating at 80 °C for 24 hours before processing and blending. The chemical composition of DSS is referred [4]. The DSS were then pre-mixed with glycerol by weight ratio of 65:35 using a speed mixer to obtain thermoplastic starch (TPS).

The banana peels were washed by using tap water and were soaked in a solution of 5% citric acid for 10 min. After that, banana peel fiber (BPF) was dried in the oven at 60 °C overnight. The dried peels were ground in the grinder and then sieved to size of 50 μm.

The LDPE/TPS blend (90/10 wt.%) and LDPE/TPS blend with BPF (0 to 40 wt.%) were then melt compounded using internal mixer (Haake Polylab System Thermo Scientific) and press molded using hot press machine (XH-406B). For all compositions, the internal mixer was performed at 50 rpm and 150 °C for 20 min and then compression molded in the electrical heated hydraulic press at 150 °C for 6 min to obtain moulded sheet (150 mm × 150 mm × 1 mm). The materials’ abbreviations and corresponding sample compositions are listed in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition (wt.%)</th>
<th>LDPE</th>
<th>TPS</th>
<th>LDPE/TPS</th>
<th>BPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LDPE/TPS</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LDPE/TPS + 10 wt.% BPF</td>
<td>-</td>
<td>-</td>
<td>90</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>LDPE/TPS + 20 wt.% BPF</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>LDPE/TPS + 30 wt.% BPF</td>
<td>-</td>
<td>-</td>
<td>70</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>LDPE/TPS + 40 wt.% BPF</td>
<td>-</td>
<td>-</td>
<td>60</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

Tensile Test. Dumbell specimens of 1 mm thickness were cut from the compression molded sheet. The tensile test was done by following the ASTM D638 standard by using Shimadzu AGS-X universal testing machine. The load used was 5 kN and the test speed is 5 mm/min.

2.2 Scanning electron microscope (SEM) test. The morphology studies were carried out by using scanning electron microscope (JSM 5600). The samples were sputter coated with carbon (Polaron SC515), then taken for microscope images at 5kV.
2.3 Fourier-Transform Infrared Spectrometry (FTIR) Test. In order to classify and observe the functional groups on the sample, Fourier Transform Infrared (FTIR) Spectroscopy (Perkin Elmer System spectrum 100; PerkinElmer, United States) was used with a resolution of 4 cm⁻¹ in a spectral range of 4000-600 cm⁻¹ using 32 scans per sample.

2.4 Soil Burial Test. Degradation behavior of all compositions carried out by soil burial test using procedures mentioned by Azahari et al. [5] with slight modification. The films measuring 20 mm x 20 mm were cut and weighed. Then, the samples of each composition were buried at depth of 50 mm in different pots filled with composted soil. The samples buried in pots and exposed to natural weather. The physical appearance of samples before and after soil burial test were observed.

3. RESULTS AND DISCUSSION

3.1 Tensile Properties. Tensile strength and elongation at break of LDPE/TPS blends with different BPF content are shown Fig. 1. It was found that by adding BPF into the LDPE/TPS as reinforcement at 10 wt.%, it did increase the tensile strength of the blend up to 6.058 MPa compared to LDPE/TPS which was 5.340 MPa. The increased TS could be attributed to the strong interfacial adhesion of the matrix with the fiber since the hydrophilic character of the system increases as BPF was added to the blend [6]. Thus, the stress transfers well from the matrix to the reinforcement. However, further addition of BPF resulted in gradual decrease of TS. This might be due to the excessiveness of BPF that caused the discontinuity of the matrix due to the phase incompatibility between hydrophilic BPF and non-polar hydrophobic LDPE [7]. This caused stress transfers to the fiber with reduction in stress concentration area as BPF tend to agglomerate and weak interfacial adhesion. The results obtained are supported by surface fracture observed under SEM. The elongation decreased as the fiber loading increased as agreement with Norshahida et al. [7]. This is because the crystallinity of fiber resulted in a decrement the polymer chain mobility and a deformability of a rigid interface between the matrix and fiber which resulted decreased the ductility of LDPE and by adding TPS into the blend, the combination of immiscible phase in LDPE matrix decreased the elongation at break.

![Fig. 1 Effect of banana peel fiber content on the tensile strength and elongation at break of LDPE/DSS blends](image-url)
3.2 Morphological Study of Tensile Fracture Surfaces. Fig. 2 shows the tensile fracture surface of LDPE, LDPE/TPS and LDPE/TPS/BPF (magnification of 350x). Based on Fig. 2(a), the surface of tensile fracture of LDPE and Fig. 2(b) shows the surface fracture of LDPE/TPS blend with 10 wt.% of TPS. It shows that the TPS was embedded in LDPE resulted the rough surface compared with LDPE morphology. The reason for surface roughness of LDPE/TPS is incompatibility between hydrophobic LDPE and hydrophilic TPS which caused a weak interfacial adhesion [6]. In Fig. 2 (c), fiber agglomeration is detected on the surface and the immiscibility of the two components caused the TS significantly decreased. Fig. 2(d) shows the surface of tensile fracture of LDPE/TPS/BPF blend with 10 wt.% of BPF. It can be observed that the fiber is embedded and well dispersed in the matrix, thus improved the TS of LDPE/TPS blend.

Fig. 2 SEM micrographs of (a) LDPE, (b) LDPE/TPS, (c) LDPE/TPS/10 wt.% BPF and (d) LDPE/TPS/40 wt.% BPF

3.3 Fourier Transform Infrared (FTIR) Analysis. Fig. 3 shows the IR spectra of the composites, whereby there are three significant peaks at 2915 cm⁻¹, 1463 cm⁻¹, 717 cm⁻¹ which indicated C-H stretching, -CH₃ bending and -CH₂- vibration, respectively. It showed the functional group of primary matrix, LDPE which is similar to a study done by Norshahida et al. [7]. Next, as shown in Fig. 3(b-c), the peaks observed at 1000 cm⁻¹ - 1263 cm⁻¹ attributed to C-O-C bond stretching and peak at 1032 cm⁻¹ represent anhydroglucose ring O-C stretch [7]. The peaks appeared when TPS firstly added in the composition, as the TPS added, the peaks shifted and it become sharper indicated additional of C-O functional group which related to amylopectin and amylose of TPS. Other prominent peaks observed at 3370 cm⁻¹ - 3385 cm⁻¹ which showed the present of O-H group. The peaks visible started at Fig. 3(b-c). The change of peaks shape and position due to intermolecular of hydrogen bond between TPS and BPF. The greater the compatibility of polymer composite, the greater would be the peak shape and shift.

3.4 Soil Burial Test. Fig. 4 shows the physical appearance of composite samples before and after exposure to soil burial test. The samples undergo 14 days buried in the soils and the samples experienced controlled environment which the soils were kept in the lab but exposed to sunlight and water.
Fig. 3 FTIR spectra of the composites of (a) LDPE, (b) LDPE/TPS and (c) LDPE/TPS/10 wt.% BPF

The weight loss and the observation on samples surface conditions were used to evaluate the biodegradability of the samples. Firstly, for LDPE/TPS blend compositions, it can be seen that as the TPS incorporated into LDPE, the biodegradability rate also increased. Fig. 4(a) showed the surface of sample after 14 days buried in soils where it shows surface discoloration and erosion indication of initial biodegradation of samples. Fig. 4(b) whereas showing a crack and surface erosion on the surface of the sample. It is believed that the fiber absorbed the moisture during exposure and accelerate the biodegradation process.

Fig. 4 The appearance of (a) LDPE/TPS and (b) LDPE/TPS/10 wt.% BPF samples after subjected to soil burial test

4. SUMMARY

The addition of 10 wt.% BPF to the LDPE/TPS blend was found to increase the tensile strength. The increment in tensile properties have been proved by the compatibility between LDPE/TPS blends and BPF shown in SEM morphology.

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Effect of Supercritical Carbon Dioxide on Tensile Properties of Durian Skin Fibre Biocomposite

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ABSTRACT. The exploration of new biocomposites that are environmental friendly is gain attention due to depletion of petroleum resources and increasing global environmental concern. Therefore, the investigation of environmental friendly and sustainable materials requires to substitute the synthetic based materials. This project is conducted to investigate the effect of supercritical carbon dioxide on tensile properties of PLA/DSF biocomposite films. The PLA/DSF biocomposites are produced via solvent casting method. Then, the samples are treated under supercritical carbon dioxide (SCCO₂) at 40 °C and at 200 bar pressure. From tensile properties, it was found that the tensile strength and modulus for untreated and treated PLA/DSF biocomposite are higher compared to net PLA which are 24.9 MPa and 23.5 MPa. Thus, the addition of durian skin fiber improved the mechanical strength PLA polymer. But, the presence of foams and pore in treated PLA/DSF biocomposites decreased its tensile properties by 1.4 MPa less compared to untreated samples as confirmed by morphological observations under scanning electron microscope.

Keywords: Durian skin fibre, Epoxidized palm oil, Tensile, Supercritical carbon dioxide;

Received: 15.10.2017, Revised: 15.12.2017, Accepted: 30.02.2018, and Online: 20.03.2018;


Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Recently, due to unstable consumption of petroleum had gain an intensive awareness towards green environment in the society by performing an upmost strategy to produce biodegradable composites packaging materials as alternatives materials for the packaging industries. The environmental concern across the globe also are worrisome [1]. This problem can be seen throughout the average rate of wastage over the time. Department of Environment from Ministry of Natural Resources and Environment already testified the highest proportion of waste approximately 56% accumulated in Malaysia is conquered by wastage dumped into landfills to decompose rather than reused or recycled product. Thus, the growing environmental issues around the world encouraged the design of materials should compatible with environment. The introduction of the biobased product which are made from recycle resources can reproduce eco-friendly product that potentially compete with synthetic-based product [2]. Biodegradable polymer films packaging offer
alternatives way to conventional packaging based on their great performance in biodegradability, compostability, processability and sustainability.

Polylactic acid (PLA) is the most generally used as biopolymer plastic due to its properties which are known as biodegradable polymer. It has great potential from an environmental point of view. Indirectly, PLA is most eligible as a candidate polymer for the advancement of biodegradable films according to its behaviour that can be readily cast into edible films via dissolving method. Despite these outstanding features, the brittle nature of PLA limits its application [1]. PLA polymer matrices has several drawbacks significantly in mechanical properties and cause unsatisfactory behaviour for the packaging application. The limitation of PLA however can be improved by the addition of reinforcement such as natural fiber [3]. Durian skin fiber (DSF) is chosen as natural fiber in this study where it has great properties in mechanical and also may reduce the material cost [4,5]. The improvement of biocomposite materials for food packaging applications by using PLA and DSF can be one of the alternatives to resolve the environmental issues. But the long period of experimental exposure of biocomposite film will affect the durability and brittleness of properties. Brittleness also affect the processability which can be modified with plasticizer. Plasticizer like epoxidized palm oil (EPO) was reported able to enhance the flexibility of polymer chain [6,7]. Natural-based plasticizer are more preferred which are categorized as non-toxicity and low migration rates [8].

The growing demand of packaging industries using natural-based additives as antimicrobial agent in food packaging applications has resulted through research exploration to improve the antimicrobial superiority on biocomposite plastic. Cinnamon essential oil (CEO) shows antimicrobial function and may assist as antimicrobial agents against food pathogen and microorganisms. It possesses a better performance in extending the shelf life of preserved food and ensure security usage of food is covered [9,10]. Antimicrobial packaging system with the presence of antimicrobial properties has ability in maintaining flavour of food and reduce microorganism activities on perishable food. Furthermore, the supercritical carbon dioxide (SCCO₂) method are used due to many advantages in particle reduction and plasticization modification on polymer. The usage of carbon dioxide as a main solvent may offer several benefits from a safety, environmental, manufacturing and economical point of view [11]. According to Comin et al. [12], solvent of CO₂ is believed to acts as plasticizer and decrease the glass transition temperature.

To date, there is no study reported on SCCO₂ aided plasticized PLA biocomposite. Therefore, this study explores the effect of supercritical carbon dioxide (SCCO₂) on the tensile properties of PLA/DSF biocomposite.

2. MATERIALS AND METHODS

2.1 Materials. Polylactic acid (PLA) was purchased from NatureWorks®, China in pellets form. Durian skin waste was collected from night market in Gombak, Selangor. Epoxidized palm oil (EPO) was obtained from Advanced Oleochemical Technology Division (AOTD), Malaysian Palm Oil Board (MPOB) in Bangi, Selangor. Chloroform was bought from Merck and Cinnamon oil essential (CEO) was supplied by local supplier from Best Formula Company.

2.2 Samples Preparation. The PLA/DSF biocomposite were produced via solvent casting method. PLA and DSF were kept in an oven at temperature 70 °C for 24h day to remove moisture. The composition of biocomposite prepared is shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PLA (wt%)</th>
<th>DSF (wt%)</th>
<th>EPO (ml)</th>
<th>CEO (ml)</th>
<th>Chloroform (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>100 wt%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>51.00</td>
</tr>
<tr>
<td>PLA/DSF/EPO/CEO</td>
<td>92 wt%</td>
<td>3 wt%</td>
<td>5 wt%</td>
<td>1 wt%</td>
<td>51.00</td>
</tr>
</tbody>
</table>

The solvent mixture was then stirred with strong agitation via magnetic stirrer on hot plate until it dissolved uniformly. Dried PLA/DSF biocomposite films were peeled off from mould after left for 24 h at
room temperature. Preparation steps of PLA/DSF biocomposite films were shown in Fig. 1. Note that treated is referred to PLA/DSF biocomposite underwent SCCO$_2$ process. While untreated is referred to PLA/DSF biocomposite without SCCO$_2$ process.

**Fig. 1** The sample preparation of PLA/DSF biocomposite films (a) stirred process with magnetic agitation on hot plate; (b) poured the sample onto flat mould and (c) left the samples for drying process

### 2.3 Supercritical Carbon Dioxide Process.

The PLA biocomposite was then underwent supercritical carbon dioxide process at temperature 40 °C at 200 bar for 2 hours. The CO$_2$ was charged into the biocomposite until the desired pressure was reached. The sample were treated through a supercritical carbon dioxide equipment with model Waters (TAP SFE Biobotanical system, IPM) at International Institute for Halal Research and Training (INHART), IIUM. The schematic diagram of supercritical carbon dioxide treatment system used in this study is exposed in Fig. 2. The tensile test was conducted based on ASTM D882 using Universal Testing Material, Shimadzu Autograph AGS-X series equipped with a 5kN load and 20 mm/min cross head speed. The biocomposites were cut into dimension according to ASTM D882. Anuar et al. (2016) reported that the thickness of sample at 0.1 ± 0.05 mm for tensile test was accepted. The surface and tensile fracture surface of PLA biocomposite was observed under scanning electron microscope (SEM) for morphological observation.

**Fig. 2** The schematic diagram of supercritical carbon dioxide equipment [13]
3. RESULTS AND DISCUSSION

The effect of supercritical carbon dioxide treatment on tensile properties of PLA/DSF biocomposite was studied and the results were compared with PLA and PLA/DSF biocomposite without treatment. The tensile strength and tensile modulus of PLA, PLA/DSF/EPO/CEO biocomposite with and without SCCO$_2$ treatment are summarized in Fig. 3. It was found that the tensile strength for untreated PLA/DSF biocomposite and treated PLA/DSF biocomposite are higher than PLA by 2.57 and 1.2 MPa. The value attained for PLA was 22.3 MPa.

The tensile properties of PLA/DSF biocomposite was the highest due to strong interaction of interfacial bonding between PLA and DSF [3]. Tensile properties will only rise when the load transfer between matrix and fiber is sufficient [14]. However, the interaction between matrix and reinforcement still poor due to hydrophobicity behaviour of PLA and hydrophilicity of DSF [15]. Therefore, the presence of epoxidized palm oil (EPO) are believed to improve interfacial adhesion and brittleness of PLA/DSF bicomposites. The improvement of tensile strength of PLA biocomposite were also reported by Ali et al. [6], Anuar et al. [16] and Chieng et al. [17]. This is because the intermolecular forces are reduced and polymer chain interaction increased with the addition of EPO which are enhance flexibility and extensibility.

The tensile properties treated PLA/DSF biocomposite with SCCO$_2$ is slightly low compared to untreated biocomposite. The behaviour of CO$_2$ tend to expand and forming the pores in biocomposite polymer [18]. It can be seen in Fig. 4 the present of foam in the PLA biocomposite. From Fig 2(b) and (d), the treated PLA biocomposite seems to have pores size compared to untreated sample based on SEM micrograph on the surface of sample. Similar morphological structures were also studied by Biani et al. [11] and Nguyen and Baird [19] on other polymer-based composites systems. According to their findings, when supercritical carbon dioxide pressure was increased, the cell sizes also tend to increase. Meanwhile, cell density of composite was slightly decreased. The low density of foam can reduce the mechanical strength of sample. Lobos and Velankar et al. [20] revealed in their investigation, the foams strength of composites may be increased by reducing the expansion. The foamed expansion occurred due to depressurize rate during releasing of carbon dioxide gas in a rapid and non-constant technique after SCCO$_2$ process was conducted. Hence, these was the main factor affected the tensile properties by treated PLA/DSF biocomposite. It is evidenced by SEM analysis on tensile fracture surface in Fig. 4 (e) and (f), the samples treated PLA/DSF biocomposites appears to have more expansion of foam and pore size compared to untreated samples.

![Fig. 3 Tensile strength, tensile modulus and strain for PLA, untreated PLA/DSF biocomposites and treated PLA/DSF biocomposite](image-url)
4. **SUMMARY**

As a conclusion, untreated and SCCO$_2$ treated PLA/DSF biocomposite are both potential for application in packaging industries based on tensile properties obtained. SCCO$_2$ treatment could represent an effective way to prepare PLA/DSF biocomposite which are characterized among high tensile properties with respect to food packaging applications.

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Microstructure and Physical Characterization of Mahang (*Macaranga*) Wood as a Core Material in Sandwich Composites

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**ABSTRACT.** Mahang (*Macaranga*) wood is one of the lesser known wood species (LKS) available in Malaysia. It is one of those underutilized fast-growing pioneering species. Categorized as light hardwood timber, mahang wood is considered as a viable alternative to be utilized in the construction of sandwich composite. Typically, the core of sandwich composite is made of balsa wood. This study aims to investigate the physical properties of mahang wood in attempt to employ this underutilized species as a core in sandwich composite. Samples of mahang wood were analysed for physical properties and the microstructure was observed under scanning electron microscope (SEM). Density of wood and core were evaluated by considering the oven dried mass and green volume of the specimens. Immersion of sample in tap water was carried out for determination of water absorption properties by considering the density change after period of immersion. Several ASTM standards were adopted to establish a valid procedure to conduct the experimental investigation. The results obtained were compared with balsa wood. Results showed that density of mahang wood falls within the range of balsa wood density. Water absorption test revealed the water absorption properties of mahang is less than balsa wood which signifies that water resistant properties of mahang is obviously better than balsa wood. Microstructure of mahang wood observed under SEM showed a resemblance between mahang and balsa wood. The relevance of mahang wood as a core in sandwich composites is clearly supported by fact that mahang wood possesses almost similar physical properties as balsa wood.

**Keywords:** Mahang (*Macaranga*) wood, Water absorption, Density, Sandwich composites;

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**1. INTRODUCTION**

The increased significant of weight reduction expand the demand for sandwich composite in the manufacturing industry. Utilization of composite during recent year has been driven by the fact that sandwich composites are capable to offer low weight structures without compromising the bending stiffness. The high bending stiffness of sandwich structure can be explained by the separation of the two adjacent skins by a thick lightweight core. Commonly used materials for sandwich composite core are balsa wood, nomex honeycomb or polyurethane foam [1,2]. Separation of skins by the core increases the moment of inertia...
whereby no significant weight added to the structure [3]. Moment of inertia is a measure to indicate the ability of a profile to resist bending. The higher the moment of inertia the more efficient the structure can resist bending and buckling loads. Adoption of sandwich composites offers a benefit of weight saving, which in turn economically reduce the fuel consumption of naval structure. Sandwich composites in naval structure often concentrated on woven fibreglass and vinyl ester face skins with balsa wood core [4]. The applications of sandwich composites in naval structure are diversified since World War II. Some applications include patrol boats, hovercraft, deckhouse, mine counter measure vessels (mcmv) and corvettes [5].

In moving towards environmental sustainability, eco-friendly materials are always preferable. Wang et al. [6] introduced an ingenious hollow sandwich columns made of glass fiber reinforced polymer skins and a naturally growing paulownia wood core. They used paulownia wood as a core due to fast growing, low density, low price, and biodegradability of paulownia wood. Likewise, Srivaro et al. [7] performed an analysis on the nature based sandwich composite made of oil palm wood core with rubber wood veneer skins. The mechanical strength tested under three point bending is predominantly depends on the core density. Taken together, these studies emerged as reliable predictors on the potential of nature based materials in sandwich composites.

Malaysia’s rainforest cover about 70% of total land area and it play host to highly diverse and unique biological species. The lesser known wood species (LKS) are still under-utilized by wood based industries due to either lesser quality or lack of information regarding these species. Focus has been placed on high quality wood such as acacia, teak, and rubber wood. Mahang (Macaranga) wood is one of those LKS massively emerged in pioneering species in Southeast Asia [8]. It belongs to hardwood category with density typically varied from 270 to 495 kg/m³ [9]. It exhibit low density, fast growing and biodegradeable qualities therfore, the main objective of this study is to investigate the microstructure and physical characterization of mahang wood in attempt to utilize this species as a core in sandwich composite.

2. MATERIALS AND METHODS

2.1 Materials and Core Fabrication. Samples were extracted from a 10 m tall mahang tree with diameter at breast height (DBH, 1.3 m above the ground) of 78 cm obtained from Agro Park of Universiti Malaysia Kelantan. Based on the periodic annual increment (PAI) of 1.5 cm per year; the age of mahang tree was estimated to be about 8 years. Prior to cutting and surfacing, the logs were marked and painted on both end to avoid excessive water loss and fungal attack. The process of cutting the log into lumbers was done by the Forest Research Institute Malaysia (FRIM). Lumbers were pre-dried in a force convection oven at 50 °C for 12 days until 12% moisture content attained. Physical tests were carried out on the clear specimens of mahang wood and core of sandwich composite (Fig. 1). Blocks of mahang wood with dimension 100 mm x 100 mm in length and width were combined into panel measures 300 mm x 300 mm for the core of sandwich composite. Epoxy resin from Fiberglast Company was used to adhesively combine the blocks. The panel was then left for 24 hours for curing process.

Fig. 1 (a) mahang wood and (b) mahang core of sandwich composite
2.2 Density. Samples of mahang wood measures 25 mm × 25 mm × 25 mm conforming to ASTM D2395 (method A) [10] were evaluated for basic density. Oven dry mass of wood sample and green volume were recorded and applied in the basic density formula as follow:

\[
\rho = \frac{m}{l \times w \times t}
\]  

Where:
\( \rho \) = Density
\( m \) = Oven dried mass of specimen
\( l \) = Length of specimen
\( w \) = Width of specimen
\( t \) = Thickness of specimen

The green volume refers to the freshly felled logs or the log that contained most of the moisture. In this experimental work, the green volume was recorded as soon as the cutting process is done to avoid any further loss of the moisture to the surrounding. The samples were then oven-dried in a force convection oven at 103 ± 2 °C until constant mass attained as required by the standard [11]. The constant mass was recorded as oven-dried mass.

Densities for mahang core specimens were evaluated as per ASTM C271 [12]. Test specimens of dimension 300 mm × 300 mm × 18 mm were pre-conditioned in an oven at temperature 40 ± 3 °C. Following this, samples were placed in a desiccator and be brought to room temperature. The samples were then carefully weighed by using electronic balance and measured the dimensions by using callipers. Recorded values were applied in the Eq. 1.

2.3 Water absorption. Water absorption test for mahang wood was carried out in accordance to ASTM D1037 [13]. Samples of mahang wood with dimensions 50 mm × 50 mm × 20 mm were immersed in tap water at temperature of 20 ± 3 °C for 24 hours. While for mahang core, samples with dimensions 75 mm × 75 mm × 15 mm as per ASTM C272 [14] were immersed in tap water of 23 ± 3 °C for 24 hours. The mass each sample was manually recorded before immersion. Since the wood and core samples were less dense than water, wire net was used to cover the sample to avoid the samples from floating on the surface of the water. Beaker was placed in a desiccator to avoid evaporation of water to the surrounding. After 24 hours, the mass of the wood samples immersed in tap water were recorded to determine the density change. Water absorption (WA) was calculated by using the following equation:

\[
WA(\%) = \left( \frac{m_1 - m_0}{m_0} \right) \times 100
\]

Where,
\( m_0 \) = Mass of specimen before immersion
\( m_1 \) = Mass of specimen after immersion
2.4 Scanning Electron Microscopy. Samples of mahang wood were observed under JEOL JSM-IT100 SEM for microstructural observation. The microscope operated at an accelerating voltage of 5-20 kV to develop an image by scanning the sample with a focused beam of high energy electrons. The samples to be observed were cut by using an industrial razor blade. A clean cut surface of mahang wood was used to obtain a fine cell detail.

3. RESULTS AND DISCUSSION

3.1 Density. As shown in Fig. 2, average density of mahang wood obtained in this study is 320 kg/m$^3$ while mahang core shows a slightly higher density.

![Fig. 2 Density of mahang wood and core](image)

Based on Malaysian Grading Rules (1984) mahang wood is classified as light hardwood (LHW) which categorized all timbers with density less than 720 kg/m$^3$ under the same class [15]. Previously published study on physical properties of mahang wood revealed the density of mahang is in the range of 270 kg/m$^3$ to 495 kg/m$^3$ [16]. In comparison to balsa, mahang wood lies in the range of balsa density which has a minimum density of 60 kg/m$^3$ and reaching up 380 kg/m$^3$ [17]. The difference in the density value between wood and core is due to the addition of epoxy resin as an adhesive to combine the blocks together while forming core. Thus, making core denser than wood. However, it is still consider as lightweight panel with density less than 500 kg/m$^3$ [18]. Low density of mahang wood and core is desirable in the construction of sandwich composite which promotes high strength to weight ratio properties when combined with high strength skins.

3.2 Water absorption. The effect of water absorption on density change of mahang wood and core is shown in Fig. 3. Water absorption for mahang wood and core are 38.15% and 25.57%, respectively.

![Fig. 3 Comparative percentage of weight gain by mahang wood and core specimens after 4 hours immersion in tap water](image)
After 4 hours of immersion in tap water the wood specimen density increases by 38.15% from original density of 325.37 kg/m$^3$. The increase in density following the immersion is due to the water absorption by the vessels which mainly function as water conducting tissue in plant. Sadler et al. [19] investigated the effect of water absorption on the density change of balsa wood. It was found that balsa density immensely increase by 74% after 4 hours immersion in water. Water absorption rate of balsa wood is significantly higher than mahang wood. This finding signifies that mahang wood has better water resistance relative to balsa. The relative density of balsa is in the range of 2.7% - 26% while relative density of mahang wood in this experimental work is 22%. The low relative density reveals that balsa wood contains most of the empty spaces in the cellular structure compare to mahang wood [20]. Water occupied the empty spaces and consequently increase the density of balsa wood tremendously. Water absorption of mahang core is rather less than mahang wood. This is due to the presence of epoxy resin which partially occupied the empty spaces and leaving the vessels with less capacity for water absorption.

3.3 Scanning Electron Microscopy. Microstructure of mahang wood in Fig. 4 depicted the main type of cells showing the presence of vessels, rays and fibers similar to Balsa wood.

![SEM micrographs of mahang wood showing the main type of cells in (a) cross-section view and (b) longitudinal view (magnification: 500x)](image)

Fibers are long hexagonal prismatic cells that run axially along the trunk. In most hardwood species, fibers are the main constituents of the wood pulps. It functions exclusively as mechanical supporting cells to support the tree. Unlike fibers, rays run radially from the central pith of the trunk. It forms brick like parenchyma cells that responsible for sugar storage. Vessels are another important cells in mahang wood. It is much larger than rays and fibers which mainly responsible to transport fluids from the roots to the crown. It runs axially along the trunk similar to fibers. The presence of vessels or known as porosity in the stem hypothesized the low density of mahang wood.

4. SUMMARY

The physical properties of mahang wood were investigated. The average density of mahang wood proved the viability of mahang wood as a biodegradable and lightweight core material. Mahang wood has lower water absorption properties than balsa wood. In the construction of sandwich composite, core material with less water absorption is desired to avoid deterioration of sandwich composite due to swelling effect. The idea of utilizing mahang wood as core in sandwich composite is strengthen by the fact that microstructure of mahang wood resembles the microstructure of balsa wood. The experimental results presented in the paper provide new insights into the potential of mahang wood as an alternative to be used as a core in sandwich composite as it possess almost similar physical properties as balsa wood. The study has gone some way towards utilizing LKS in attempt to add value to those species.
REFERENCES

Tensile Properties of γ Irradiated And Non-Irradiated Poly (L-Lactide) Carboxymethyl Starch And Nano-Hydroxyapatite Composite Film

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Abstract. A film of poly (L-lactide) (PLLA), carboxymethyl starch (CMS) and nano-hydroxyapatite (nHA) was prepared by casting evaporation method. The use of natural resources of CMS blending with PLLA induced the pore in the potentially used in tissue engineering applications. PLLA were blend with CMS in a solution form and added with nHA particles. The film was irradiated with gamma (γ) at 10, 30, 50 and 80 kGy doses. Pores with diameter in the range of approximately 20-50 µm was observed. Low tensile strength was obtained CMS was introduce into PLLA matrix, however improves by addition of nHA. Increasing of γ irradiation exceeded 10 kGy leads to decreasing in tensile strength. Glass transition temperature, T_g, crystallization temperature, T_c and enthalpy of crystallization indicating the changes in degree of crystallinity due to the degradation occur in when the samples were undergo irradiation.

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1. INTRODUCTION

PLLA is linear aliphatic polyester with a large number of applications ranging from medical implant material, drug delivery system and tissue engineering scaffold. PLLA as much great interest due to its biocompatibility, biodegradability and proven to be safe use in human body. Successful application as medical implant makes this material more attractive and also to be modified with other material to improve their applications in the medical field [1]. The blending PLLA either with other polymeric material or composited with other material has been main subject to many researcher recently. PLLA blending with PDLA [2], PLLA and PLCL as a scaffold materials[3], DLLA-PEG-PDLLA-b-PLLA used as a drug delivery system [4], PLLA and HA/TCP [5-8] and PLLA/MgO composite [9]. The used of ionizing radiation were also been implemented either to induce the cross linking or to tailor the degradation profile of implant material [10-12].

The properties of the PLLA and many polymeric material including mechanical behaviours, thermal and degradation properties are strongly depend to the crystalline and morphology. The crystallization rate of PLLA is very slow; meaning that it is very hard to achieve high crystallinity in PLLA[13]. Blending with other polymer, composited with other material and the application of ionizing radiation such electron beam [14,15], and gamma radiation [16-18] be able to modify its crystallization. It is well known that the biodegradability of PLLA is strongly related to its crystallinity, high order structure, blending ratio and morphology. Inside the body, PLLA degrade to lactic acid through chain scission due to hydrolytic attack on their ester bond and enter tri-carboxylic acid cycle follow by metabolism process and subsequently eliminated from the body as carbon dioxide and water.
The aim of this work is to study the blending between the PLLA, CMS and nHA in the form of porous film. Recently the blend of natural polymer and synthetic for both organic and inorganic resources were synthesized from sago starch widely used in pharmaceutical product and wound healing materials and food technology. CMS remain as alternative to synthetic polymer due to its biocompatibility, degradable, non-toxic and inexpensive as well. CMS commonly produce via synthesis by chemical modification reaction. Carboxymethylation process of starch is one of the procedures to functionalize this material to provide valuable properties as biomaterial. During carboxymethylation the hydroxyl group (O-H) in starch molecule was substituted with carboxymethyl group (CH$_2$COOH) to produce CMS\[19\]. In this study the PLLA, PLLA/CMS and PLLA/CMS/HA film were prepared by solvent casting evaporation techniques. The tensile properties of PLLA with addition with CMS and nHA at various irradiation doses were investigate.

2. MATERIALS AND METHODS

PLLA with inherent viscosity 2.32 dl/g were obtained from BioInvigor (Taipei, Taiwan). Nano-Hydroxyapatite with particle size less than 200 nm was purchased from Sigma Aldrich (USA). CMS was prepared from local sago starch. Sago starch was slurred in 300 ml of isopropanol added with NaOH about 30% in reactor flask equipped with reflux condenser and burette. In this work, the detail carboxymethylation process of sago starch was done as described by Yaacob et al. \[19\]. 7% concentration PLLA were prepared by dissolving the granule PLLA in dichloromethane. Films were prepared by casting evaporation method by mixing 20% of CMS v/v in with present of 0.1% of nHA. They were mixed and then stirred for 24 hours later rolled to form a film of 200 µm thickness and dried for 24 hours. The thickness of the film reduces in the range of 50 - 70 µm after the drying process.

Samples were irradiated at different doses of 10, 30 50 and 80 kGy. Irradiations were carried out in research loop facility at Malaysian Nuclear Agency Gamma Sterilization Plant with $^{60}$Co sources. The irradiation was carried out at dose rate 1.67 kGy h$^{-1}$, the measurement of dose rate by using ceric cerous dosimeter in order to measure the effectiveness of doses absorbed by samples.

Changes in thermal properties, glass transition temperature ($T_g$), cold crystallization temperature ($T_c$), melting temperature ($T_m$), enthalpy of crystallization ($H_c$) and enthalpy of melting ($H_m$) were investigated using TA Instrument (Q20, USA). Samples were purged with nitrogen gas approximately 35 ml min$^{-1}$ to avoid any oxidation during the heating. About 2.35 mg samples were heated from 20 to 300 ºC at the heating rate of 10 ºC min$^{-1}$.

The SEM (Quanta 400, FEI, USA Germany) was used to evaluate the morphology of film porosity. The images were collected at 2000x, magnification at 10 kV. Tensile testing was conducted using 50 N load cell (Model UUK 5, Korea) equipped with Ezi Step micro stepper motor system (Fastec, Korea). A screw type crosshead and attached with data logger OMRON RX-RX25. The elongation was determined by 1.0 mW Omron laser detector with detection limit 2.5 ms 600 nm$^{-1}$. The tensile test conducted at 0.5 mm min$^{-1}$ of crosshead velocity. Samples were punch into rectangular shape with dimension of 5 x 40 mm. Stress and strain curve were then calculated based on the thickness of the film.

3. RESULTS AND DISCUSSION

The films that produce by cast evaporation technique segregate into two layer; polymer rich phase and polymer lean phase due to the 3 phase system which are PLLA, CMS and nHA particles. CMS is not dissolve in PLLA solution because of the different solvent. PLLA is hydrophobic whereas nHA and CMS have a hydrophilic structure. During evaporation polymer rich phase is transform into matrix and polymer lean phase will produce the porous structure \[20\]. Fig. 1 shows the pore induced in PLLA/CMS and PLLA/CMS/nHA compared to dense film of PLLA of none irradiated samples. Generally, introducing the CMS into PLLA reduced the tensile strength due to the generating of porous structure within the sample. Tensile properties can be improved by addition of HA nano particle (nHA). From our observation, PLLA matrix contributes most to of the properties to bulk composite sample. Fig. 2(a) exhibits tensile strength of the PLLA/CMS/nHA, PLLA/CMS and PLLA samples for non-irradiated and irradiated samples at various irradiation doses.
Porosity affected the tensile property by reducing the strength by 55% from 34.4 to 15.2 MPa for non-irradiated PLLA and PLLA/CMS respectively. Addition of nHA in PLLA/CMS sample reducing the porosity therefore increase the tensile strength up to 28.4 MPa. The morphology of the PLLA/CMS/nHA samples as shown in Fig. 1(c). Another possible reason to the increasing of tensile strength is the ability of nHA penetrating the amorphous region thus prevent mobility of the polymer chain during tensile test [21,22].

**Fig 1** The SEM micrograph of (a) PLLA, (b) PLLA/CMS and (c) PLLA/CMS/HA of non-Irradiated sample produced by casting evaporation method.

Tensile strength was observed reducing in all irradiated samples except for sample irradiated at 10 kGy (Fig.2). The tensile strength increase about 23%, 44% and 6.5% at lower doses (10 kGy) and reduce down about 27%, 15% and 28.7% at higher doses (80 kGy) for PLLA, PLLA/CMS, and PLLA/CMS/HA, respectively. The effect of ionizing radiation to polymer either can be degradation or crosslinking, in fact this mechanism can occur simultaneously [12,16,23]. If the chain scission is predominant than the crosslinking, the degradation will be take places. Massive degradation will lower the mechanical strength in contra to the crosslinking [23,24].

**Fig. 2** (a) The ultimate strength and (b) Strain of PLLA, PLLA/CMS and PLLA/CMS/HA of both non-irradiated and irradiated at 10 and 80kGy

The possible reason of increasing in tensile strength at 10 kGy is suggested due to some part of the polymer chain occure a crosslinking as in the increasing of $T_m$ as indicate in DSC thermogram (Fig 2b) [11].
The present of nHA particle in the sample promoting the stiffness and reduce the plasticity thus reduce in strain. Fig 2b exhibits the decreasing in strain when nHA was introduce in PLLA/CMS. nHA penetrated into amorphous region thus retarded the movement of the molecular chain with the sample and increased the stiffness which lead to the brittle failure of PLLA/CMS/nHA sample [22]. Nano HA particles together with irradiation would destroy the molecular to shorter chain with open structure that lead to rapid failure.

The thermal stability of PLLA and PLLA/CMS/nHA were investigated via DSC thermogram for both irradiated and non-irradiated samples as shown in Fig. 3. PLLA is a semi crystalline polymer, exhibits both endothermic and exothermic peaks which attribute to amorphous and crystalline region. The crystalline region consists of more oriented chains and closely pack compared to amorphous regions [25,26]. Peaks appeared at 63.6, 104.2 and 157.5 ºC for the PLLA samples corresponding to temperature of glass transition, Tg, cold crystallization, Tc and melting, Tm. The Tg values was slightly lower when PLLA was blended with CMS and also in addition of nHA. By irradiating the samples the Tg were significantly decrease and even more by decreasing the doses to the increasing of irradiation doses. The decreasing of Tg values can be explained by degradation that occurred in the amorphous region from fragmentation of polymer chain [13,24].

Fig. 3 DSC thermogram of irradiated and non-irradiated samples, (a) PLLA and (b) PLLA/CMS/nHA at 10 and 80kGy

The increasing of crystallization peak after irradiation process can be explained by the increasing of the crystallization enthalpy. The sharp peak indicated that higher rate of crystallization upon heating. The energy from the ionizing radiation resulted in chain scission due to energy exceed the electron binding energy [27]. The polymer chain is fragmented into shorter chain, the higher the energy received the shortest the chain, this is known as degradation mechanism [24]. During heating, the fragmented chain re-oriented into a crystallization phase. Shorter chain would increase the crystallization rate thus produced the sharp peak in DSC thermogram. The more fragmentation occurs the higher enthalpy produce during heating in DSC analysis as exhibited in Fig 3a. Higher doses (80 kGy) produce sharp crystallization peak indicated the occuring of a massive degradation. The crystallization enthalpy of PLLA increased from 24.9 to 43.7 Jg⁻¹ for non-irradiated and irradiated samples at higher doses respectively, and 11.9 to 19.2 Jg⁻¹ for PLLA/CMS/nHA. The fragmentation of the of the chain would ease the mobility of the molecule prior to heat and lower the Tg (Fig. 3). The Tg value decreased from 63.6 to 59.8 ºC for PLLA and 60.9 to 58.1 ºC for PLLA/CMS/nHA for pre and post irradiation at 80 kGy.

Partially chain scission occurred at lower doses because of low energy received by the polymer chain: If took place only in amorphous region, retarded the mobility of the polymer chain upon heating and increased in tensile strength at lower doses [25]. Loo et. al. [25] suggested that, the polymer chain in the crystalline region were close one another, the free radical either hydroxyl group or alkyl will trap in crystalline region.
promote recombination. The recombination within the free radical would prevent the degradation thus contributed to the increasing of tensile strength.

4. SUMMARY

The PLLA/CMS/nHA porous film were produced by casting evaporation method subsequently irradiated by γ at various irradiation doses. Introducing CMS into PLLA matrix reduce the tensile strength due the present of porosity and can be improved by addition of nHA. Lower irradiation doses may increase the tensile strength whereas higher irradiation doses reduce the strength of samples due to massive destruction in polymer chain. DSC thermogram indicated the degradation occurs at higher doses.

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AC Susceptibility of the Magnesium Diboride (MgB₂) Added on Bi₁.₆Pb₀.₄Sr₂Ca₂Cu₃O₆ Superconductor

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ABSTRACT. This study have used ac susceptibility technique to measure the transition through the whole volume of the MgB₂ added on Bi₁.₆Pb₀.₄Sr₂Ca₂Cu₃O₆ superconductor for additions at x= 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10 wt.%. Transition curve can be divided into two parts which are real part, χ′ and imaginary part, χ″. From the real part, χ′ found that two steps transition corresponds to the temperature of onset diamagnetism, T_C-ON and phase lock-in temperature, T_CJ. The results indicate that the transition have optimum value with x= 0.02 wt.% addition at 109 K (T_C-ON) and 107 K (T_CJ). From these results displays allows the determination of Josephson current, I_o at 92.37 Ampere. The smaller range between T_C-ON and T_CJ indicate higher I_o corresponds to intrinsics properties of grains. While imaginary part, χ″ showed two peaks of coupling peak temperature, T_p related to the magnitude or strength of the pinning force. As the fields increases, T_p decreases for the lower temperature when applied ac field from 0.05 Oe to 2.00 Oe. The decreasing temperature attributed to the absorption of magnetic energy of the superconductor from the AC field. These results indicate the optimum T_p for pure sample belonging to displays the good coupling effect between the grains.

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1. INTRODUCTION

Intrinsic and extrinsic properties are the nature contains grains, grain boundaries and coupling between grains can be measured using ac susceptibility techniques. This technique offered additional advantages because the samples is contactless and the whole are measures. The curve can provide information on coupling diamagnet shielding for intrinsic and feature of coupling losses which common extrinsic behavior [1]. AC susceptibility measurement have been widely used to study flux dynamics of high temperature superconductors since this contactless measurement revealed a detailed information on critical current density, pinning strength, flux creep, activation energy, volume fraction of the grain etc. [2]. In this paper, ac susceptibility measurement as a function of temperature and ac field and its effect on the coupling of the grains were discussed. Nikolo and Goldfard [3] were discussed on the Aderson flux creep model that ac loss peak shift to higher temperature shown the flux creep enhance the critical current density. The major
limitation of inter and intra granular capability is the flux pinning capability need to improve by overcome the rapid decrease in the critical current density. The addition could produce such defects within superconducting grains as dislocations or stacking faults, which enhance the flux pinning and critical current density [4]. The aims of this work were studied the intrinsic and extrinsic properties on the MgB$_2$ added with B$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ using applied fields dependence AC susceptibility. We have also determined the Josephson current, $I_J$ based on equation (1) effectively controlled the grains morphology and thus the grain coupling and hence the superconducting properties.

2. MATERIALS AND METHODS

Samples (B$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$)$_{1-x}$ (MgB$_2$)$_x$ were prepared by solid state reaction method. Samples with the nominal ratio B$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$, and CuO powder was mixed. Then the powders were milled using ball for 24 hours. The mixture was first calcined at 800 °C for 20 hour, followed by calcined at 820 °C for 10 hours and finally calcined at 840 °C for 4 hours with intermediate grinding to ensure homogeneity. The (B$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$)$_{1-x}$ (MgB$_2$)$_x$ with $x = 0.00$, $0.02$, $0.04$, $0.06$, $0.08$ and $0.10$ wt.% added then the powder were pressed into pellet and sintered at 845 °C for 96 hours and annealing at 830 °C for 30 hours. AC susceptibility of the entire volume of the samples were measured using CryoBIND (Cryogenic Balanced Inductive detector) SR830 lock in amplifier at frequency of 240 Hz with driving fields range from 0.05 Oe to 5.00 Oe to investigate coupling peak temperature, $T_p$, onset temperature of onset diamagnetism, $T_{C\text{-ON}}$; Phase lock-in temperature, $T_{CJ}$ of the materials.

3. RESULTS AND DISCUSSION

Typical AC susceptibility curves were observed for all samples which are the two drops in real part, $\chi'$ accompanied by bell-shape in imaginary part, $\chi''$ can be seen in Fig. 1, its shows the temperature dependence curves for pure samples. In polycrystalline high temperature superconductor, normally real part $\chi'$ depicts diamagnet shielding of the samples while imaginary part $\chi''$ indicates the hysteretic losses due to vortex motion. The real part depicts the diamagnet shielding currents in intra and inter granular superconducting region. The imaginary part indicates losses for intra and inter granular vortices [5].

All the summarize data of coupling peak temperature ($T_p$), onset temperature of onset diamagnetism ($T_{C\text{-ON}}$), phase lock-in temperature ($T_{CJ}$) and Josephson current ($I_J$) in Table 1 extract from the graph real part, $\chi'$ and imaginary part, $\chi''$ of susceptibility versus temperature for samples B$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ added with (MgB$_2$)$_x$ at $x = 0.00$, $0.02$, $0.04$, $0.06$, $0.08$ and $0.10$ wt.% The temperature of onset diamagnetism, $T_{C\text{-ON}}$ was observed at 107 K, 109 K, 108.5 K, 108.3 K, 108.1 K and 108.0 K for addition MgB$_2$ at $x = 0.00$, $0.02$, $0.04$, $0.06$, $0.08$ and $0.10$ wt.% The second drop from $\chi'$ which reflected to phase lock-in temperature, $T_{CJ}$ occurred at lower temperature was observed at 105.5 K, 107 K, 105.2 K, 104.5 K and 103 K for samples $x=0.00-0.08$ wt.%. There was no superconducting behavior for sample with $x=0.010$ wt.% thus indicating that the samples have lost their superconductivity. This might be related to the quality of the grain [6].

From the imaginary part $\chi''$ showed the intergranular coupling peaks, $T_p$ shifted towards lower temperature when increasing the field from 0.05 Oe to 1.00 Oe, and with increasing additions of MgB$_2$. The decrease of the temperature is proportional to the magnitude or strength of the pinning forces [7]. The result for addition with $x=0.02$ wt.% showed the highest temperature at 107 K, 105.5 K, 101.0 K, 95 K and 90 K at different applied fields for 0.05 Oe, 0.10 Oe, 0.5 Oe, 1.00 Oe and 2.0 Oe. These explained by apply lower fields, magnetic penetration into the sample at higher temperature however when apply higher fields the magnetic start expels the field from the interiors known as Meissner effect. By increases the additions also show the coupling slightly decreases the temperature.
Fig. 1 Real part, $\chi'$ and imaginary part, $\chi''$ of susceptibility versus temperature, $T$ at various magnetic fields for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_n$

The results plotted in Fig. 2 shown the variation of the superconducting diamagnet ($T_{C\text{-ON}}$), phase lock-in temperature ($T_{CI}$) and Josephson current ($I_o$) versus amount of MgB$_2$ additive. The width between $T_{C\text{-ON}}$ and $T_{CI}$ narrow for pure $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_n$ but for addition with 0.02 wt.% while the width slightly wide for addition 0.04 wt.% till 0.10 wt.% . Wide separation of $T_{C\text{-ON}}$ and $T_{CI}$ loss peaks showed poor coupling between the grains. The variation of $I_0$ decreased as addition increases at 119.83 μA, 93.27 μA, 56 μA, 48.46 μA and 35.97 μA for all samples. The higher of $I_0$ indicates a good links and hence the good coupling between the grain occur due to the layer consist polycrystalline phase. For samples with Bi-2223 phase dominancy the weak link is probably S-N-S types will correspond to higher $I_0$ whereas lower $I_0$ in the Bi-2212 phase dominancy the weak link is probably S-I-S types, respectively [8]. As we can see from Table 1, the Josephson current $I_0$ calculated based on eqn. (1) [9]

\[
I_0 = 1.57 \times 10^{-8} \frac{(T_{C\text{-ON}})^2}{(T_{C\text{-ON}} - T_{CI})}
\]  

(1)
The strong dependence of coupling $T_P$ with the various amount of applied field are observed in Table 1 was found that the result is shifted toward lower temperature. The amount of shifted to lower temperature as the higher applied fields is proportional to the magnitude or strength of the pinning force. The large of the shifted of the temperature, the weaker pinning force and hence the smaller intergranular critical current density [10].

**Table 1** Summarize data of coupling peak temperature ($T_P$), onset temperature of onset diamagnetism ($T_{C-ON}$), Phase lock-in temperature ($T_{CJ}$) and Josephson current ($I_o$)

<table>
<thead>
<tr>
<th>Sample x</th>
<th>0.00</th>
<th>0.20</th>
<th>0.40</th>
<th>0.06</th>
<th>0.08</th>
<th>0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_P$ (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>105.0</td>
<td>107.0</td>
<td>105.0</td>
<td>101.0</td>
<td>97.0</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>104.0</td>
<td>105.5</td>
<td>103.5</td>
<td>99.0</td>
<td>95.0</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>101.0</td>
<td>101.0</td>
<td>99.0</td>
<td>92.0</td>
<td>88.0</td>
<td>-</td>
</tr>
<tr>
<td>1.00</td>
<td>99.0</td>
<td>95.0</td>
<td>93.0</td>
<td>86.0</td>
<td>80.0</td>
<td>-</td>
</tr>
<tr>
<td>2.00</td>
<td>95.0</td>
<td>90.0</td>
<td>88.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$T_{C-ON}$ (K)</td>
<td>107.0</td>
<td>109.0</td>
<td>108.5</td>
<td>108.3</td>
<td>108.1</td>
<td>108.0</td>
</tr>
<tr>
<td>$T_{CJ}$ (K)</td>
<td>105.5</td>
<td>107.0</td>
<td>105.2</td>
<td>104.5</td>
<td>103.0</td>
<td>-</td>
</tr>
<tr>
<td>$I_o$ (μA)</td>
<td>119.83</td>
<td>93.27</td>
<td>56.00</td>
<td>48.46</td>
<td>35.97</td>
<td>-</td>
</tr>
</tbody>
</table>

**Fig. 2** The variation of the superconducting Diamagnet ($T_{C-ON}$), Phase lock-in temperature ($T_{CJ}$) and Josephson current ($I_o$) dependence on sample (x) wt.% of MgB$_2$
SUMMARY

Polycrystalline superconducting samples of \((\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_\delta)_{x}(\text{MgB}_2)_{1-x}\) were applied various fields and the AC susceptibility studies carried out the important properties of these materials. We demonstrated that AC susceptibility technique are powerful tools to study wider aspects of superconductor, by investigated the role of superconducting grain and their coupling in bulk polycrystalline samples. Nature of the grain boundaries and flux pinning mechanism through remain same. The grain boundary was very much required to unleash the potential of high temperature superconductor.

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Crystalline Phase, Surface Morphology and Electrical Properties of Monovalent Doped Pr$_{0.75}$Na$_{0.25}$Mn$_{1-y}$Co$_y$O$_3$ Ceramics

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ABSTRACT. This paper reports effects of cobalt (Co) doped at Mn-site of Pr$_{0.75}$Na$_{0.25}$Mn$_{1-y}$Co$_y$O$_3$ ($y = 0, 0.02$ and $0.05$) on structure and electrical properties along with the surface morphology. All the samples were synthesized using standard solid state reaction method. Powder X-ray diffraction measurement shows that all samples were crystallized in an orthorhombic structure with $Pnma$ space group. The unit cell volume was decreased suggestively due to the different ionic radius between Mn and Co as Co increases. Resistivity measurement shows that the $y = 0$ sample exhibits an insulating behavior down to lower temperature and interestingly the metal-insulator (MI) transition was found at 108 K and 84 K for $y = 0.02$ and $y = 0.05$ respectively. The shifting of the MI transition to lower temperature indicates a weakening of the double-exchange mechanism. On the other hand, scanning electron microscope (SEM) measurement showed that a different surface morphology was observed for all samples. A different pattern of grain boundaries was observed with increasing of Co content. Grains connection of $y = 0$ samples was observed slightly denser compare to the $y = 0.02$ and $0.05$ samples in conjunction with increasing of the value of porosity. This can be suggested due to the successful of doping of Co ions in the compound.

Keywords: X-ray diffraction, Scanning electron microscope, Double-exchange mechanism;

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1. INTRODUCTION

Mixed valence perovskite manganites with general formula RE$_{1-x}$A$_x$MnO$_3$ (where RE= Pr, Nd, La; and A= Ca, Sr, Ba) received noticeable attention due to varieties of physical and chemical properties as well as potential applications in technology such as magnetic sensor, magnetic recording, etc [1-3]. The Pr-based manganites have been studied widely as they exhibit charge ordering (CO) which can be destabilized or destruct in order to tune the physical properties [4] and Pr$_{0.75}$Na$_{0.25}$MnO$_3$ has caught attention as this compound is CO insulator at relatively high temperature, $T_{CO} \sim 220$ K compared to antiferromagnetic interaction with Neel temperature, $T_N \sim 180$ K [5,6].

The doping at Mn-site with other transitional metal ions whether magnetic or non-magnetic ions could be a very effective ways to alter the properties and charge ordering of the manganites due to the changes of Mn$^{3+}$/Mn$^{4+}$ ratio [7]. Generally, the Curie temperature ($T_C$) as well as metal-insulator transition temperature ($T_{MI}$) will decrease dramatically when other elements are substituted at Mn site due to the destroyed double-
exchange ferromagnetism [8]. For instance, the CO of Nd$_{0.75}$Na$_{0.25}$Mn$_{1-y}$Cr$_y$O$_3$ [9] is said to be decreased as the concentration of Cr$^{3+}$ increased. The metal-insulator (MI) transition of the samples appeared at ($x = 0.04$) and disappeared with further Cr doping. Besides, the electrical study of La$_{0.8}$Ca$_{0.2}$Mn$_{1-y}$Cr$_y$O$_3$ shows the $T_{MI}$ shifts towards lower temperature as the Cr content increased probably due to the weakening of double exchange (DE) mechanism by reducing the ratio of Mn$^{3+}$/Mn$^{4+}$ [10]. However, the behavior of CO affected by the elemental substitution at Mn-site of mixed valence perovskite manganites is still not clearly understood.

Recently, a mixed valence perovskite manganites has become the focus of investigation as the system was reported to exhibit a variety of magnetic and electrical transport properties [11,12]. For instance, N. Dhahri et al. [13] reported decreasing $T_{MI}$ varied from 360 K to 210 K as the Co concentration increased in La$_{0.6}$Pb$_{0.33}$MnO$_3$ most probably due to the enhancement of superexchange and weakening of DE mechanism as Co replaces Mn site. Similar observations also have been reported in La$_{0.7}$Sr$_{0.3}$MnO$_3$ where the $T_c$ decreased gradually with increasing Co content due to the reduction of ferromagnetic (FM) interaction thus enhanced the antiferromagnetic interactions between Co and Mn ions [14]. By considering the literatures mentioned above, we expect the Co doping in the compound Pr$_{0.75}$Na$_{0.25}$MnO$_3$ may influence the physical properties of the materials. However to the best of our knowledge, such study on the Pr$_{0.75}$Na$_{0.25}$MnO$_3$ has not been reported. Thus, the doping effect of Co at Mn-site on the Pr$_{0.75}$Na$_{0.25}$Mn$_{1-y}$Co$_y$O$_3$ would be particular interest as it is expected to induce the MI transition as well as suppress the CO state. In addition, the monovalent doped manganites is believed having advantage of creation or the required concentration in Mn$^{3+}$/Mn$^{4+}$ ions with relatively small doping concentration. In this paper, the crystal structure, morphology and electrical transport properties of monovalent doped materials, PNMCoO are reported. In addition, values of density and porosity are also presented and discussed.

2. MATERIALS AND METHODS

The manganite samples of Pr$_{0.75}$Na$_{0.25}$Mn$_{1-y}$Co$_y$O$_3$ ($x = 0, 0.02,$ and $0.05$) were synthesized using standard solid state reaction method. A stoichiometric amounts of high purity ($\geq 99.99\%$) Pr$_2$O$_3$, Na$_2$O$_3$, MnO$_2$ and Co$_2$O$_3$ were ground in agate mortar with pestle and calcined in air at 1000 °C by using Protherm furnace Model PLF130/15 for 24 hours with heating rate of 15 °C/min and slowly cooled to room temperature at rate of 1 °C/min followed by several intermediate grindings process. The obtained powder were compacted into pellets with 13 mm diameter and thickness around 3 mm under 5 tons and then sintered at 1200 °C for 24 hours. X-ray diffraction (XRD) was performed using Bruker D8 Advance Diffractometer system. The radiation employed was Cu-Kα ($\lambda = 0.15406$ nm) which were operated at 40 KV and 40 mA. The sample was scanned continuously in the range of $20^\circ \leq 2\theta \leq 80^\circ$ with a scanning rate of $2^\circ$/min. The XRD patterns was then analyzed by using XPert HighScore software to confirm the crystalline phase of the samples. Electrical resistivity measurement were carried out using the DC electrical resistivity measurement along with four-point probe technique. The measurement was performed in the temperature range of 20 - 300 K using a four point probe technique in a Janis model CCS 350T cryostat. The morphology of the synthesis samples were determined by using Phenom ProX, scanning electron microscopy (SEM) with 5Kx magnification. Bulk density of the samples were determined by employing the Archimedes principle using acetone as the liquid buoyant. The percentage of porosity was calculated by using this relation.

$$\text{Porosity}\% = \left(\frac{\rho_{\text{theoretical}} - \rho_{\text{bulk}}}{\rho_{\text{theoretical}}}\right) \times 100\% \tag{1}$$

Where $\rho_{\text{theoretical}}$ and $\rho_{\text{bulk}}$ are the theoretical and bulk density respectively.

3. RESULTS AND DISCUSSION

The powder XRD patterns for all the Pr$_{0.75}$Na$_{0.25}$Mn$_{1-y}$Co$_y$O$_3$ ($0 \leq y \leq 0.05$) samples are shown in Fig. 1. XRD analysis revealed all samples consist of essentially single phase and crystallized in orthorhombic structure.
with Pnma space group reliable with the structure reported from the previous study [15]. Table 1 shows the values of MI transition temperature \((T_{MI})\), lattice parameters, calculated unit cell volume \((V)\), density \((D)\) and porosity of each samples. It can be seen that, the values of \(V\) was observed to be decreased as the concentration of Co increased, which points to the possibility that Co ions with smaller ionic radius (0.61 Å) substitutes Mn ions with larger ionic radius in the lattice structure. Successful of substitution for Mn\(^{3+}\) has also been previously reported [16]. Apart from that, the decrease in values of \(D\) with Co content shows a good agreement with the calculated unit cell volume indicating that Co\(^{3+}\) which has smaller ionic radius compared to Mn\(^{3+}\) is successfully doped in the system which is in line with the previous study [17].

![XRD patterns for Pr\(_{0.75}\)Na\(_{0.25}\)Mn\(_{1-y}\)Co\(_y\)O\(_3\) (0 ≤ \(y\) ≤ 0.05)](image)

**Fig. 1** XRD patterns for Pr\(_{0.75}\)Na\(_{0.25}\)Mn\(_{1-y}\)Co\(_y\)O\(_3\) (0 ≤ \(y\) ≤ 0.05)

**Table 1** M-I transition temperature \((T_{MI})\), Lattice parameters, unit cell volume, density and percentage of porosity of Pr\(_{0.75}\)Na\(_{0.25}\)Mn\(_{1-y}\)Co\(_y\)O\(_3\) (0 ≤ \(y\) ≤ 0.05)

<table>
<thead>
<tr>
<th>Sample ((y))</th>
<th>(T_{MI}) (K)</th>
<th>Lattice parameter</th>
<th>(V) ((\text{Å}^3))</th>
<th>(D) ((\text{g/cm}^3))</th>
<th>Percentage of porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(y = 0)</td>
<td>-</td>
<td>(a) (Å) ± 0.001</td>
<td>(b) (Å) ± 0.002</td>
<td>(c) (Å) ± 0.001</td>
<td>228.2 ± 0.1</td>
</tr>
<tr>
<td>(y = 0.02)</td>
<td>108</td>
<td>5.444</td>
<td>7.696</td>
<td>5.445</td>
<td>227.9 ± 0.1</td>
</tr>
<tr>
<td>(y = 0.05)</td>
<td>84</td>
<td>5.443</td>
<td>7.680</td>
<td>5.444</td>
<td>227.6 ± 0.1</td>
</tr>
</tbody>
</table>

The effect of Co-doped on temperature dependence of electrical resistivity for all samples are shown in Fig. 2. It was found that, the \(y = 0\) sample showed an insulating behaviour as there are no MI transition observed in the temperature range of 80 K - 300 K. Interestingly the \(y = 0.02\) and \(y = 0.05\) samples showed distinct a metal-insulator transition at 108 K and 84 K respectively suggestively due to the DE mechanism. Meanwhile, the shifting of the MI transition to lower temperature as Co increased could be suggested due to replacements of Co ions at Mn site which leads to the depletion of the Mn ion ratio and the decreasing of resistivity can be connected to the hopping process. Thus, the DE is weakened and caused to the destruction of long range ferromagnetic order [12,19,20].
The effect of Co-doped on the surface morphology of the $y = 0.05$ fractured samples are shown as in Fig. 3. Different surface morphology characterized by a change in grain boundary and the grain size as well as apparent porosity was observed for all samples. The $y = 0$ sample showed a uniform grain compared to the $y = 0.02$ sample. This can be said the uniformity and disorder of the grain size of the samples change according to the concentration of the Co doped most probably due to the difference of ionic radii between $\text{Co}^{3+}$ and $\text{Mn}^{3+}$ in line with the previous study [20].

Fig. 2 Temperature dependence of electrical resistivity of $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$ ($0 \leq y \leq 0.05$)

Fig. 3 SEM images with 10kx magnification for $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$ samples (a) $y = 0$, (b) $y = 0.02$ and (c) $y = 0$. 

(a) 

(b) 

(c)
However for \( y = 0.05 \), the observation of grain boundaries was not clearly seen. Apart from that, the calculated porosity as shown in Table 1 was increased from 1.75% to 8.96% with increasing of Co content in line the apparent porosity as observed in SEM morphology indicated a successful doped of Co in the Mn-site in the compound.

4. SUMMARY

In conclusion, crystalline phase, electrical properties and surface morphology of the monovalent doped of \( \text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-x}\text{Co}_x\text{O}_3 \) (\( y = 0, 0.02 \) and 0.05) samples have been investigated. Powder X-ray diffraction measurement show that all the synthesized samples were crystallized in the orthorhombic structure with \( \text{Pnma} \) space group. Analysis of lattice parameters and unit cell volume from the XRD results showed these values were decreased in conjunction with the value of calculated sample of bulk density suggestively due to smaller ionic radii of \( \text{Co}^{3+} \). Increasing of Co content form \( y = 0.02 \) to \( y = 0.05 \) caused a MI transition to shifted to lower temperature which can be suggested due to the weakening of DE mechanism. On the other hand, investigation on the surface morphology of \( \text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-x}\text{Co}_x\text{O}_3 \) samples showed an improvement of grain boundaries with increasing Co content accompanying with the increasing values of calculated porosity.

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Deposition of TiO$_2$/ZnO Thin Films using Spin-Coating Method

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ABSTRACT. Thin film technology is important to semiconductor devices, optical coatings, and corrosion protection and also important within physical science. Thin films commonly used in metal oxide material as a layer or bilayer to improve the performance of films. In this study, TiO$_2$ and ZnO were synthesized by using sol-gel method and deposited using spin coating technique by using glass substrate. The sol-gel TiO$_2$ has been produced by using titanium (IV) butoxide, N-butanol, acetic acid and distilled water in molar ratio 2:20:1:1 meanwhile zinc acetate dehydrate, iso-propanol, diethanolamine and distilled water with molar ratio 1:20:1:1 was used to produced sol-gel Z. The calcination temperature were used for first layer of TiO$_2$ from 400°C to 600°C and for the second layers of ZnO are 500°C and 600°C. A combination of characterizations such as X-ray diffraction (XRD), atomic force microscopy (AFM), field-emission scanning electron microscope (FESEM), and ultraviolet-visible spectrophotometry (UV-Vis) were used. The XRD analysis confirmed that TiO$_2$ with anatase structure and ZnO with hexagonal wurtzite were present. The XRD intensity increases with increasing of calcination temperature. The surface roughness analysis by AFM shows the TiO$_2$/ZnO thin films surface was improved with increasing the calcination temperature. All the result suggested that the use of bilayer thin films effectively enhanced the quality of films crystallinity and optical properties as compared to a single layer thin films.

Keywords: Thin films, Bilayer, Multilayer, Titanium dioxide (TiO$_2$), Zinc Oxide (ZnO), Sol-gel;

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1. INTRODUCTION

A thin film is a thickness layer of films where the metal oxide material has been used as a layer and deposited onto the substrate. Generally, the deposition of thin films used metal oxide material as a layer or bilayer thin films because it improved the performance of films. The layer of thin films has been deposited with different substrate such as glass [1,2], quartz [3] and silicon wafers [2]. Moreover, chemical composition widely used for thin film application such as sol-gel [4,5], electro-deposition [6], chemical vapor deposition (CVD) [1,7], impregnation [8] and atomic layer deposition [9].

In this study, titanium dioxide (TiO$_2$) and zinc oxide (ZnO) has been used as bilayer thin films. Generally, TiO$_2$ is a white solid organic and also known as titania. TiO$_2$ is a one of semiconductor material widely used to improved the performance in film thickness such as crystallite size [10], morphology [10,11], and optical...
properties. Moreover, transmittance in visible region, chemical stability and high reflective index actually good for optical thin films [4]. Generally, TiO₂ have three different phase crystalline structures such as rutile, anatase and brookite. Generally, anatase and brookite in metastable form and by using calcination process, the phase able to transform both structure into stable rutile form [12]. Zinc oxide (ZnO) is one of metal oxide widely used thin films proces. The advantages of using this semiconductor as additive for our case study because this material are cheap [13], non-toxic [13] and low cost attractive material [8]. Zinc oxide (ZnO) was used as additive because also used in electrical and optical application where it improve the optical absorption property [14] and excellent in ultraviolet photosensitivity [9].

Sol-gel method is one of liquid chemical mixture to formed TiO₂ and ZnO solution. Generally, this method widely used in thin films because these technique effective for bilayer and multilayer thin films surface structure, low cost [5,6,10], high purity [5,13] and easy to control the reaction condition structure at low temperature [6]. These method actually suitable for combined metal oxide because it increased the thickness layer and also the porosity of the thin films. Besides that, deposition technique widely applied for thin films such as spin coating [2,5,15] and dip coating [1,16]. Spin-coating defined as method to produced uniform organic films in large areas on the substrate by using spinning process and dip-coating is one of coating process and usually this process used for complex shape substrate. The methods was used to characterize the structure and optical properties of bilayer TiO₂/ZnO thin films by using X-ray diffraction (XRD), atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM).

2. MATERIALS AND METHODS

The TiO₂/ZnO thin films were prepared by sol-gel method with pre-deposited TiO₂ at different calcination temperatures from 400°C to 600°C. The sol-gel of TiO₂ was prepared by using titanium (IV) butoxide and n-butanol at room temperature. Then, acetic acid and distilled water were added dropwise into the precursor under continuous stirring at room temperature for 2 hours to produce homogenous TiO₂ sol-gel. The ZnO sol-gel was prepared using zinc acetate dehydrate and isopropanol. The diethanolamine and distilled water were added into the ZnO precursor solution under strong stirring and heated at 60 °C for 2 hours. The resultant of both TiO₂ and ZnO sol-gel were kept ageing at room temperature for 24 hours. The microscope glass slides were used as substrates. The substrates were cleaned using ethanol and acetone then rinsed with deionized water. The bilayer TiO₂/ZnO thin films with pre-deposited TiO₂ were deposited using spin coater (MTI; VTC-50A). The deposition of thin film was started with deposited TiO₂ pre-deposited layer on substrate. The spinning of coating speed used was 3000 rpm for 30 s. After that, the film was dried at 100 °C in oven. The TiO₂ pre-deposited layer then calcined at 400 °C, 500 °C, and 600 °C before deposited with ZnO sol-gel. By using the same glass substrate coated with pre-deposited TiO₂, the glass was placed again on spin coater to deposit with ZnO sol-gel to forming TiO₂/ZnO thin film. Then, the TiO₂/ZnO thin film was post-calcined at temperature 500 °C and 600 °C. The TiO₂/ZnO thin films were characterized and analyzed in detail as follow. The crystalline phases of the thin films were identified through XRD (Bruker AdvanceD8). The surface roughness and morphology of the grain sizes were studied by using AFM(XE-100) and FESEM, respectively.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis of TiO₂/ZnO Thin Films. Bilayer of TiO₂/ZnO thin films was deposited using glass substrate and the crystal structures of bilayer were analysing by XRD. All XRD analyses confirmed that TiO₂ was present with an anatase crystal structure and ZnO was present with wurtzite crystal structure. No other phase rutile or brookite was determined in the result. XRD peak of TiO₂ matched with anatase of JCPDS 00-021-1272 and ZnO pattern matched with the wurtzite of JCPDS 00-036-1451.
Fig. 1 shows XRD pattern of TiO$_2$/ZnO thin films where the calcination temperature of first layers TiO$_2$ increased from 400°C to 600°C and for second layers of ZnO maintain at 500°C. The results show increases of peak intensity after calcination process. It reveal the intensity of anatase peak of $\theta = 25.28^\circ$, 37.80°, 62.69°, and 68.76° are attributed to the (101), (004), (204), and (116). For hexagonal wurtzite intensity peak of $\theta = 31.77^\circ$, 34.42°, 36.25°, 47.53°, 56.60° and 67.96° are assigned to (100), (002), (101), (102), (110) and (112), respectively. It shows that the crystallinity of the TiO$_2$ film improved with deposition of Mechiakh et al.[10] and Xu et al.[17] also found the similar result where the calcination temperature has influenced the intensity on the diffraction peaks.

Fig. 1. XRD pattern of TiO$_2$/ZnO thin films (a) TiO$_2$ (400°C)/ZnO (500°C), (b) TiO$_2$ (500°C)/ZnO (500°C) and (c) TiO$_2$ (600°C)/ZnO (500°C)

Fig. 2 shows XRD pattern of TiO$_2$/ZnO thin films for TiO$_2$ layers at 400°C, 500°C, and 600°C and ZnO at 600°C. It shows that the XRD pattern is similar with Fig. 1 and the intensity is significantly enhanced by increasing the annealing temperatures. Fig. 2 shows the intensity of anatase peak of $\theta = 25.28^\circ$, 37.80°, 53.89°, 55.06° and 62.69° are attributed to the (101), (004), (105), (211), (204) and (116), respectively. For hexagonal wurtzite intensity peak of $\theta = 31.77^\circ$, 34.42°, 36.25°, 47.53°, 56.60°, 67.96° and 69.1° are assigned
to (100), (002), (101), (102), (110), (112) and (201), respectively. The highest intensity peak for TiO$_2$ are at $2\theta = 25.28^\circ$ (101) and for ZnO at $36.25^\circ$ (101). It shows when the calcination temperature increases, the intensity of some peak also increase. In addition, Shi et al.[18] also has similar result where the intensity improved when temperature increase and the crystallinity quality of ZnO film has been improved where TiO$_2$ film used as a buffer layers. In addition, Hussin et al.[19] was observe with increases the crystallite size also improved crystalline quality of TiO$_2$/ZnO bilayer. Moreover, crystallization of thin film shows thickness deposition and annealing process play important roles to improve the performance of thin films.

3.2 Surfaces Morphology of TiO$_2$/ZnO Thin Films. The AFM characterization was carried out on bilayer TiO$_2$/ZnO thin films with different calcination temperature. Fig. 3 shows the images of single layer TiO$_2$ and bilayer TiO$_2$/ZnO thin films. It can see that the surfaces roughness become smoother after applied the calcination process. The lower roughness value represents good homogeneity of the TiO$_2$ particles on the surface. The layer of TiO$_2$ show smooth surfaces but with bilayer, the roughness of thin films becomes more smooth. The result shows the decrease of RMS values single layer TiO$_2$ (600°C) from 5.333nm to 2.578nm for bilayer TiO$_2$ (600°C)/ZnO (600°C). The grain size and average surface roughness performance increases when the buffer layer has been used significant with enhancement in crystallinity. In addition, the calcination temperature influences the decreasing of surface roughness. Ibrahim et al.[20] also concluded that the annealing temperature strongly affects the structure of thin films.

![AFM morphology](image)

**Fig. 3.** AFM morphology (a) single layer TiO$_2$ (600°C), (b) TiO$_2$ (600°C)/ZnO (500°C) and (c) TiO$_2$ (600°C)/ZnO (600°C)
Based on the result shown in Fig 3, RMS values slightly decrease after single layer TiO$_2$ films was deposited with ZnO layer. Hussin et al.[19] found the similar results, which the value of RMS and grain size improved when applied bilayer thin films and the particle size reaction also depend on deposition temperature and impurities from the grain boundaries.

The FESEM images in Fig. 4 shows the effect of calcination process on the TiO$_2$/ZnO thin films. The particle and boundary clearly show in the images with different size of grain boundary. It shows when the temperature increase, the size of particle become bigger and the gap between boundaries becomes smaller. Xu et al.[21] have similar result where the calcination temperature influences the size of particle.

AFM results for grain size also has significant result with FESEM result where surface roughness improved and grain size reduced from 22.228 nm for TiO$_2$ (400°C)/ZnO (500°C) to 9.114nm for TiO$_2$ (600°C)/ZnO (500°C). TiO$_2$ (600°C)/ZnO (600°C) grain size also reduced from 16.673nm of TiO$_2$ (400°C)/ZnO (600°C) to 5.886nm TiO$_2$ (600°C)/ZnO (600°C). The calcination process influences the growth of particle size significantly with AFM result of surfaces roughness becomes smoother. The particles for single TiO$_2$ thin films show the homogeneous particle and after deposition with ZnO, the grain size becomes irregular and increases the particle size of TiO$_2$/ZnO thin films.

4. SUMMARY

TiO$_2$/ZnO thin film had been successfully growth on the glass substrate using spin coating method. XRD result shows the intensity of peak improved with bilayer TiO$_2$/ZnO thin film. The RMS value decrease for single layer TiO$_2$ (600°C) from 5.333nm to 2.578nm for bilayer TiO$_2$ (600°C)/ZnO (600°C). It shows the surface morphology become smooth with deposition with ZnO layer. The transmittance spectra of TiO$_2$/ZnO thin film shows the improvement of transmittance after applied the calcination process. High transmittance and good conductivity makes TiO$_2$/ZnO thin film widely used in optical application especially in solar cell.
Bilayers TiO$_2$/ZnO thin films show better properties compared with single layers of thin films. It proved that, TiO$_2$ thin films improved the crystallinity structure, surfaces roughness, grain boundary size and transmittances by using ZnO as bilayer of the thin films.

REFERENCES


Effect of Borosilicate Glass Addition on the Dielectric Properties of CCTO-Glass Composites for DRA Applications

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ABSTRACT. The effect of borosilicate glass addition on the dielectric properties of CCTO-glass composites for DRA applications was studied. CCTO ceramics were prepared via solid state reaction method. The raw materials of CCTO were wet mixed for 24 hours and then dried overnight in oven. CCTO mixtures were calcined at 900 °C for 12 hours. The borosilicate glass, taken from laboratory beaker was grinded by using planetary ball mill machine to form a finer powder. Then the glass powder was mixed with CCTO's calcined powder for 24 hours. The mixed powder was compacted at 250 MPa and then was sintered at 1040 °C for 10 hours. X-Ray Diffractometer (XRD) analysis showed the formation of CCTO phase and minor secondary phase of CuO were obtained by pure CCTO and CCTO-borosilicate glass composites samples. Observation on Scanning Electron Microscopy (SEM) micrographs showed large grain size of CCTO was reduced with increasing borosilicate glass addition (0.01-1.0 wt.%). The εr of CCTO was increased while the tan δ of CCTO was decreased with small addition of borosilicate glass. The resonance frequency of CCTO was moves to lower frequency with increasing of glass addition until 0.1 wt.%, but it moves to higher frequency with increasing of glass addition up until 1.0 wt.%. The radiation pattern shows that each sample can radiate the signal equally on E- and H-planes.

Keywords: CaCu3Ti4O12, Borosilicate glass, Dielectric properties;

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1. INTRODUCTION

Recently, wireless communication systems are growing rapidly where antenna is considered as one of the key devices for wireless communication systems. The trend of wireless communication devices is moving towards miniaturization in order to accommodate smaller designs and limited space. As being reported by Subramanian et al. [1], high dielectric constant, εr (~ 10⁴) had been found on the oxide of CaCu3Ti4O12 (CCTO) at low frequencies (1 KHz) and nearly constant over large temperature range from room temperature to 300 °C. Such material is very promising for the application as capacitor and dielectric resonator antenna (DRA). The important properties required for the ceramic material to be used as DRA are high εr, low dielectric loss (tan δ) and low temperature coefficient. However, even though CCTO is known to have high εr, it is also
identified to have high tan δ (>0.05). Yuan et al. [2] and Didry et al. [3] reported that tan δ of CCTO from their researches was around 1.0 at 1 MHz. Usually, high $\varepsilon_r$ will result in higher tan δ because of inherent material properties. This phenomenon (high tan δ) happened not only for CCTO, but for other dielectric materials as well. Tan δ can be affected by several extrinsic factors, such as porosity, microstructural defects, impurities and microcracks [4].

Based on the previous studies, there were alternative ways to produce DRA with better properties; which is by using DRA composites. Even though there were various reports on ceramic composites used as DRA [5,6], there were no specific study on effect of borosilicate glass addition on the dielectric properties of CCTO and suitability for DRA application. Glass is known to have low tan δ and can improve the densification of ceramic materials. Previous study by Prakash and Varma [7] find that boron oxide and silicon oxide based glass can effectively reduce tan δ of CCTO from 0.12 to 0.06. Since the performance of antenna is evaluated by the dielectric properties ($\varepsilon_r$ and tan δ) of the material, thus borosilicate glass addition might help to modify the dielectric properties of CCTO.

2. MATERIALS AND METHODS

CCTO ceramics was prepared via solid state reaction method. The raw materials of CaCO$_3$ (Sigma Aldrich, >99%), CuO (Sigma Aldrich, >99%) and TiO$_2$ (MERCK, >99%) powder was wet mixed for 24 hours and the mixture was dried overnight in oven. The dried mixtures then were calcined at 900 °C for 12 hours. The borosilicate glass (Pyrex™), taken from laboratory beaker was grinded by using planetary ball mill machine to form a finer powder. Subsequently, the glass powder was mixed with CCTO's calcined powder for 24 hours in the ratio corresponding to the following chemical composition: (100-x) % CaCu$_3$Ti$_4$O$_{12}$ + x % glass additives (wt.%), where x = 0, 0.01, 0.1, and 1.0 respectively. The mixed powder was pressed into pellets under a pressure of 250 MPa. The sample was labelled as CCTO for pure CCTO sample while Boro0.01, Boro0.1 and Boro1 were stand for the samples of CCTO with addition of 0.01, 0.1 and 1 wt.% of borosilicate glass, respectively. The pellets then were sintered at temperature 1040 °C for 10 hours. The phase formation of the pure CCTO and CCTO-borosilicate glass composites were analyzed by using X-ray Diffraction (XRD) (model: Bruker Advance D8) while Scanning Electron Microscopy (SEM) (model: TM 3000) was used to observe the microstructures of the samples. For electrical measurement analysis, the dielectric properties of the samples were measured by using impedance analyzer machine (model: 4291B Hewlett Packard) at 1 GHz and for DRA behavior, the measurement was took placed by using network analyzer (model: HP8720D), spectrum analyzer (model: Agilent E4405B) and Swept Signal Generator (model: Agilent 83260B) machines.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD pattern of pure CCTO and CCTO-borosilicate glass composites after being sintered at at 1040 °C for 10 hours. The amounts of glass added were 0.01, 0.1 and 1.0 wt.%. XRD analysis in Fig 1 showed that CCTO and CCTO-borosilicate glass composites samples present the formation of CCTO phase (ICDD Data File Card No. 01-075-2188) with minor peaks of CuO phases (ICDD Data File Card No. 00-045-0937). The minor CuO phase presented for each sample is expected come from the CuO compound that segregated at the grain boundary of CCTO. Previous studies [8-12] also reported that the presence of CuO compound was observed at the grain boundary of CCTO after being sintered at 1040 °C for 10 hours. According to Yuan et al. [1], the intergranular CuO phase is due to the instability (or activity) of Cu ions in the CCTO lattice. Cu ions were first separated out from CCTO at ~1000 °C, then were ousted to the surface layer of the pellet and mostly segregated at the grain boundaries, and were finally oxidized to CuO compound.

Fig. 2 shows the SEM images of the sintered pure CCTO and CCTO-borosilicate glass composites samples, respectively. It can be observed that the grain size of CCTO becomes smaller with the increasing amount of borosilicate glass addition. Further addition of borosilicate glass contributed to the smaller grain size of CCTO. CCTO sample had the largest average grain size of 96.6 µm while Boro0.1 had
smallest average grain size with 54.05 µm. The glass addition seems to be segregated with CuO at the grain boundaries and restrict the CCTO’s grain growth. Several researchers [13-15] stated that with more addition of glass into the BaSrTiO₃ (BST) and CCTO ceramics, the segregation of glass at the grain boundaries hinders the movement of ceramic particles, hence restricting the ceramic grain growth and reduce the grain size of BST and CCTO ceramics, respectively.

Fig. 1 XRD pattern of sintered CCTO and CCTO-borosilicate glass composites samples

Fig. 2 SEM micrographs of CCTO and CCTO-borosilicate glass composites samples with different glass composition of (a) 0 wt.%, (b) 0.01 wt.%, (c) 0.1 wt.% and (d) 1.0 wt.%
Table 1 shows the \( \varepsilon_r \), tan \( \delta \) and resonance frequency of CCTO and CCTO-borosilicate glass composites samples. It shows that as the composition of borosilicate glass in CCTO increased, the \( \varepsilon_r \) of CCTO was increased as well while the tan \( \delta \) of CCTO was decreased when all samples were measured at 1 GHz. The \( \varepsilon_r \) of CCTO was increased from 86 to 100 while the tan \( \delta \) of CCTO was decreased from 0.62 to 0.38 after the addition of 1.0 wt.% of borosilicate glass. The \( \varepsilon_r \) of CCTO had increased while the reduction of tan \( \delta \) of CCTO-glass composites because due to the addition of borosilicate glass improved the densification and reduce the porosity of the CCTO. Besides, it also was due to the properties of borosilicate glass that has low tan \( \delta \) were added into the CCTO ceramics [7].

This table also shows the resonance frequency of CCTO moves to lower frequency from 9.51 GHz to 9.02 GHz with increasing of glass addition until 0.1 wt.%. Instead, the resonance frequency of CCTO was increased until 10.56 GHz when 1.0 wt.% of borosilicate glass was added into CCTO. The resonance frequency shifting was within the range of 9 to 11 GHz. According to International Telecommunication Union (ITU), this operating frequency is under the X-bands category [16]. Fehine et al. [5] stated that the shifting of the resonance frequency is caused by differences of \( \varepsilon_r \) value of YIG ceramics as a function of doped Gd\(_3\)Fe\(_5\)O\(_{12}\) compound where high \( \varepsilon_r \) move the resonance frequencies to lower frequencies. Based on the dielectric results shown in Table 1, small addition of borosilicate glass increased the \( \varepsilon_r \) of CCTO, thus contributed to lower resonance frequency of CCTO-borosilicate glass composites samples compared to the pure CCTO sample. But, when the addition of each glass was up to 1.0 wt.%, the \( \varepsilon_r \) decreased, thus the resonance frequency of CCTO moves to the higher frequencies of 10.56 GHz.

Table 1 \( \varepsilon_r \), tan \( \delta \) and resonance frequency of CCTO and CCTO-borosilicate glass composites samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \varepsilon_r ) at 1 GHz</th>
<th>tan ( \delta ) at 1 GHz</th>
<th>Resonance frequency (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCTO</td>
<td>86</td>
<td>0.62</td>
<td>9.51</td>
</tr>
<tr>
<td>Boro0.01</td>
<td>37</td>
<td>0.43</td>
<td>9.19</td>
</tr>
<tr>
<td>Boro0.1</td>
<td>96</td>
<td>0.40</td>
<td>9.02</td>
</tr>
<tr>
<td>Boro1</td>
<td>100</td>
<td>0.38</td>
<td>10.56</td>
</tr>
</tbody>
</table>

The radiation pattern in different plane of view of pure CCTO ceramics and CCTO-borosilicate glass composites samples were illustrated in Fig. 3. The measured radiation patterns were taken at the respective resonance frequency of each sample as shown in Table 1. For E-plane cut (Fig. 3(a)), it was observed that each sample that have been set up as DRA radiated the signal equally especially at the front and at the back lobes. It shows that each sample had a strong signals on the front and the back. However, there were dip at 90° and 270°, indicated that the transmission/reception signal by the sample was weak.

Meanwhile, Fig. 3(b) shows the H-plane cut of radiation pattern for the same samples. It can be observed that the radiation patterns for all samples were nearly identical between each other where the signal was radiated on the top of the plane. Similar kind of results also have been reported by Wan Ali et al. [6]. Furthermore, it can be observed that the radiation pattern of CCTO was increased after the addition of various glasses for both E- and H-planes. So, it can be said that the addition of borosilicate glass can help to improve signal strength to the CCTO when it is used as the DRA.
SUMMARY

CCTO and CCTO-borosilicate glass composites were successfully prepared via solid state reaction method. From the XRD analysis, the formation CCTO phase alongside with minor CuO phase were seen for each sample which were sintered at 1040 °C for 10 hours. SEM micrographs show that the grain size of CCTO becomes finer with increasing glass concentration. The $\varepsilon_r$ of CCTO was increased while the tan $\delta$ of CCTO was decreased with small addition of borosilicate glass. The resonance frequency of CCTO was moves to lower frequency with increasing of glass addition until 0.1 wt.%, but it moves to higher frequency with increasing of glass addition up until 1.0 wt.%. The radiation pattern shows that each sample can radiate the signal equally on E- and H-planes. Thus, it shows that the borosilicate glass addition into CCTO can give the great effect on the dielectric properties of CCTO ceramics for DRA applications.

Fig. 3 Radiation pattern of CCTO and CCTO-borosilicate glass composites samples as DRA in different cut plane (a) E-plane and (b) H-plane
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Effect of CuO doped TiO\textsubscript{2} on Morphology, Crystal Structure and Photocatalytic Activity

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ABSTRACT. Copper oxide doped Titanium Dioxide (CuO= 0-1.0wt.%) powders were prepared using sol-gel method and all the powder were sintered at 500 °C. The samples were characterized using X-ray diffraction(XRD), scanning electron microscopy(SEM), Brunauer-Emmett-Teller (BET) and UV/Vis spectrophotometer. The doping concentration of CuO gave significant influenced on the structural properties of TiO\textsubscript{2}. The lattice parameter, particles size and specific surface area of TiO\textsubscript{2} size were increased with increasing CuO concentration. The degradation rate of methylene blue (MB) was calculated to investigate the photocatalytic activity of CuO doped TiO\textsubscript{2}. The degradation rate were increased when the concentrations of CuO increased.

Keywords: Photodegradation, Photocatalytic activity, Anatase, Microstructural;

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1. INTRODUCTION

TiO\textsubscript{2} had been recognized as one of the semiconductor metal oxide due to its unique properties like wide bandgap (3.20eV), strong ultraviolet absorptivity, good photocatalytic activity, non-toxicity and long term chemical stability [1-2]. It is desired for photocatalysts to have high reaction for solar spectrum ranges. Thus, simultaneous catalytic process could be run naturally by sunlight. However, the wide band gap of anatase phase (3.2eV) became limited in order to get higher photocatalytic performance. The previous research had provided some promising methods to enhance the UV light photo activity such as metal and non-metal doping, dye sensitization, and semiconductor coupling method [3]. The properties of TiO\textsubscript{2} also reported to be influenced by the synthesize method like sol-gel, hydrothermal or reverse micelle method. Currently, the modification methods by metal ions was being considered where the process required the higher temperature of calcination temperature.

Previous study proposed that the metal doping can effectively reduced the band gap of TiO\textsubscript{2} in order to increase the number of photogenerated electron-hole pairs separation [4-5]. It was reported by Sangpour et al. [6], the effect of photocatalytic activity on copper (Cu) and silver (Ag) doped TiO\textsubscript{2} were performed in the following order Cu: TiO\textsubscript{2} > Ag: TiO\textsubscript{2} > TiO\textsubscript{2}. Accordingly, Cu-doped TiO\textsubscript{2} was found to be promising materials for high photocatalytic activity[7]. It was well reported that mesoporous materials with larger surface area
with relatively regular channel structure are good materials for catalyst [8]. Therefore, morphological and surface analysis is vital tool in enhancing photocatalytic activity. While, Nakata et al. [9] revealed the significant role of polymeric template and calcination temperature on producing high crystallinity and large surface area of synthesized TiO₂.

In the present study, copper oxide doped TiO₂ powders was prepared using sol-gel method with different dopants concentration from 0-1.0wt.% and sintered at 500 °C. Different concentration of CuO was doped to investigate the effect on structural, morphological and photocatalytic performance. The structural properties of powders were characterized using X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) while the photocatalytic performance was investigated using UV/vis spectrophotometer. The photocatalytic activities of CuO doped TiO₂ were evaluated by photo degradation of methylene blue (MB).

2. MATERIALS AND METHODS

2.1 Sample Preparation. TiO₂ was synthesized through the sol-gel method by the hydrolysis of titanium isopropoxide (Ti(OC₃H₇)₄,12.8 mL). Titanium isopropoxide was added into the mixture solution of 18.6 mL of isoprophyl alcohol and 20.6 mL of acetic acid. Then, a mixed solution of 18.6 mL alcohol dissolved with copper nitrate trihydrate (Cu(NO₃)₂·3H₂O) was added into the solution according to the anticipant Cu content (0.2%-1.0%, weight fraction). Finally, a few drops of deionized water was dropped in the solution while stirring. Stirring was held for the whole course and continued for 1 hour. After stewing for 24 hours, the solution became gel and was dried in an oven at 80 °C for 24 hours to form the powder. The powder was then put in a muffle furnace and sintered at 500 °C for 6 hours to acquire the Cu-doped TiO₂ powders with different CuO contents from 0.2wt.% to 1.0wt.%.

2.2 Characterization. XRD patterns were obtained with a diffractometer on Shidmadzu XRD 6000 2500 V using Cu Ka radiation. UV-vis adsorption spectra were recorded using a Genspec III (Hitachi, Japan) spectrometer. Scanning electron microscopy (SEM) images of the product were taken on a field with an accelerating voltage of 20 kV. Specific surface area was determined by BET.

2.3 Photocatalytic activity. The photocatalytic activity of TiO₂ and CuO doped TiO₂ was evaluated by the degradation of MB in solution under illumination of UV light (wavelength about 365nm). The UV lamp was placed horizontally hung. A 500ml beaker contain reaction solution were stirring using magnetic stirrer which irradiated under UV light. The distance from the beaker to the lamp was 30cm. In this experiment, the TiO₂ powder was added to aqueous of MB, and the initial concentration of MB and amount of TiO₂ and CuO/TiO₂ were set at 20ppm and 5mg per little, respectively. The reaction time were ranged from 0 to 180min. The degradation of MB was calculated using formula: Degradation = (A₀ - A)/A₀, where A₀ and A were the absorbance of the primal and remaining MB respectively. The absorbance then was measured with UV/vis spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Phase structure. The phase and structure analysis of the samples were investigated by X-ray diffraction pattern in Fig. 1 for different weight percent of CuO. All peaks observed were indicated to anatase structure of titanium dioxide. There was no Cu peak observed in this pattern observed indicated that Cu was doped into TiO₂ lattice. The average crystallite sizes of TiO₂ and 0.2 wt.%-1.0 wt.% CuO were calculated using Debye-Sherrer equation. The increased of crystallite size due to the presence of Cu species in the TiO₂ matrix. Pham et al. [1] reported that (101) plane of Cu doped materials was slightly shifted to higher diffraction angles when the Cu content increased. They also confirmed that Cu was incorporated into TiO₂ lattice. Other researchesfound that Cu²⁺ could be substituted in Ti⁴⁺ position due to similar ionic radii which is Ti = 0.68Å and Cu = 0.72Å. The diffraction peak decreased in intensity and became broadened as the Cu content was
increased shows that the average size of TiO$_2$ particles decreased [10]. In Table 1, the crystallite size increased with increasing copper oxide concentration from 102.2 up to 260.8. The rietveld refinement were carried out using tetragonal structure with space group I41/amd (141). The lattice parameter (a, b, and c) and microstructural parameter including crystallite was refined.

Table 1 Lattice parameter and crystallite size of doped and undoped TiO$_2$

<table>
<thead>
<tr>
<th>Doping concentration (wt.%)</th>
<th>Lattice parameter, a (Å)</th>
<th>Lattice parameter, b (Å)</th>
<th>Lattice parameter, c (Å)</th>
<th>Crystallize size (Å)</th>
<th>Reliability</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.78686</td>
<td>3.78686</td>
<td>9.51762</td>
<td>102.2</td>
<td>12.1314</td>
</tr>
<tr>
<td>0.2</td>
<td>3.78847</td>
<td>3.78847</td>
<td>9.50429</td>
<td>105.8</td>
<td>11.3611</td>
</tr>
<tr>
<td>0.4</td>
<td>3.79087</td>
<td>3.79087</td>
<td>9.49885</td>
<td>119.4</td>
<td>11.4029</td>
</tr>
<tr>
<td>0.6</td>
<td>3.79093</td>
<td>3.79093</td>
<td>9.48808</td>
<td>138.6</td>
<td>12.4353</td>
</tr>
<tr>
<td>0.8</td>
<td>3.79057</td>
<td>3.79057</td>
<td>9.48510</td>
<td>195.3</td>
<td>12.6082</td>
</tr>
<tr>
<td>1.0</td>
<td>3.79204</td>
<td>3.79204</td>
<td>9.47465</td>
<td>260.8</td>
<td>12.8860</td>
</tr>
</tbody>
</table>
3.2 Morphological analysis. Fig. 2 shows SEM images of TiO$_2$ and CuO doped TiO$_2$ samples sintered at 500°C for 6 hours. From SEM micrographs (Fig.2(a)-(f)), the particles sizes were increase with increasing CuO concentration and the changes were clearly seen for sample 1.0wt.%CuO. Colon et al. reported that BET surface area values of powders increased with increasing Cu-doping concentration [11]. As shown in Table 2, the specific surface area increased with increasing CuO concentration. It was increased from 18.245 m$^2$/g for 0wt.%CuO up to 47.1855 m$^2$/g for 1.0wt.%CuO.

![SEM micrographs of (a) TiO$_2$, (b)0.2wt.%CuO, (c)0.4wt.%CuO, (d)0.6wt.%CuO, (e)0.8wt.%CuO, and (f)1.0wt.%CuO](image)

Table 2 Specific surface area of 0-1.0 wt.%CuO/TiO$_2$

<table>
<thead>
<tr>
<th>CuO concentration (wt.%)</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m$^2$/g)</td>
<td>18.245</td>
<td>23.0288</td>
<td>31.5431</td>
<td>41.7041</td>
<td>42.9819</td>
<td>47.1855</td>
</tr>
</tbody>
</table>

3.3 Photocatalytic activity. The photocatalytic activity of TiO$_2$ and CuO doped TiO$_2$ was study by observing degradation of MB under UV light irradiation. Fig. 3 shows the photocatalytic activity of CuO-doped TiO$_2$ with different CuO weight percent and undoped TiO$_2$ on the degradation of 20mg/L MB. From the graph, the degradation rate of MB increased with increasing the weight percent of CuO content from 0.2 to 1.0 wt.%.
The photocatalytic performance increase from 0.2 wt.% CuO until 1.0 wt.% CuO and best photocatalytic performance shows by sample with 1.0 wt.% CuO. The absorbance spectra of CuO-doped TiO$_2$ enhanced light harvest in both UV and visible light regions that enable much more light energy to be utilized for photocatalysis thus, increased the photocatalytic performance. Besides that, Cu species such as CuO, Cu$_2$O, and metallic Cu have smaller band gap and higher work function than bare TiO$_2$, where the electron can transfer from the conduction band of TiO$_2$ to metallic copper ion. This phenomenon results in the formation of Schottky barrier in the metal-semiconductor contact region, which then facilitated the charge separation, and hence enhances the photocatalytic performance of TiO$_2$ [12].

![Fig. 3 Photodegradation of methylene blue (MB) using CuO doped TiO$_2$ with different CuO contents and undoped TiO$_2$ as catalyst](image)

4. SUMMARY

The CuO doped TiO$_2$ samples were successfully prepared by sol-gel method and sintered at 500 °C. The synthesized samples were confirmed in anatase phase of TiO$_2$ for doping range 0 - 1.0 wt.% of CuO. The largest crystallite size was recorded by sample 1.0 wt.% CuO with 260.8 Å. The highest specific area was 47.185 m$^2$/g recorded by 1.0 wt.% CuO. The increasing of CuO content in TiO$_2$ obviously increased the photocatalytic performance of TiO$_2$. The highest photocatalytic performance was presented by 1.0 wt.% CuO doped TiO$_2$ which degraded more MB compared to others. Higher photocatalytic activity can increase water splitting performance for gas production.

ACKNOWLEDGEMENTS
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Humidity Sensing Properties of CCTO Thin Films Grown by Radio Frequency Magnetron Sputtering: Substrates Dependent

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ABSTRACT. CCTO thin films are of great importance for applications in various electronic devices. CCTO thin films with 200 nm thickness were grown on ITO and Al2O3 substrates by RF magnetron sputtering at 300 °C. The crystallographic properties of the films were studied by X-ray diffraction (XRD), and their morphologies were investigated by field emission scanning electron microscopy (FESEM). The I-V characteristic were measured by using direct current (DC) analysis method at humidity range of 30–90% relative humidity (RH). The XRD and FESEM results indicate that the CCTO thin films are polycrystalline nature, and porous for both substrates. The average crystallite size was 30 nm and 50 nm for CCTO deposited on ITO and Al2O3 substrate, respectively, as it is in good agreement with the FESEM results. The response times, recovery time and sensitivity were obtained 12 s, 500 s, and 17, respectively for 200 nm CCTO thin films deposited on ITO substrate, while those sensing properties were 30 s, 450 s, and 75 for CCTO thin films deposited on Al2O3 substrate. The CCTO thin films deposited on Al2O3 substrate show better I-V characteristics than that deposited on ITO substrates.

Keywords: CCTO, RF magnetron sputtering, Structural, I-V characteristic;

Received: 15.10.2017, Revised: 15.12.2017, Accepted: 30.02.2018, and Online: 20.03.2018;

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1. INTRODUCTION

The CaCu3Ti4O12 (CCTO) thin film with cubic structure is a novel electroceramic material with high dielectric permittivity (ε) and moderate dielectric loss (δ)[1,2]. Contrast to other metal oxide thin film materials, the CCTO thin film usually exhibits better chemical resistance, and thermal stability than electrolyte and organic polymer sensors. Recently, CCTO-based materials has concerned a great attention in the various applications from capacitor [3,4], to sensors [5,6] due to its distinctive electronic, physical and sensing properties. However, fabrication of the reliable CCTO thin film based possible device applications require to understand the factors influencing on the structural, morphological and properties of the thin films that are sensitive to the process conditions [7,8].

The substrate is an important factor which should be taken into consideration. As we all know, the thin films with better crystallinity will show excellent properties. Different substrates will led the change in crystallinity of thin films. Several researchers have reported the effect of the substrates on the different properties of the thin films. The suitable substrate cause better crystallinity and large grain size, leads to
better humidity sensing properties, and increment in other properties for thin films. However, so far there is no effort to study the influence of substrate on properties of CCTO thin film.

In this work, cubic structure CCTO thin films had deposited on ITO and Al$_2$O$_3$ substrates by RF magnetron sputtering at substrate temperature 41 ºC. The effect of different substrates was investigated by studying the structural, morphological, and humidity sensing properties.

2. MATERIALS AND METHODS

2.1 CCTO thin film humidity sensor preparation. The CCTO thin films with 200 nm thicknesses were deposited on ITO and Al$_2$O$_3$ substrates by RF magnetron sputtering system. The cylinder shaped pure CCTO (99.9%) target with a thickness of 0.19 inch and diameter 3 inch was used. The ultrasonically cleaned ITO and Al$_2$O$_3$ were used as substrates and fixed in rotatable substrate holder. The distance between target and substrate was kept constant approximately 120 mm. The sputtering chamber was first pumped down from atmospheric pressure to a base pressure of 30 × 10$^{-5}$ mbar. Then Ar gas was introduced into the chamber at a rate of 65 standard cubic centimeter per minute (SCCM) and when the pressure reached 2 × 10$^{-5}$ mbar, the RF power supply was switched on and kept at 150 W. Sensor fabrication and humidity measurement using these CCTO thin film sensors was carried out by a climate chamber (Memmert HPP108) which was the same as our previous work [9]. The sputtering conditions for thin film deposition are summarized in Table 1.

Table 1 Sputtering condition for CCTO thin film deposition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>CCTO (99.9% purity)</td>
</tr>
<tr>
<td>Substrate</td>
<td>ITO, Al$_2$O$_3$</td>
</tr>
<tr>
<td>RF power</td>
<td>200 W</td>
</tr>
<tr>
<td>Sputtering gas</td>
<td>Pure argon (10 SCCM)</td>
</tr>
<tr>
<td>Deposition time</td>
<td>60 min</td>
</tr>
<tr>
<td>Operation pressure</td>
<td>1.23 × 10$^{-5}$ mbar</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>41 ºC</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction and morphology analysis. The X-ray diffraction (XRD) patterns of the sputtered CCTO thin film on ITO and Al$_2$O$_3$ substrates is shown in Fig. 1 (a, b). Diffraction peaks of the film can be specified to body centered cubic perovskite related structures (ICDD data card no. 98-005-8088) with space group of Im-3. As shown in Fig. 1, the four comment peaks with hkl value (022), (013), (123), and (244) are observed for CCTO thin films. The intensities of peaks are sharps and narrow, approving that the samples are in high quality and good crystallinity. Furthermore, the crystallite size (D) can be calculated according to the Williamson-Hall [10] Eq. (1):

$$\beta \cos \theta = \frac{\lambda}{D} \cos \theta + (4 \varepsilon \sin \theta)$$

Whereby, $\lambda$ is the X-ray wavelength (0.15406 nm), and $\beta$ is the full width at half maximum [FWHM] of the film diffraction peak, and $\theta$ is the Bragg diffraction angle. The values of D can be obtained through the extrapolation and shown in Table 2. The extra peaks also were observed in Fig. 1 (a and b) that is belong to substrates.

Fig. 2 (a and b) illustrates FESEM images of the sputtered CCTO thin film on ITO and Al$_2$O$_3$ substrates. The CCTO thin film layer present uniform surface morphology. The average grain size is 30 and 50 nm distribute on the film surface for ITO and Al$_2$O$_3$ substrates, respectively that was measured by ImageJ software. It can
be obviously perceived that CCTO thin films layer are intergranular porous. The thickness of the CCTO thin films was measured by thin film analyzer (Filmetric, F20) and found to be 200 nm.

Table 2 XRD data for CCTO films on ITO and Al₂O₃ substrates for comment peaks

<table>
<thead>
<tr>
<th>Substrate</th>
<th>2θ (°)</th>
<th>d-spacing (Å)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>(022)</td>
<td>24.5</td>
<td>38.7</td>
</tr>
<tr>
<td>Alumina</td>
<td>(022)</td>
<td>34.6</td>
<td>38.3</td>
</tr>
</tbody>
</table>

3.2 Humidity sensitivity of CCTO thin film

3.2.1 Response/Recovery Time. Response time is defined as the time taken by the sensor to achieve 90% of the final steady resistance value, while the recovery time is the time required for the sensor to return 30% above the original resistance value in air. The humidity sensing properties of CCTO thin films was analyzed at constant temperature (30 °C). Under these conditions, the response/recovery time were measured at voltage 3 V and humidity range 30 – 90% RH. The electrical characteristics of CCTO thin films are shown in Figs. 3 and 4. The response time is 12 s and 40 s while the recovery time is 500 s and 450 s, CCTO thin film deposited on ITO and Al₂O₃ substrates, respectively.

Fig. 1 X-ray diffraction patterns of the sputtered CCTO thin films layer on (a) ITO substrate and (b) Al₂O₃ substrate
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3.2.2 Sensitivity. The humidity sensitivity ($S_H$) is measured by using Eqs. 2 and 3 and response curve (Fig.3). $S_H$ is defined as the change in the resistance of the sample per unit change in the applied relative humidity.
The $R_{LH}$ is the resistance of the sample measured at lower humidity ($R_{LH} = 30\% RH$) and $R_H$ is the resistance of the sample at any relative humidity (RH%). It is found that, $S_H$ is about 17, 75 for CCTO thin film with 200 nm deposited on ITO substrate and $Al_2O_3$ substrate respectively, at 30-90% RH. CCTO deposited on $Al_2O_3$ substrate shows better $S_H$ that is attributed to grain size effect. Because of small grain size, the film with 200 nm thickness has large grain boundary density.

**Fig. 4** Humidity behavior CCTO thin film deposited on $Al_2O_3$ substrate at relative humidity 90%–30% and 3 V (a) Response and (b) recovery curve

### 4. SUMMARY

CCTO thin film layer with 200 nm thicknesses was successfully deposited on ITO and $Al_2O_3$ substrates by RF magnetron sputtering process at 300 °C and power 150 W. The FESEM shows the CCTO thin film layer are intergranular porous microstructures, uniform, and porous with average grain size is 30 and 50 nm for ITO and $Al_2O_3$ substrates respectively. CCTO thin film deposited on $Al_2O_3$ substrate shows better humidity sensing properties.

### ACKNOWLEDGMENTS

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Impact of High Electron Radiation on Electrical properties of 4H-Silicon Carbide Schottky Diodes

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ABSTRACT. In this work, investigates of the electron irradiation effects on the electrical characteristics of 4H-SiC Schottky diodes has been done. Commercial 4H-SiC Schottky diodes were electron irradiated with the dose of 6 MGy, 9 MGy, 12 MGy and 15 MGy using EPS-3000 electron beam machine. Electrical characterization of post irradiation diodes showed that the forward bias (FB) current decreased while reverse bias (RB) leakage current increased. The series resistance was also increased as well as the electron fluence increased. The increases of resistance indicated that the RB leakage current was increased. It was believed that both electron-induce displacement and the formation of generation-recombination (G-R) centres as the cause of the carrier density decreased.

Keywords: 4H-silicon carbide, Schottky diode, Electron irradiation, Current-voltage;

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DOI: 10.30967/ijcrset.1.S1.2018.251-255

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1. INTRODUCTION

Diode is one of the main component in an electronic circuit. Utilizing diode in harsh radiation environment may create electrical damages to the diode which affects the properties, reliability and lifetime. Therefore, it is very important to investigate radiation sustainability of diode which operated under radiation. Various diodes materials have been studied for application under harsh radiation environment. 4H-Silicon Carbide (4H-SiC) Schottky diodes have been shown to be the most suitable candidate for this purpose due to its high radiation hardness, superior thermal and electrical characteristics such as wide band gap, higher thermal conductivity, high critical breakdown field, saturation electron drift velocity, electron mobility, chemical stability and mechanical strength. Therefore, 4-H Schottky diodes are promising be used for satellite-based systems, high temperature detectors and nuclear power industries [1-3]. Schottky diode is devices that has similar operation to a conventional p-n junction diode, but differs in its structure because consist of metal-semiconductor junction which plays important role [4]. This paper reports on the impact of radiation damage on the device performance of 4H-SiC Schottky diodes, which are irradiated at room temperature with 3 MeV electrons.

2. MATERIALS AND METHODS

Diodes used in this study were high voltage and high-speed switching commercial 4H-SiC Schottky diodes. The electrical characteristic was measured by Keithley instrument 4200 SCS. Electron irradiations were done using EPS-3000 EBM at Malaysian Nuclear Agency. The radiation energy was 3 MeV, while the
accumulated radiation dose ranged from 6 MGy to 15 MGy. The repetitive reverse voltage $V_{RRM}$ of commercial 4H-SiC diodes was 600V and Forward Current $I_{F}(AV)$ was 1.7A. The ideality factor ($n$) saturation current ($I_s$) and series resistance ($R_s$) have been determined by fitting the linear and high injection region of the forward bias I-V curves while barrier height ($\Phi_b$) was calculated.

![Outline and Inner Circuit of Commercial 4H-SiC Diode](image)

**Fig. 1** Outline and inner circuit of commercial 4H-SiC diode

Fig. 1 shows the outline and inner circuit diagram of commercial 4H-SiC diode used in this work. Pre-irradiation I-V measurements were carried out for all samples. The series resistance $R_s$ was measured by using relationship as follow:

$$R_s = \frac{C}{N_D}$$

(1)

where $C$ is a constant that depends on the relationship between dopant density and resistivity and on the diode geometry, $N_D$ is the dopant density [5].

3. **RESULTS AND DISCUSSION**

Fig. 2(a) shows the forward bias (FB) current-voltage (I-V) characteristics of pre and post irradiated 4H-SiC Schottky diodes. The results indicated that semilogarithmic FB of I-V curves decrease and shift towards higher voltages as the radiation dose increased. Current-voltage curves also exhibit a linear behaviour at low injection regions. In case of irradiation with 6, 9 and 12 MGy, semilogarithmic FB of I-V curves increase up to 0.5 V then start to saturate. However, irradiation with 15 MGy, FB of I-V curve starts to saturate at 0.4 V. It’s also noted that the behaviour of I-V curves is dominated by the series resistance $R_s$ at high voltages. Fig. 2(b) shows the reverse bias of I-V measurements indicated that the increasing of RB current as well as irradiation dose increased. The decrease of forward bias current for high fluence is related to the increased of the resistance, while the decrease of the barrier height is mainly responsible for the increasing of the reverse bias current.
Fig. 2 (a) Semilogarithmic forward bias I-V and (b) Semilogarithmic reverse bias I-V curves of pre and post irradiation.
Table 1 Electrical parameters of 4H-SiC Schottky diodes extracted from I-V characteristics

<table>
<thead>
<tr>
<th>Radiation dose (Gy)</th>
<th>Ideality factor, $N$</th>
<th>Barrier height, $\Phi_b$ (eV)</th>
<th>Saturation current, $I_s$ (A)</th>
<th>Series resistance, $R_s$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non irradiated</td>
<td>1.04</td>
<td>1.20</td>
<td>4.22x10^{-15}</td>
<td>1.3</td>
</tr>
<tr>
<td>6M</td>
<td>1.05</td>
<td>1.24</td>
<td>8.51x10^{-16}</td>
<td>11.0K</td>
</tr>
<tr>
<td>9M</td>
<td>1.05</td>
<td>1.24</td>
<td>8.51x10^{-16}</td>
<td>33.2K</td>
</tr>
<tr>
<td>12M</td>
<td>1.09</td>
<td>1.22</td>
<td>2.09x10^{-15}</td>
<td>109K</td>
</tr>
<tr>
<td>15M</td>
<td>1.10</td>
<td>1.23</td>
<td>1.40x10^{-15}</td>
<td>15M</td>
</tr>
</tbody>
</table>

Fig. 3 Relation between series resistance $R_s$ and radiation dose

The drastic increase of the leakage current is most likely because of new defect levels that act as efficient carrier traps and recombination centers. Benkovska et al. [6] observed that after irradiation of 9 MeV, series resistance and leakage current of 4H-SiC Schottky diodes increased as a result of deep energy levels originated in the structure. Generally, the results show that the barrier height was decreased while the ideality factor was increased. On the other hand, Benkovska et al. [6] reported that the leakage current of 4H-SiC Schottky diode decreased after irradiation with 6 MeV and significant decrease in barrier height because of irradiation induced traps at the interface. The decrease of leakage current can be explained as a result of dopant deactivation caused by radiation. Therefore, radiation induced defects in 4H-SiC promote interaction electrically with dopant, leading to its deactivation and finally reduce of free-carrier concentration. In turn, it
contributes to the decrease of the leakage current in reverse bias [5]. The increasing of series resistance is also related to the free carrier deactivation. Radiation induced displacement damage gives rise to carrier removal which decreases the effective dopant density based on the formula,

\[ ND = N_D^0 - A\Phi \]  

where \( N_D^0 \) is the dopant density before irradiation, \( \Phi \) is the radiation fluence, and \( A \) is the rate of carrier removal [5]. It also indicated that the decreasing of effective dopant density leads to the increase of the series resistance. Çınar et al. [2] studied the effect of the electron irradiation on the series resistance of Au/Ni/6H-SiC and Au/Ni/4H-SiC Schottky contacts reported that an increase in series resistance was due to the reduction of the mobility and the free carrier concentration. Dachev et al. [7] was also reported that the decreasing of the electrical characteristics for both diodes is because of the concentration carrier reduction due to the trapping effect of the irradiation induced defects.

4. SUMMARY

4H-SiC diodes were irradiated with high dose electron radiation and electrical characteristics was successfully analysed. The results clearly indicated that the forward bias current significant degraded due to an increase in the series resistance \( R_s \). The results also observed that reverse bias leakage current increased due to the density of generation-recombination (G-R) centres increased associated with the electron-induce displacement damage. However, the degradation of barrier height (\( \Phi_b \)) was not significant, both saturation current (\( I_s \)) and ideality factor (\( n \)) were also not noticeable degraded.

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REFERENCES

Improved Performance of Dye Sensitized Solar Cell with Nb-Doped TiO$_2$ Photoanodes using Solid State Method

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**ABSTRACT.** A series of Nb-doped TiO$_2$ (0.25-1.75 wt.% of Nb) were synthesized via solid state technique and used for the development of photoanodes in dye-sensitized solar cells (DSSCs). The X-ray diffraction patterns of the Nb-doped TiO$_2$ were almost exactly matched to pure anatase TiO$_2$ with no Nb$_2$O$_5$ peaks observed. It was found that, 1.0 wt.% Nb had the highest energy conversion efficiency ($\eta$) of 1.40%, short current density ($J_{SC}$) of 5.00 mA/cm$^2$ and open circuit voltage ($V_{OC}$) of 0.33V. From electrochemical impedance (EIS) measurements, the presence of Nb dopants has enhanced the cell performance by improving the charge transport and retarding the recombination process in the photoanode.

**Keywords:** Nb-doped TiO$_2$, Photoanode, Dye sensitized solar cell;

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1. **INTRODUCTION**

Dye-sensitized solar cells (DSSCs) have received great attention due to the low cost and easy fabrication process as well as its high power conversion efficiency [1]. A typical DSSC consists of multiple components i.e. transpiring conducting glass which usually utilizes fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO), mesoporous metal oxide layer developed from TiO$_2$ that acts as photoanode, sensitzers (dye molecules), electrolyte (iodide-tri iodide electrolyte is mostly used) and counter electrode. TiO$_2$(anatase) has been widely used as photoanode to ensure the transfer of photo-excited electrons. Due to its outstanding optical and electrical properties, TiO$_2$ has been extensively investigated as one of the most promising wide band gap semiconducting materials in photocatalysis and photovoltaic applications [2]. As a result, single-crystal TiO$_2$ is preferred as it can provide direct electrical pathways for photo-generated charges and avoid electron scattering or trapping [3]. When electron transport is oriented, the DSSCs can enhance performance in photoelectric conversion.

Modification of photoanode in previous studies using TiO$_2$ based photoanodes has shown that doping with various metals could enhance some of the photovoltaic properties of the cell. Xiang et al. [4] reported the negative shifting of TiO$_2$ conduction band (CB) as a result of tantalum (Ta) doping; this was due to an increase in open circuit voltage ($V_{OC}$) which increased the energy conversion efficiency. Kim et al. [5] reported improvements in photoelectric performance of DSSCs using chromium (Cr)-doped TiO$_2$ semiconductor as
photoanode. Lu et al. [6] and Nikolay et al. [7] synthesized niobium (Nb)-doped TiO₂ using the co-hydrolysis method and found an improvement in electron injection and transport due to the increase in electrical conductivity, shift of E_F and conduction band minimum (CBM).

However, it is difficult to obtain high crystallinity and size uniformity using the co-hydrolysis method; besides that, it also inevitably generates structural defects in TiO₂ which affects the electron injection and transportation. Doping via the co-hydrolysis method also tends to cause deep dopants energy which may not be available for electron injection and transportation. Moreover, the preparation of Nb-doped TiO₂ using the co-hydrolysis method is expensive and niobium chloride (NbCl₅) is unstable and not suitable for use in mass production [8]. Much research has been conducted on the photovoltaic performance of Nb-doped TiO₂ photoanode but its fabrication using the solid state method has not been reported. Fabrication using the solid state method tends to produce a homogeneous powder with high crystallinity structure and is less complicated compared to the co-hydrolysis method.

2. MATERIALS AND METHODS

2.1 Preparation of Natural Dye Sensitizers

Preparation and characterization of E. conferta as sensitizers can be found in our previous work [9].

2.2 Preparation of Nb-doped TiO₂. TiO₂ doped with 0.25-1.75 wt.% of Nb were synthesized via the solid state method. The mixture was prepared using the ball mixing method. The mixture was filled into 250 ml polyethelene containers with zirconia balls with a ball to powder weight ratio of 10:1. Zirconia balls were used as a mixing media due to its high degree of hardness and to minimize contamination. The containers were placed on the ball mixing roller and mixed for 6 hours at 120 rpm and annealed at 600 °C for 6 hours.

2.3 Preparation of Photoanode and Assembly of DSSCs.

FTO conductive glass with a sheet resistance of ~7Ω/cm² was cleaned in a detergent solution, rinsed using deionized water and ethanol and then dried. TiO₂ paste was prepared with 0.3 g of TiO₂, 0.5 ml acetic acid, 1:1 (5 ml) mixture of deionized water and ethanol and was ground for 20 min. Triton-X was added (0.5 ml) to the mixture and continued to be ground until a homogenous paste was achieved. The TiO₂ pastes were deposited onto FTO glass using the doctor blade technique. The coated films were sintered at 450 °C for 30 min. The same method was applied for the 0.25-1.75 wt.% Nb-doped TiO₂, respectively. The sintered photoanode electrodes were immersed in E. Conferta dye solution for 24 hours at room temperature. The sensitized electrodes were rinsed using ethanol to remove unanchored dye. The counter electrode was obtained according to methods employed in previous work [9]. A drop of redox electrolyte was cast on the surface of the sensitized photoanodes. The counter electrode was then clipped onto the top of TiO₂ working electrode with a cell active area of 6.5 cm², and then sealed using slurry tape.

2.4 Cell Characterization. Phase identification of the nanomaterials were studied using Bruker D8 Advance which was operated in Bragg Brentano geometry and exposed to CuKα radiation (λ = 1.540Å). The X-ray diffraction (XRD) pattern was scanned with step size of 0.02° (2θ) at a fixed counting time of 71.6 s from 10° to 90° 2θ. The resulting powder diffraction patterns were analyzed using Highscore Plus software. The photocurrent-voltage (J-V) curves of DSSCs were recorded with a computer-controlled digital source meter (Keithley 2400) under an irradiation of 100 mW cm⁻². The charge-transfer resistance of a DSSC was analyzed by electrochemical impedance spectroscopy (EIS, GamryREF 3000, USA) under a light intensity of 100 mW cm⁻² in a frequency ranging from 0.1 Hz to 100 kHz with an AC amplitude of 10 mV.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis. Fig. 1(a) shows the XRD patterns of the undoped TiO₂ (0 wt.% Nb) and Nb-doped TiO₂ (0.25-1.75 wt.% Nb). The peaks indicate that the complete anatase structure after doping with Nb showed no characteristic peaks of Nb₂O₅ in Nb-doped TiO₂ even at 1.75 wt.% Nb. In Fig. 1(a), the lattice distortion is
due to the defects (vacancies, interstitials and substitutions) which can cause shifts in XRD peak positions, depending on the type of strain in the crystal, such as tensile or compressive strain. This shift proves that the \( \text{Nb}^{5+} \) was successfully inserted into the crystal lattice of TiO\(_2\). An observation of the enlarged image shown in Fig. 1(b) indicates a shift in peak positions as well as change in peak broadening. Based on the line from Fig. 1(b), the peaks start to shift when 0.25 wt.% onwards of Nb was doped into the TiO\(_2\). This shows that the Nb doped into the TiO\(_2\) lattice and is evident by the shift in peak position towards a higher angle. In addition, the full-width at half maximum of XRD patterns of the sample are sharpened with the increase of Nb doping concentration which might be attributed to the increased of crystallite size. By using Debye-Scherrer equation, the crystallite sizes of these samples are listed in Table 1. The introduction of Nb into TiO\(_2\) can inhibited the crystallite size. This is in line with the peak shifted as shown in Fig. 1(b). The lattice constant \((a\text{ and }c)\) and cell volume also increases when the amount of Nb increases. Therefore, there have significant changes in crystal parameters when the amount of Nb increases based on lattice constant and crystallite size analysis which affect the performance of DSSC.

![Fig. 1](image)

**(a)** XRD patterns of 0-1.75 wt.% Nb-doped TiO\(_2\) and (b) Shifts in peak position and changes in peak broadening are depicted through enlarged view of (101) peaks for undoped TiO\(_2\) and Nb-doped TiO\(_2\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average crystallite size (nm)</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt.% Nb</td>
<td>8.51</td>
<td>3.784</td>
<td>9.49</td>
</tr>
<tr>
<td>0.25 wt.% Nb</td>
<td>9.16</td>
<td>3.784</td>
<td>9.50</td>
</tr>
<tr>
<td>0.5 wt.% Nb</td>
<td>9.16</td>
<td>3.785</td>
<td>9.50</td>
</tr>
<tr>
<td>1.0 wt.% Nb</td>
<td>11.00</td>
<td>3.785</td>
<td>9.50</td>
</tr>
<tr>
<td>1.25 wt.% Nb</td>
<td>11.00</td>
<td>3.785</td>
<td>9.51</td>
</tr>
<tr>
<td>1.50 wt.% Nb</td>
<td>11.00</td>
<td>3.785</td>
<td>9.51</td>
</tr>
<tr>
<td>1.75 wt.% Nb</td>
<td>11.25</td>
<td>3.786</td>
<td>9.52</td>
</tr>
</tbody>
</table>
3.2 Photovoltaic Performance of DSSC. In order to determine the photovoltaic performance, the current density-voltage (J-V) curves of DSSC based on undoped and Nb-doped TiO$_2$ electrodes with different amounts of Nb dopant are shown in Fig. 2 and the photovoltaic properties are shown in Table 2. As shown in Table 2, the highest $V_{oc}$ is found in the DSSC with 0.5-1.0 wt.% Nb-doped TiO$_2$. Higher $V_{oc}$ value indicates the large energy difference between the conduction band of TiO$_2$ and the iodine redox potential. Due to the difference energy levels, the recombination of injected electron in the conduction band of TiO$_2$ with the oxidized electrolytes is prevented and resulting in higher efficiency for 1.0 wt.% Nb-doped TiO$_2$ [8].

![Fig. 2 The photocurrent density-photovoltage (J-V) of the fabricated DSSC using undoped and Nb doped TiO$_2$](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$/V</th>
<th>Efficiency, $\eta$ (%)</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt.% Nb</td>
<td>3.20</td>
<td>0.32</td>
<td>0.80</td>
<td>6.1407</td>
</tr>
<tr>
<td>0.25 wt.% Nb</td>
<td>4.30</td>
<td>0.30</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>0.5 wt.% Nb</td>
<td>5.00</td>
<td>0.33</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>1.0 wt.% Nb</td>
<td>5.00</td>
<td>0.33</td>
<td>1.40</td>
<td>8.8314</td>
</tr>
<tr>
<td>1.25 wt.% Nb</td>
<td>4.90</td>
<td>0.32</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>1.50 wt.% Nb</td>
<td>4.80</td>
<td>0.32</td>
<td>1.23</td>
<td>7.3451</td>
</tr>
<tr>
<td>1.75 wt.% Nb</td>
<td>4.50</td>
<td>0.30</td>
<td>1.08</td>
<td></td>
</tr>
</tbody>
</table>

Improvement of $V_{oc}$ also due to introduction of Nb into TiO$_2$ lattice improves the photo response due to additional energy levels was created within the band gap of TiO$_2$. The internal resistance decreases due to Nb dopants modified the electronic structure of TiO$_2$ therefore increase the $V_{oc}$. The highest $J_{sc}$ of DSSC with 0.5-1.0 wt.% Nb-doped TiO$_2$ gave the highest value of 5.00 mA/cm$^2$. High $J_{sc}$ values indicate high electron collection efficiencies which function as faster electron diffusion rates. The increase of $J_{sc}$ and $V_{oc}$ produced high efficiency which increases the performance of photovoltaic. Nb doping also reduces the concentration of
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ny oxygen vacancies at the TiO₂ surface [10]. Therefore, the space charge region widened to suppress recombination at the TiO₂-electrolyte interface and leads to the increment of V_{OC} [11]. The decrease in Voc and J_{sc} is also due to how Nb would have acted as a new recombination center thus reducing the number of charge carriers [12].

![Nyquist plots of DSSCs measured under illumination conditions for undoped and Nb-doped TiO₂](image)

**Fig. 3** Nyquist plots of DSSCs measured under illumination conditions for undoped and Nb-doped TiO₂

Electrochemical impedance spectroscopy (EIS) measurement was carried out to investigate the TiO₂/dye/electrolyte interfacial charge transfer kinetics. Fig. 3 shows the Nyquist plots for DSSC using undoped and Nb-doped TiO₂ photoanodes. In Fig. 3, the charge transfer resistance related to the recombination of electrons (R_{CT}) at the photoanode/dye/electrolyte interface is determined using the semicircles at the intermediate frequency regions. The R_{CT} value for 1.0 wt.% Nb is the lowest compare to other dopants. It proves that electron transfer becomes faster within the TiO₂ film, implying that the film conductivity was improved [13]. Based on this result, it can be correlated that Nb dopant has improved the capacitance of the device leading to higher J_{SC} and V_{OC} values. However, when doping amount increases (1.25 wt.% Nb onwards), the R_{CT} increases due to the formation of more defects in the semiconductor. Higher R_{CT} value corresponds to lower probability in recombination of the electrons. The low recombination of electron leads the decreases of J_{SC} and V_{OC} values due to high recombination process.

4. **SUMMARY**

The performance of Nb-doped TiO₂ synthesized using the solid state method as photoanode promoted and favoured electron transformation. The DSSC with 1.0 wt.% Nb-doped TiO₂ improved the J_{SC} and V_{OC} and produced the highest efficiency of about 1.40%. The improvement of J_{SC} is related to the enhancement of electron injection and transportation. The reduction in the concentration of oxygen vacancies at the TiO₂ surface is correlated to Nb doping. Therefore, the space charge region was found to widen up and suppress electron recombination at the TiO₂-electrolyte interface and increase the value of Voc.

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Optical Characteristics of ITO/NTCDA Film for Defence Technology Application

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ABSTRACT. The interface structure between inorganic/organic layer governed microscopic and physical property of many organic based devices. The 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) is strong electron acceptor and its thermal stability can be explored in electro-optics application and laser material. In this study, optical characteristics of NTCDA film at interface of indium tin oxide (ITO) was demonstrated. The film was processed using ethanol and toluene solvents at 1:1 ratio before spin coated on 180 nm thickness ITO substrate. Hexamethyldisilaze (HMDS) was used to surface functionalized the ITO substrate. Analysis of AFM images showed the NTCDA film grown on ITO substrate at grain size approximately 0.5-1.5 μm. The onset of the absorption band shifted around 0.11 eV upon HMDS modification at interface of NTCDA film and ITO substrate indicating electronic modification on the bulk NTCDA film. Structural conformation was studied using the infrared absorption. Other than strong absorption peak at 1783 cm⁻¹ that belonged to vibrational mode of the C = O functional group of the NTCDA, the fingerprint peaks of NTCDA on FTIR spectra were present with or without HMDS modification. This study showed the bandgap tuning of organic semiconductor film using surface functionalization technique as potential material processing in defence technology application.

Keywords: Organic semiconductor, Surface functionalization, Spin coating, Optical characteristic;

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1. INTRODUCTION

Since the last decade, thin films of molecular organic semiconductors are attracting much interest for electronic and optoelectronic applications [1]. Technologies such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic field-effect transistors (OFETs) have been steadily evolving and penetrating the mainstream consumer electronics market [2-3]. Organic device is more preferable because of easy fabrication. For example, OFETs can be manufactured near room temperature on plastic and rubber. This temperature is not possible for silicon-based device [4]. Solution processing are also possible in wide range of organic materials. This technique has the advantageous to be applied in existing thin-film coating technologies from inkjet and screen printing for individual substrates to continuous roll-to-roll manufacturing using slot-die coating, gravure printing or doctor-blading [5]. Other than potential
applications as flexible displays, RF-ID components and e-papers, the organic semiconducting materials has been explored for photonics, electro-optics and laser materials [6-7]. The material can be fabricated into eyes protection devices and sensors for intense laser beams that is useful in military and weaponry purpose [6]. Styrylbenzene derivatives luminescent material is candidate laser active materials [6]. Lasing threshold was reduced by controlling the bandgap of small molecular materials and conjugated polymers [7].

Organic semiconductor molecule, 1,4,5,8-naphthalene-tetracarboxylic dianhydride, C_{14}H_{4}O_{6}(NTCDA) is a prototype n-conjugated molecule that has been investigated in both experiments and theories [8]. Previous researches found that compounds containing six-membered imide rings have possible application in optoelectronics and photonic technology [9]. One advantage of NTCDA is its thermal stability that allows thermal treatment up to ~450 °C without chemical or physical decomposition [10]. The intermolecular interaction between NTCDA molecule and various surfaces such as Au, Ag and Al had been widely investigated. A study by Tonner et al showed the NTCDA monolayers interacts with substrate Ag(111) via non-directional van der Walls forces and covalent bonding of the acyl oxygen atoms with underlying Ag atoms [11]. The information was extracted using the infrared absorption data.

For devices, there is not only physical but electronic barriers exist at interfaces between dissimilar material such as between inorganics and organics, ITO is included [12]. The indium tin oxide (ITO) is n-type semiconductor with bandgap of ~ 4 eV. In order to overcome the barrier, interactions at the interface can be modified so that desired electronic property such as electronic bandgap can be realized. One way is to attach a functional organic on the electrode surface such as hexamethyldisilazane (HMDS). The HMDS is a self-assembled monolayers (SAMs) [13]. HMDS is safe and non-corrosive, therefore, it have been used widely as photoresist adhesion-promoting agent [14]. HMDS also will produced lower porosity on film grown with it. The HMDS treatment at interface of substrate and organic film not only improve the quality of the organic semiconductor film but also increase charge carrier density by decreasing the interface trap density. Investigation done by Fiorillo et al showed the surface of Si substrate becomes silated and non-polar surface upon treatment of HMDS. It was found to reduce surface energy of Si substrate [13].

In this study, the organic film were fabricated by solution-processed method using spin coater. Spin-coating technique is easy, versatile, inexpensive and highly effective for depositing uniform thin film reproducibly. This fabrication method is convenient for rapid device testing purpose. The film thickness can varied from 20 – 200 nm. Previous study shows electrical performance of spin coated OFET strongly correlated with the morphology and solid-state order of the deposited semiconductor layer [14]. Here, the solution was spin-coated on indium tin oxide (ITO) substrate of organic field-effect transistor (OFET) following solution deposition of HMDS. Optical characterization on spin coated NTCDA film reported in this paper is a part of initial procedure preceeding the investigation of the film property at nanoscale.

2. MATERIALS AND METHODS

The processing of organic semiconductor solution was produced under atmospheric condition. Here, 0.08 wt.% of NTCDA in powder form (95%, Sigma Aldrich) was dissolved in 1:1 ethanol and toluene solvent [9]. Hexamethyldisilazane, HMDS (95%, Sigma Aldrich) was used as received. The brown powder of NTCDA did not immediately dissolved in the solvents but the aggregates slowly dissapeared after continuous stirring at constant temperature of 100 °C. Fig. 1 shows the transformation of NTCDA aggregates in this processing condition. At 120 H stirring, the aggregates size distribution varied from 1 μm to 20 μm. The aggregates can be origin of many linear and non-linear optical phenomenon. The final solution was taken when the aggregates were no longer visible under observation of 10× magnification optical microscope as shown in Fig. 1 (b). The organic films were spin coated at low speed frequency of 500 rpm. The ITO substrates were cleaned with acetone and isopropanol prior film deposition. HMDS were spin-coated on ITO to form uniform
monolayer on the substrate. Finally, the films were dried at 25 °C and later 120 °C to allow solvent evaporation. The thickness of spin coated NTCDA film was determined by Atomic Force Microscope (AFM). Optical characterization of NTCDA solution was done by UV-Vis spectrometer (Genesys TM6, Thermo Scientific) while morphology of NTCDA thin film were characterized by using optical microscope, UV-Vis-NIR (Lamda 950, Perkin Elmer), and Fourier transform infrared spectroscopy (FTIR).

3. RESULTS AND DISCUSSION

The surface area of polycrystalline ITO thin film was scanned using AFM. The thickness of the thin film is 180 nm, a typical thickness for anode of OLED. The bare ITO are homogenous film with surface roughness up to 30 nm. The average grain size of the ITO was determined to be 0.2 µm as shown in 5 µm × 5 µm AFM image below (Fig. 2(a)). Meanwhile, Fig. 2 (b) shows a new surface image obtained after deposition of NTCDA film. This film was deposited with HMDS treatment on the ITO surface. The analysis on the 10 µm × 10 µm surface shows the roughness of the film is approximately ~200 nm with grain size of 0.5-1.5 µm. The roughness of the surface was determined using the difference between the highest and lowest point of the film thickness. The NTCDA film produced from this processing condition was not homogenous as well as having large grain and this usually leads to short-circuit in devices.

The thickness of the organic film was determined using the line scan of 10 µm × 25 µm surface image (Fig. 2 (c)). It can be estimated from the line profile that film thickness is approximately ~125 nm thick. The top line profile belonged to Line A on the image of NTCDA film. It can be seen that the film grew thicker toward the film’s edge. Line B contained the surface roughness information both the film and the substrate. Because the film did not covered the whole surface area of the ITO, the surface becomes really rough. In the microscopic point of view, the NTCDA molecules may not form good intermolecular interaction with the ITO’s surface. This type of non-uniformity at the interface can damage the organic device. On the other hand, the organic semiconductor molecules is known to stack vertically in crystalline manner due to non-covalent π-π stacking interactions provided by the aromatic rings of NTCDA [12]. The information on the crystalline stacking could only be confirmed using XRD or FESEM measurement.

In Fig. 3, three UV-Vis absorption spectra were used to study electronic structure of single layer NTCDA film (Spectrum A), NTCDA solution (Spectrum B) and HMDS surface modified NTCDA film (Spectrum C). The UV-Vis-NIR measurement of the films were taken with ITO substrate as reference, thus optical property of the ITO became negligible. Spectra comparison is made in order to check the electronic modification after the NTCDA solution is deposited as film as shown in Fig. 3(a). Since the absorption spectrum indicates molecular electronic transition, the onset of absorption is considered as gap of semiconductor. In the visible light region, the absorption edge of both spectra overlapped at 3.1 eV indicating no electronic change in the NTCDA film. This finding is true for bulk NTCDA as the compound is stable in both solution and solid state. However, there were noticeable absorption at 400 nm-600 nm in Spectrum B originated from the film thickness. Meanwhile, Spectrum C was obtained from the NTCDA film fabricated on surface functionalized ITO.
comparison at the absorption edge in Fig. 3 (b), there exist a small shift ~0.11 eV of electron energy. This change of optical characteristics may indicated electronic modification of bulk film originated by improved molecular order at the interface. The bathochromic shift was also seen in P3HT:PCBM thin film due to conformational order in macroscopic scale that result into different energy level distribution. The modification at the surface using HMDS had caused the collection of the irradiation to be broadened and difference in HOMO and LUMO levels to be smaller, thus lowering the bandgap of the NTCDA film.

**Fig. 2** (a-b) Surface images 3D of 10 µm × 10 µm from atomic force microscope of bare ITO and NTCDA thin film on ITO, respectively. (c) Line profiles at edge of organic film and substrate
The vibrational measurement in organic samples is important to study structural change in interest material. The analysis of vibrational spectra is also useful to determine whether the solvents are still present or have completely evaporated during the drying process. First of all, smooth vibrational spectrum of polycrystalline ITO thin film was obtained to be used as reference. In the spectra of bare ITO in Fig. 4, three distinct peaks were detected at 2840 cm\(^{-1}\), 2950 cm\(^{-1}\) and 2970 cm\(^{-1}\). These vibrational peaks belonged to stretching C-H bond. Meanwhile, the spectrum of NTCDA film on ITO shows sharp absorption peaks that were absence in spectrum of bare ITO. One of these absorbance peaks located at \(\sim 1783\) cm\(^{-1}\) wavenumber that indicated the presence of C = O stretching due to the dianhydride carbonyl group of NTCDA structure \([2]\). A medium peak at \(\sim 1583\) cm\(^{-1}\) and \(\sim 1300\) cm\(^{-1}\) indicated C-O stretching vibration and C – O – C stretching NTCDA, respectively. The assignments and strength of these peaks were similar to the one in powder form indicated similarity in molecular packaging. However, there can be a weak interaction between the ITO and NTCDA as seen in the presence of several stretching modes absence in spectrum of the powder. This information most likely implied the NTCDA molecule lied flat on the substrate as seen in ref. 11. Small peaks at \(\sim 3087\) cm\(^{-1}\) were detected in the region of C-H stretching vibration. This peak maybe related to the one observed in spectrum of bare ITO earlier. The peak shifts in this second spectra might be due to the possible migration of the electrons at the interface between ITO and NTCDA.
The possibility of conformational re-arrangement occurring in HMDS-modified NTCDA film was further investigated using the vibrational spectra. Once again, comparison was made as shown in Fig. 5. Similar peaks were observed implying not much change had occurred at molecular order in the film. However, it is noted that vibrational peaks at \(\sim 3087 \text{ cm}^{-1}\) and \(1518 \text{ cm}^{-1}\) had disappeared when the ITO's surface was treated with HMDS. No peak shift was observed. The disappearance of the peak might be related to changing thickness of the organic layer. The range about \(1500 \text{ cm}^{-1}\) to \(500 \text{ cm}^{-1}\) is called fingerprints region where the peaks are more complicated and hard to take out the individual bonds. However, this region are important since it consists of bending vibrations of the molecule that produced pattern of the compound itself. Previous study showed that NTCDA spectrum produced unique pattern at the fingerprint region before comparing with Li and Ni metals where the spectrum is slightly changed after mixed with metal compounds \([9]\). So, it can be concluded from the peaks in region between \(1500 \text{ cm}^{-1}\) to \(600 \text{ cm}^{-1}\) that NTCDA molecule was not modified throughout the entire filming process.

![Fig. 5 Infrared absorption peaks of NTCDA films](image)

4. SUMMARY

Thermal and chemically stable NTCDA molecule was studied as potential material in defence application. The organic semiconductor can be tuned to achieve desired electronic property. Two stacking layer films of ITO and NTCDA were fabricated using the spin coating process. Self assembled monolayers of HMDS was introduced to study the effect of surface functionalization on the interfacial electronics and optical property. The morphology of NTCDA film grown on the ITO showed high porosity and undesirable morphology to be implemented as device. The morphology can be improved with the use of HMDS at the interface. A bathochromic shift of 0.11 eV was found upon HMDS modification at interface of NTCDA film and ITO substrate indicating electronic modification on the bulk NTCDA film. From the infrared absorption spectra, it can be concluded that there is small possibility of molecular re-arrangement of the NTCDA film. There is a need of detailed measurement of XRD and FESEM to check structural conformation under this modification.

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ABSTRACT. This study was determined the influence of radiation and non-radiation work activities over 222Rn concentration levels in soil at selected areas in Universiti Sains Malaysia Health Campus. Radon Sentinel 1030 monitor was used to determine 222Rn concentrations emanated from soil collected at Radiology Department and Nuclear Medicine Department (red areas), hospital lobby, hostel and Registry Department (public areas) and isolated area. Each reading was recorded within 30 min time intervals in a close perspex room for 5 consecutive days to obtained average 222Rn concentrations reading. The results show the Radiology Department and hostel have obtained least amount of 222Rn concentrations, which were 0.287 pCi/L and 0.246 pCi/L. Concentration of 222Rn at Nuclear Medicine Department was 0.304 pCi/L, whereas 0.289 pCi/L in isolated area. Insignificant reading at Radiology and Nuclear Departments prove the proper application of radiation protection principle has been applied such as half value layer rule for wall thickness. Meanwhile, Registry Department and hospital building (public area) showed the highest concentration of 222Rn which were 0.561 pCi/L and 0.462 pCi/L due to the natural environmental radiations that are mainly depending on geographical conditions, as the random properties of 222Rn emanations cannot be controlled.

Keywords: α-Particles, Radiation protection, Environmental radiations, Health implications;

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1. INTRODUCTION

Radon (222Rn) is one of the radioactive gases that contributes towards background radiations [1-2]. It is occurred naturally in the environment from the Uranium-238 decay series in the soil that originate from the Earth’s crust. As the 222Rn exists in soil, it will leave the soil grain by α-recoil process and moves towards atmosphere [3]. Emanation of radon towards surrounding poses high risk for health due to the successively decay of their daughters of alpha (α) particles [1]. The inhalation of the gas and its decay products into the respiratory system will be absorbed by the lung tissues and unfortunately increases the risk of lung cancer and other health problems [2, 4-7]. Theoretically, the 222Rn concentrations might be influenced by its location,
based on the activity that has been conducted such as mining industry and radiations work. Human-made of radioactive chemicals have enter the environment from activities such as mining and the use of radioactive materials in nuclear medicine, military, industrial applications, consumer products and nuclear power generation. The radiations most commonly emitted by radionuclides are alpha particles, beta particles and gamma rays. The radiation exposure is harmful to human health.

Through this research, we were revealed the $^{222}$Rn concentrations level of soils originated from six different locations and generally classified; a: red areas (radiation working areas; x-rays, ultrasound, unsealed radioactive sources), b: isolated area (no development and human activities area) and c: public areas (human activities area, building area, residential area). The data presented should be the base line in considering any radiation protection and initial awareness among the related group of people at related locations in Universiti Sains Malaysia Health Campus.

2. MATERIALS AND METHODS

This research work was conducted to determine the $^{222}$Rn concentrations among different locations of soil samples in Health Campus, Universiti Sains Malaysia, Kubang Kerian, Kelantan, Malaysia. In this study, soil samples were collected from six different locations and categorized into three general areas which are red, isolated and public areas. The samples were dried to reduce and remove the moisture into the soil as shown in Fig 1. Radon Sentinel 1030 monitor manufactured by Sun Nuclear Corporation, United State of America (USA) was used to measure the $^{222}$Rn concentrations emanated from the selected soils in a close perspex box as shown in Fig. 2.

![Fig. 1 Soil samples after drying process for $^{222}$Rn measurements collected from six different locations](image)

Radon Sentinel 1030 monitor was setup to record $^{222}$Rn concentrations within 30 min time interval. Each soil sample was measured within 24 hours for 5 consecutive days. Hence, there were 240 $^{222}$Rn data has been recorded for each sample. Average of $^{222}$Rn concentrations has been obtaine using Eq. 1:

$$\text{Average } ^{222}\text{Rn} = \frac{\text{Cumulative } ^{222}\text{Rn readings}}{240}$$

(1)

The average of $^{222}$Rn concentrations for each sample collected in read areas, public areas and isolated area have been presented in Table 1.
Fig. 2 Radon Sentinel 1030 monitor was used to determine $^{222}\text{Rn}$ concentrations level emanated from collected soil samples

3. RESULTS AND DISCUSSION

Registry Department and hospital building (public area) showed the highest concentration of $^{222}\text{Rn}$ which was 0.561 pCi/L and 0.462 pCi/L as shown in Table 1 and plotted in Fig. 3. This is due to the natural environmental radiations that are mainly depending on geographical conditions, as the random properties of $^{222}\text{Rn}$ emanations cannot be controlled [8].

Table 1 Average of $^{222}\text{Rn}$ concentrations obtained from soil sample at six selected locations.

<table>
<thead>
<tr>
<th>Location of soil collected</th>
<th>Average of $^{222}\text{Rn}$ concentrations level (pCi/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear</td>
<td>0.304</td>
</tr>
<tr>
<td>Radiology</td>
<td>0.287</td>
</tr>
<tr>
<td>Hospital</td>
<td>0.462</td>
</tr>
<tr>
<td>Hostel</td>
<td>0.246</td>
</tr>
<tr>
<td>Registry</td>
<td>0.561</td>
</tr>
<tr>
<td>Isolated</td>
<td>0.289</td>
</tr>
</tbody>
</table>

In addition, the soil characteristics such as porosity at Registry Department is one of the major factor in emanating the higher $^{222}\text{Rn}$ concentration. Thus, $^{222}\text{Rn}$ was easily emanated from the sand and released to the surrounding through common ways [9]. Average concentration of $^{222}\text{Rn}$ at Nuclear Medicine Department was 0.304 pCi/L since the soil sample was collected around the delay tank of radioactive waste. In this issue, $^{131}\text{I}$ and $^{99m}\text{Tc}$ were used as unsealed radioactive sources for patient treatment and the waste product were drained in the delay tank. The exposure rate decreased due to the attenuation by the wall of delay tank itself.
In other way, good material selection to develop the tank wall might be one of the main factor in preventing the radiations to pass through.

Fig. 3 $^{222}\text{Rn}$ concentrations level of soils based on selected locations

Meanwhile, average $^{222}\text{Rn}$ concentration in isolated area was 0.289 pCi/L, which is a little bit higher than red area. This is due to the presence of naturally occurred radioactive nuclides in soil such as $\text{Ra}^{226}$ and $\text{U}^{238}$. Decay chain of these radioactive nuclide occurs with varying degrees of concentration (random) in earth crust [11-12]. However, concentration of $^{222}\text{Rn}$ in hostel was the least compared to the other places. This is due to the trapped air in one place. Slow movement of wind will carry the contaminated air and distribute towards environments.

Moreover, average of $^{222}\text{Rn}$ concentration at Radiology Department seems unexpected reading with lower record than unusual radiations area (isolated area) with 0.287 pCi/L. With heavily usage of x-ray modalities for medical diagnostic, the productions of α-particle as secondary radiation due to material interactions with x-rays should be higher and expected to interfere the $^{222}\text{Rn}$ data has been obtained. Conversely, there are no significant results recorded which means the secondary particles has almost been prevented, but secondary x-rays and Compton scattering might be dominant.

4. SUMMARY

Radiology Department and hostel showed the least amount of average $^{222}\text{Rn}$ concentrations, which were 0.287 pCi/L and 0.246 pCi/L. Theoretically, aggressive used of ionizing and non-ionizing modalities in the department should contribute to the higher $^{222}\text{Rn}$ measurements. However, the graph in Fig. 3 has shown insignificant findings at Radiology Department. This is due to the proper application of radiation protection principal such as half value layer of wall thickness in preventing the unwanted of wave and mostly particle radiations. Concentration of $^{222}\text{Rn}$ in hostel was the least compared to the other places. This is due to the trapped air in one place. Slow movement of wind will carry the contaminated air and distribute towards environments. Meanwhile, average $^{222}\text{Rn}$ concentration in isolated area was 0.289 pCi/L, which is a little bit higher than red area. This might be due to the presence of naturally occurred radioactive nuclides in soil such as $\text{Ra}^{226}$ and $\text{U}^{238}$.

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Dynamic Testing for Compatibility Assessment of Non-Metal Automotive Components with Biodiesel Fuel: A Concept Study

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ABSTRACT. Over the years, concern on the compatibility issue of the blended biodiesel fuel with non-metal material components in diesel engine vehicles had received many attentions. Assessing the compatibility of non-metal material components like elastomer and plastics usually rely on the measurement of mechanical and physical properties such as tensile strength, elongation, hardness, surface morphology, weight and volume changes. These properties are typically measured after the static immersion test is done accordingly to the ASTM D471. However, data and results given from the static immersion test is only applicable when the samples are in a static condition and not in a dynamic situation. Thus, this paper attempts to review some common issues related to the biodiesel fuel and non-metal components and introducing the dynamic testing approach that can be applied when assessing the compatibility study of biodiesel fuel with some potential problems that might be encountered.

Keywords: Biodiesel fuel, Compatibility, Dynamic test rig, Non-metal automotive components;

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1. INTRODUCTION

Due to the lessen of fossil fuel resources, alternative or renewable fuel is not a new topic and received many interests in Malaysia. Blended biodiesel fuel derived from palm oil, for example, is widely used as transportation fuels in Malaysia and other countries. It is widely acknowledged that pure biodiesel or higher blended biodiesel fuel will be used for the increment of the energy sources for transportation in the near future.

Theoretically, biodiesel is referred as methyl ester of a fatty acid (or shortly known as FAME) which have to fulfill the ASTM D6751 specifications for use in diesel engines. Previous studies show that biodiesel helps to reduce carbon dioxide and other pollutants emission from engines [1]. Another advantage of biodiesel is, it does not require extensive engine modification in the diesel engine and can performs better due to the high cetane number [2]. It is also one of the most promising alternative fuels for diesel engines since there will be no underwater plantation, drilling and refinery. In other words, biodiesel would make an area become independent of its need for energy as it can be produce locally depending on the feed stock available in that area.

Blended biodiesel fuel is where pure biodiesel fuel (B100) is blended with diesel fuel and signified as "BXX" (e.g., B5, B10, B20), where "XX" is denoted as the volume percentage of the biodiesel content in the
The implementation of blended biodiesel fuel is due to rapid growth of the studies on the production of blended biodiesel fuel from various feedstock either edible or non-edible and on the fuels efficiency in the diesel engine vehicles. In order to ensure that the blended biodiesel fuel can be used in diesel engine vehicles, the fuel properties must be corresponded to the standard provided, the ASTM D7467 [5] that covers fuel blended with the grades of 6 to 20 volume percent (%) biodiesel.

Any fluids can cause chemical degradation, swelling, cracking and extraction of additives of elastomers or rubber and plastics. The absorption of fluid into the polymer network of the elastomer can caused swelling. A general rule is that polar substances dissolves better in polar liquids and non-polar substances dissolves better in non-polar liquids [6]. As noted, the chemical structure of biodiesel is chemically different than diesel and contains more polar esters. Therefore swelling of polar elastomers is greater in biodiesel than in diesel. Swelling is observed when more liquid is absorbed than soluble components are being extracted from the rubber. Opposing, the volume decreases might be due to soluble components being replaced by less dense solvent molecules or that the extraction of additives is greater than the absorption of solvent [6]. Volume change is increased at higher temperatures [7].

The difference of chemical composition in biodiesel fuel shows an important reason for why the compatibility of non-metals material in diesel engines should be further studied. Nevertheless, the compatibility of biodiesel with non-metals components that includes elastomers and plastic that are widely used in diesel engines has not been fully explored, and to date, few papers discussing this issue have been published.

2. NON-METALS COMPATIBILITY.

The effect of biodiesel or blended biodiesel fuel on engine performances and emissions had been undertaken in a gradually trend and gives several good examples. However, little or not much information is known about the effect of biodiesel fuel on the non-metal automotive components like elastomer or rubber compound and plastic that usually applied as fuel transportation or sealing elements and fuel tank in the diesel engine vehicles. Fig. 1 shows some of the non-metal automotive components found in the fuel system of diesel engine.
The resistance of some non-metal automotive components like elastomer or rubber compounds are thoroughly analyzed because of the importance of these compounds in fuel system components of diesel engine as hoses, seals, and tubes. For example, nitrile butadiene rubber (NBR) is used widely to fabricate vehicular hoses and gaskets, and these components come into constant contact with fuels when the engine is running [9].

Several studies had listed out the common issue observed on engine components with the used of biodiesel fuel. Terry et. al had identified that usually there will be a possibility of the fuel injector blockage and excessive fuel injector wear corrosion on the fuel injection equipment components and significantly resulted on the elastomer and rubber seal failures [10].

Concern arises from the fact that diesel fuel and biodiesel fuel have different chemical structures and consequent different effects on the non-metal automotive components. It is because there must be a reaction occurred between the alternative fuel and the non-metal automotive components in the fuel system of diesel engine vehicles. Relatively the presence of alcohol and fatty acid methyl ester in the biodiesel fuel, potentially can deteriorates the element and may affect the material on the components of the fuel system in the diesel engine vehicle. Besides that, blended biodiesel fuels might be aggressive towards the components in the fuel system of diesel engine due to the difference of chemical composition in biodiesel fuel. Even the biodiesel fuel is mixed with the diesel fuel in small amounts, material compatibility is still one of the important issue whenever the fuel composition is changed in the fuel system [11]. This is because many components in the fuel system of diesel engine vehicles are specifically designed to run on diesel fuel which are known by the automotive industry. Moreover, biodiesel fuels are prone to oxidation upon exposure to air and storage conditions which can increase the total acidity and risk of degradation of automotive parts and components made from materials like copper and nitrile rubber [12] in the fuel system of diesel engine vehicles [13]. Previous review [14] identified that most automotive rubbers tend to swell, deteriorates and degrade when being exposed to the blended biodiesel fuel.

3. STATIC IMMERSION TEST.

Assessing the compatibility of blended biodiesel fuel with non-metal material components is challenging and needs a lot of data and information. Since the duration of usage of the non-metal components are typically some years, thus it is not realistic to perform tests for such a long time. To estimate how well a material will perform during its life time, accelerated tests are used, where there is a standard used in the industry on how to perform these tests. Usually, static immersion test are done by completely soaking the test pieces in different reference tested fuels samples at specified time and temperature upon the fuel system of diesel engine vehicle condition. The effect of fuels on the non-metal compounds are evaluated by measuring certain mechanical properties like mass change, volume change, surface morphology, hardness and tensile-stress properties [15-17]. ASTM D471 [18] provides test methods and guideline procedure on exposing the specimens to the influence of liquids or fuels for a duration of times and temperature. However there are drawbacks of this immersion test. The disadvantages of this test is that the experimental conditions are differ from the real service conditions in the fuel system of diesel engine vehicles and hence the results can be clashed. Furthermore, literatures search on the fundamental durability and resistance study of non-metal components in biodiesel fuel in dynamic condition also has shown the scarcity of publications in this field. Therefore, there is a need to study the degradation and durability of non-metal components in biodiesel fuels and to provide comparative data on the dynamic condition.

Micallef, G. [19] have compared standard laboratory testing (according to standard ASTM D2240 hardness, ASTM D412 stress-strain and ASTM D471 fluid immersion) with testing under service conditions for different fluoroelastomers in different fuels. Under service conditions, water contamination is expected, especially in biodiesel since water is more soluble in biodiesel than in diesel. The water contaminated fuel
gave a large deterioration of some of the elastomers compared to standard laboratory tests and it is suggested that the water causes hydrolysis of esters in biodiesel which open up for other chemical reactions than in fuel without water. This is one of the issue of how real service conditions can give differences in properties of the non-metal automotive components.

4. DYNAMIC TEST RIG.

Fig. 2 shows the design of preliminary test rig developed for the dynamic test. This test rig is developed to undertake the compatibility of non-metal automotive component with biodiesel fuel and design based on the existance fuel system of diesel engine. The experimental test rig is also suitable to conduct various test runs under different working conditions in comparison with that of a diesel operated engine. It can be seen that the proposed test rig is a closed loop test and consist of the fuel storage tank, measuring equipments and of course the test piece of non-metal automotive components.

![Diagram](image)

**Fig. 2** Experimental dynamic test rig

This test was done dynamically in many cycles and certain period of times for different type of fuels. The fuel from the tank will be transporting and pass through the test piece of non-metal automotive components that is connected to the stainless steel tubing and then the fuel will be returning back to the storage dynamically for a period of time. A filter is located before the tank to minimize the contamination of the fuels. During this test, the samples of non-metal automotive components was maintained at specific temperature or at ambient temperature (25 °C) depending on the application. The variable parameter like pressure and flow
rate were adjusted accordingly by pressure gauge and flow meter. The sampling points were located before and after the tested piece for fuel properties determination and results comparison purposes.

As in the static test, before the test started, the mass, volume, inner diameter and cross-section diameter of the fuel hose were measured as the initial data. After certain period of time and cycles, the samples were picked up and dried by air. Then, immediately after the test piece is removed from the tested fuel, the mass, volume, inner diameter and cross-section diameter of it were measured and several analysis and mechanical properties were performed for comparison purposes.

5. SUMMARY

This paper managed to highlight the common issues regarding to the compatibility of non-metal components in diesel engine with biodiesel fuel. As mention previously, non-metal automotive components presence in the fuel system of diesel engine vehicles are not in a static condition. Thus, with the dynamic test rig approach that considering different parameters such as temperature, pressure, fuel composition and time exposed, we can simulate as far as possible the actual and real operational condition before carrying out in the field trials. This attempt will simplify some of the confusion surrounding dynamic testing on the non-metal automotive components in the fuel system. Moreover, data from the dynamic condition would give quantitative information to the diesel engine vehicles users. However, a systematic and deep investigation on the proposed dynamic test rig needs to be done with extra data and empirical work to check the accuracy and that would give valuable information and better understanding of the compatibility assessment of non-metal components with biodiesel fuel.

REFERENCES


Characterisation of Al$_{65}$Cu$_{20}$Fe$_{15}$ Quasicrystal Alloy Synthesised via In-situ Casting under Standard Room Ambient and Argon Enriched Atmosphere

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ABSTRACT. Characterisation on a series of bulk Al$_{65}$Cu$_{20}$Fe$_{15}$ quasicrystal alloy synthesised via in-situ induction casting under argon (Ar) enriched atmosphere and standard room ambient as the focal point of this research. The significance of atmospheric inertness in the course of induction casting process as well as the impacts of subsequent heat treatment at 650 °C under 5 hours dwelling duration on the metallography of Al$_{65}$Cu$_{20}$Fe$_{15}$ quasicrystal alloy were investigated through VPSEM coupled with EDX as well as XRD. The Al$_{65}$Cu$_{20}$Fe$_{15}$ quasicrystal alloy specimens produced by induction casting under critically controlled inert environment and standard room ambient as well as subjected to posterior heat treatment process were inspected via vickers hardness test in accordance to ISO 6507-1:1997. Research findings inferred that inert atmospheric condition during induction casting is critical for the formation of icosahedral, $i$ phase and served as oxidation retardant to the Al-Cu-Fe ternary system alloy, while the subsequent heat treatment at 650 °C promoted the grain growth of Al$_{65}$Cu$_{20}$Fe$_{15}$ icosahedral quasicrystalline compound.

Keywords: Quasicrystal, Al-Cu-Fe, In-situ Casting, Argon, Heat treatment;

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1. INTRODUCTION

Solid state matters were fundamentally classified into 3 major categories, namely crystalline group, non-crystalline group and quasicrystalline group. Crystalline structures are mainly characterised by the integral construction of either atoms, molecules or ions in a definite geometrical pattern [1,2]. The particles in crystalline systems are uniformly positioned to form long range order of 2 dimensional (2D) as well as 3 dimensional (3D) crystal network with infinite repetition of unit cells that may possess 2, 3, 4 as well as 6 fold axis of non-trivial rotational symmetry [1,2]. Non-crystalline solids on the other hand exhibit randomly configured network of particles throughout the amorphous system without long range repetition of unit cells and features only 1 fold axis of rotational symmetry [1,2].

Differing from crystalline solids which are systematically governed by long range repetitive array of atomic pattern, as well as amorphous solids with relatively random atomic regularity, quasicrystalline solids does not possess rotational axis and comprised of long range aperiodic yet ordered atomic configuration [3-5]. Quasicrystals may be sub-classified into 2 categories, namely the 2 dimensional (2D) polygonal or dihedral quasiperiodic group which composed of octagonal, decagonal as well as dodecagonal configuration with 1 periodic direction perpendicular to the quasiperiodic layers as well as 3 dimensional (3D) polyhedral
quasiperiodic group which composed of icosahedral configuration with no periodic direction [3,4]. The lattice arrangement of crystalline matters were often described with generic models of regular tiling involving only one kind of unit cell with 2, 3, 4 and 6 fold rotational symmetry, meanwhile, quasicrystalline structures violated the conventional crystallographic restriction theorem by exhibiting Penrose tiling patterns involving two or more kind of unit cells, where the primary tiling units may possess 5, 8 10 and 12 fold rotational symmetry, while the secondary tiling units represented by voids or overlapping cells [4,5].

The first profound research on quasicrystal was pre-eminently contributed by Professor Dan Shechtman through the characterisation of rapidly solidified Al-Mn intermetallic compound synthesized via melt-spinning process [6]. The employment of melt-spinning technique allowed the molten Al-Mn composite to be rapidly quenched and solidified within milliseconds, hence resulted in the formation of metastable binary phase Al-Mn quasicrystal with icosahedral diffraction symmetry [6].

Quasicrystals in general exhibit extreme hardness, high electrical resistance, energy absorption, low coefficient of friction, thermal conductivity as well as density and accompanied by adversities such as brittleness and metastability [7,8]. Up to date, quasicrystal technology have been employed particularly on the aspect of non-stick surface coating for culinary kitchenware products via sputter deposition technique under Argon (Ar) enriched atmosphere as well as atomic dislocation impedance for steel reinforcement mechanisms [9]. The abundance of unique nanoclusters present in several quasicrystals had drawn massive interest and instigated immense scientific exploration on the materials, hence unleashed their potential to serve as catalysts for the synthesis of carbon nano-tubes (CNT) and facilitate the steam reformation process for the production of methanol [10-12].

The foremost scientific investigation emphasising on the formation of icosahedral, i quasicrystalline phase in Al-Cu-Fe ternary system was primarily conducted by Tsai et al. (1987) [13,14]. Tsai et al. (1987) revealed that the laboratory synthesised specimens of Al₆₅Cu₂₀Fe₁₅ compound which undergo rapid solidification as well as conventional cooling through natural convection are mainly dominated by icosahedral, i quasicrystalline phase and accompanied by the presence of relatively minute amount of several highly complex crystalline phases [13-15]. It had been discovered that Al-Cu-Fe ternary system remarkably outshined other quasicrystalline structures by exhibiting significantly high thermal stability of up to approximately 890 °C at relatively narrow composition domain, hence suggesting that the material may potentially be viable for numerous engineering applications and dispelled the notion on quasicrystals of being inherently metastable [14-16].

2. MATERIALS AND METHODS

2 distinctive Al₆₅Cu₂₀Fe₁₅ quasicrystal alloy ingots (represented by mole fraction) with the elemental composition of aluminium (Al), copper (Cu) and iron (Fe) purity level inspected via glow discharge spectrometry (GDS) as depicted in Table 1 were synthesized via in-situ casting as illustrated by the schematic diagram in Fig. 1. The significance of atmospheric inertness in the course of casting process on the properties of Al₆₅Cu₂₀Fe₁₅ quasicrystal alloy was studied by manipulating the input flow rate of argon (Ar) gas into the confined induction furnace during its operation at 0 ml/s and 20 ml/s in order to simulate standard room ambient and highly inert atmospheric condition respectively. The concentration of the inert gas within the confined induction furnace operated at 2000 Hz were ensured to be constant by maintaining the flow rate of Argon (Ar) gas throughout the entire casting process. The temperature profile of both Al₆₅Cu₂₀Fe₁₅ quasicrystal alloy samples were captured during the on-site casting process which comprised of melting, solidification and cooling in sequence by using a type R thermocouple connected to data logger.

Full annealing process were performed in order to microstructural homogeneity of the Al₆₅Cu₂₀Fe₁₅ quasicrystal specimens by relieving their internal stress, while promoting chemical equilibrium by increasing
the interstitial diffusion rate of particles within the ternary alloy system [16]. The heat treatment process in this research involved critical elevation of the Al₆₅Cu₂₀Fe₁₅ quasicrystal alloy specimens temperature up to 650 °C in conjunction to locate the ideal temperature vicinity in promoting the grain growth of icosahedral, i quasicrystalline phase in Al-Cu-Fe ternary system as defined by Faudot et al. (1992) [7]. The Al₆₅Cu₂₀Fe₁₅ quasicrystal alloy specimens were subjected to heat dwelling at the particular ambient for up to 5 hours duration, followed by prolonged cooling to room temperature.

**Table 1** GDS analysis of raw materials

<table>
<thead>
<tr>
<th>Element</th>
<th>Purity Level [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium (Al)</td>
<td>98.9</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>99.9</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>98.2</td>
</tr>
</tbody>
</table>

**Fig. 1** Schematic diagram of in-situ casting setup

**Fig. 2** ×1000 magnified morphology of Al₆₅Cu₂₀Fe₁₅ synthesised in standard room ambient (a) without subjected to heat treatment (b) subjected to heat treatment at 650 °C

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Fig. 3 ×1000 magnified morphology of Al$_{65}$Cu$_{20}$Fe$_{15}$ synthesised in argon enriched atmosphere (a) without subjected to heat treatment (b) subjected to heat treatment at 650 °C. Variable pressure scanning electron microscopy (VPSEM) coupled with energy dispersive x-ray spectrometry (EDX) as well as x-ray diffraction (XRD) were performed to characterise the metallography of Al$_{65}$Cu$_{20}$Fe$_{15}$ quasicrystal alloy synthesised under both standard room ambient and inert atmospheric condition. Vickers hardness inspection were performed on all categories of specimens in accordance to ISO 6507-1:1997 by using Shimadzu DUH-211 micro hardness tester, while the post-indentation morphology of specimens were analysed via optical microscope [17,18].

3. RESULTS AND DISCUSSION

The ×1000 magnified morphology of Al$_{65}$Cu$_{20}$Fe$_{15}$ quasicrystal alloy synthesised under standard room ambient and argon enriched atmosphere were shown in Fig. 2 and Fig. 3, while the corresponding EDX analysis and XRD pattern were depicted in Fig. 5 and Fig. 6. It is deduced that the Al$_{65}$Cu$_{20}$Fe$_{15}$ quasicrystal alloy synthesised via on-site casting in the absence of inert atmospheric condition were highly dominated by "region iii", identified as the bright clusters of oxidized compound as depicted by the morphology in Fig. 4.

Fig. 4 ×5000 magnified microstructure of oxide clusters on Al$_{65}$Cu$_{20}$Fe$_{15}$

The Vickers hardness value for each categories of Al$_{65}$Cu$_{20}$Fe$_{15}$ quasicrystal alloy specimens collected through the semi-destructive experiment were computed and analysed via box and whiskers plot as depicted in Fig. 7. The formation of higher intensity of oxide compound in the Al$_{65}$Cu$_{20}$Fe$_{15}$ quasicrystal synthesised under standard room ambient resulted increment in terms of hardness magnitude of the alloy. Meanwhile, heat treatment process conducted at elevated temperature which promoted minute oxidation and the formation of icosahedral phase further impart hardness to the quasicrystal alloy. The exhibition of uneven
edges around the vicinity of mechanical imprint, accompanied by the propagation of cracks observed through the post-indentation topography captured at ×100 magnification scale as shown in Fig. 8 conjectured that the compound to be brittle.

Fig. 5 EDX analysis (a) overall region (b) region i (c) region ii (d) region iii
Fig. 6 X-ray diffraction pattern

Fig. 7 Vickers hardness box and whiskers plot
Fig. 8 × 100 magnified post-indentation topography of Al_{65}Cu_{20}Fe_{15}

4. SUMMARY

It is inferred that the application of argon gas had effectively displaced the gaseous elements in surrounding atmosphere, hence substantially retarded oxidation on the Al-Cu-Fe ternary system alloy in the course of in-situ casting, while increased the apparent diffraction intensity of icosahedral, i phase Al_{65}Cu_{20}Fe_{15} compound. Cost effective semi-inert gas such as nitrogen may be employed in heat treatment process with dwelling temperature of no higher than 700 °C whenever appropriate to prevent oxidation and contamination to the aluminium rich Al-Cu-Fe quasicrystal specimens.

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Characterisation of Encapsulation Citronella Oil with Gelatin-Chitosan

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ABSTRACT. Citronella oil is one of the essential oils has been known recently due to its applicability in food and pharmaceutical industry. The main problems of essential oil are unstable and fragile volatile component. They could be degraded easily by oxidation, volatilization, heating and light if they are not protected from external factors such as encapsulation. Microencapsulation is a method whereby one material or mixture of the materials is coated by other material. This method is designed for protection, isolation and assist in storage. In the present study, the gelatine-chitosan microcapsules were prepared by complex coacervation. The morphology of the microcapsule, the mean particle size of microcapsules, thermal stability and release rate and release mechanism of the microcapsules were investigated. On the optical microscope, the microcapsules were spherical shape and irregular size. The release of citronella oil from the capsules can be seen clearly with the rupture of spherical shape within two weeks. The mean particle size by the volume for this microcapsules is 363.176 µm which at acceptable range of particles size by the complex coacervation which is at range 1-500 µm. The span values more than two indicated that different width of size distribution shows not much difference and can be accepted. Analysis of result of thermal analysis reveal that incorporation of citronella oil by the microencapsulation process results in a complex coacervation with high thermal stability compared with the free oil, indicating that microcapsules protect the oils, making it more resistant to evaporates.

Keywords: Microcapsules, Citronella oil, Complex coacervation, Gelatin, Chitosan;

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1. INTRODUCTION

Many active compounds present in pharmaceutical, cosmetics and food products (essential oils and flavor) are unstable compounds. They can suffer oxidation or volatilization or react with other formulation components. Microencapsulation is a feasible alternative to increase the stability of these compounds. There is a few works in literature on the encapsulation citronella oil. Some aspects of the microencapsulation process still need to be better understood as well as the influence of the process on the oil characteristic [1]. The most important aspect in microencapsulation of given essential oil is to prevent the deterioration of the oil during the encapsulation step [2, 3]. The choice of microencapsulation methods is very much depend on the nature of core material [4]. Among the microencapsulation technique, the complex coacervation is suitable for encapsulate the high value active molecules and unstable substances such as polyphenols which are the major constituent in citronella oil [5]. Complex coacervation involved neutralization of two oppositely charge polymer in aqueous solution. The concentration of the wall material and pH of coacervation are the most important characters in the microencapsulation by coacervation. Furthermore, an additive which is cross linking agent such as formaldehyde or glutaraldehyde normally use as to harden the wall around the
core material [4]. Basically, the complex coacervation consist of three steps: formation an oil-in-water emulsion, formation of the coating and stabilization of the coating[6]. From the literature, the most favorable coating were the gelatin and Arabic gum [7,8,2]. Recently the microencapsulation with gelatin and chitosan also been considered by the researcher because the properties of gelatin and chitosan that contain thermal stability as when combine together to form the wall [3].

2. MATERIALS AND METHODS

2.1 Preparation of encapsulation citronella oil by complex coacervation

Materials. The materials used as wall materials in this research were Gelatine-B (type B, 260 bloom, from bovine) was supplied from Halagel Sdn. Bhd and Chitosan (R&M Chemical). Essential oil used as a core material was citronella essential oil (CO) which was extracted from lemongrass. Glutaraldehyde (50% aqueous solution) was used as a cross linker. Other reagents involved were distilled water, ethanol, acetic acid solution (1%v/v), hydrochloric acid (HCl) and sodium hydroxide (NaOH).

2.2 Encapsulation procedure. The encapsulated citronella oil (ECO) was made through the complex coacervation process. In this process the substances that were used are citronella oil, gelatin type B and chitosan.

2.3 Preparation of encapsulation solution. Before starting encapsulation process, preparation for two main solution A and solution B must been done first. Solution A were prepared by 30 min soaking 3.5 g of gelatin-B in 350 ml of deionized water prior one hour stirring at 50°C until the solution were fully dissolved. Solution B was prepared by dissolving 0.1 g of chitosan in 100 ml of acetic acid aqueous solution for more 12 hours at the room temperature.

2.4 Microencapsulation CO by complex coacervation using chitosan-gelatin (B). There were seven steps involved in the complex coacervation including emulsification, coacervation, pH adjusting, dilution, cooling, cross linker and harvesting. After harvesting process, the processed mixtures was transferred into a separating funnel and undergo settling process for 24 hours. Three layers occurred whereby the top layer contains capsule in oil layer, middle layer contains water and diluted excess polymer and lastly bottom layer contains concentrated excess polymer. The bottom layer and middle layer were drained off and the top layer was rinsed with distilled water three times

2.5 Assessment of microcapsule morphology. The shape and morphology of ECO can be determined by using optical microscope (RZ-5, Meiji Techno, Japan).

2.6 Particle size and particle size distribution. Particle size and particle size distribution were determine by a laser particle size analyzer (Mastersizer 2000, Malvern Instrument Ltd., UK) at 1 min, 2500 rpm.

2.7 Thermal stability. The thermal stability of the microcapsules was studied by thermogravimetric analysis (TGA, SDTA851, and Mettler Toledo. The thermal behavior of gelatin, chitosan, citronella oil and microcapsules were analyzed by using heating rate 10 °C min⁻¹, temperature range between 25 -550 °C.

3. RESULTS AND DISCUSSION

3.1 Morphology of encapsulated citronella oil. The encapsulation of citronella oil by complex coacervation and using gelatin - chitosan as core shield was successfully. Fig. 1 shows the microcapsules of citronella oils under optical microscope.

Fig. 2 shows that the CO capsules are in spherical shape which having irregular size. Some of the capsules were attached together causing agglomerate due to the hardened free gelatin –B after cooling until the settling process. Agglomeration of the capsules during the wall formation was a common phenomenon in many microencapsulation process [10]. As the wall of the materials change from liquid to solid form, they often went through a sticky stage which makes the agglomeration difficult to avoid [10]. After the microcapsules were dispersed under the water, the spherical microcapsules can be seen clearly. Also the
color of citronella oil from the picture shows the yellow color indicated the origin color of citronella oil. It can be observed clearly in Fig. 2.

![Microscopic image of microcapsules](image1)

**Fig. 1** The microscopic image of the microcapsules under optical microscope: (A) Microcapsules form agglomerates and (B) Microcapsules dispersed under water

![Image of microcapsules dispersed in water](image2)

**Fig. 2** The picture of the microcapsules dispersed in water

### 3.2 Particle size and Particle Size distribution

It was observed from Fig. 3 that this distribution is a unimodal distribution. Unimodal distribution is a distribution with one clear peak or most frequent peak. The values increase at first, then rising to single peak then after that they decrease [11]. At the Malvern laser diffraction, the particle size was expressed as mean diameter over the volume distribution $d(4,3)$ and size distribution (span) were calculated by equation 1.

\[
\text{Span} = \left( \frac{D(0.9) - D(0.1)}{D(0.5)} \right)
\]

whereby $D(0.9)$, $D(0.5)$ and $D(0.1)$ are the particle diameters at 10%, 50% and 90% of undersized particle calibration curve, respectively. In this experiment, the mean particle over volume is 363.176 µm. It twice from the reported by other researcher [12] but still considered moderate rate of microencapsulation that have been reported by other researcher whereby the range of microencapsulation by using complex coacervation is from 1 to 500 um [9].

Fig. 3 also shows that same particle size distribution measurement was quantified both relative to the total of particles and the volume of particles. It was observed 10% of total volume particles have diameter less than 2 um, 50% total of volume have diameter below 267 um, meanwhile 90% of total volume particles has diameter less than 700 um. It represent 5.52% of the particles by volume. This indicated that microcapsules
contain the particle size acceptable range from 1 μm to 500 μm. The span values for this experiment is 2.6 and that means the different width of size distribution is not far and can be acceptable. The more values of span, the wider of distribution. Fig. 4 shows the mean particle size, particles size distribution and span.

Table 1 show microcapsules mean particles size obtained for two replicants of experiment. Although the obtained distribution has wide dispersions, the results pointed out for a good reproducibility.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>363.2</td>
</tr>
<tr>
<td>2</td>
<td>212.8</td>
</tr>
<tr>
<td>Average</td>
<td>288</td>
</tr>
</tbody>
</table>

### 3.3 Thermal stability of microcapsules

Thermograms become an important part for analysis of microcapsules formation. It is also provides information on each constituent of microcapsules which can used for their comparison. Fig. 4 shows the TGA curves and their first derivatives as function of time. Table 2 summarizes the most important thermographic results.

![TGA curves and their first derivatives](image)

**Fig. 4** The TGA curves and their first derivatives as function of time for gelatin, chitosan, citronella oil and encapsulation of citronella oil.

The thermogravimetric curves in Fig. 4 and Table 2 disclosed the distinct mass reduction or losses for each component and indicated the thermal decomposition in different stages. Citronella oil present mass reduction in single stage, while chitosan, gelatin and encapsulation of citronella oil present two stages [13].

Mass losses of citronella oil started at about 44 °C and it end at 268 °C. Analysis of thermogram curve and its first derivative shows oil evaporated completely. Thus, this oil is highly volatile and its need to extend the
durability when will be used for other applications. It is slightly higher from reported by previous study [13]. Analysis of thermogram curve and its first derivative shows that the oil completely evaporated. This oils is highly volatile and requires protection to extend its durability when applied to surface. This act can be understood more by looking to the thermal behavior of jasmine oil [14]. It’s indicating that the most of the mass of the jasmine oil was lost below 150 °C and not tolerant with thermal durability.

For gelatin and chitosan, the first mass loss stage indicates evaporation of all the residual water present in these compounds [15,16]. The liberation of humidity seen in TGA and DTG curves in Fig. 4 occurs in initial temperature range of analysis, approximately above the boiling temperature. For this case, the mass loss of gelatin extend to 219 °C and 109 °C for chitosan. Quantitatively mass loss for gelatin is 3% and chitosan is 7% from 20 mg samples.

Pyrolysis of gelatin and chitosan occurs in the same decomposition temperature range 240 °C to 450 °C. These two compound present different behavior in decomposition zone. For mass loss (44% and 34%, respectively) and the residual mass is 55% and 65%, respectively.

In the thermogram for the microcapsules, two thermal events are also observed: the first stage of mass loss at the 35 °C boiling and below 225 °C [6]. In this stage 72% mass loss occurred. The second stage of mass loss occurred in the upper temperature range, beginning at 225 °C and extended to 410 °C. At this stage, likely most of the most of the protein chain such as gelatin and chitosan have been degraded. At this stage 24% of mass loss occurred. Active core material begin to degrade. Fig. 4 also shows that in the second stage of curve for this microcapsules occurs in a few seconds due to the high volatility of citronella oil. It can also been observed in the corresponding first derivative curve.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Thermogravimetric data for citronella oil, gelatin, chitosan and microcapsules</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stage 1</strong></td>
<td><strong>Citronella</strong></td>
</tr>
<tr>
<td>ΔT_{decomposition}</td>
<td>44 -265 °C</td>
</tr>
<tr>
<td>T_{Max}</td>
<td>265 °C</td>
</tr>
<tr>
<td>Mass Loss</td>
<td>84%</td>
</tr>
<tr>
<td><strong>Stage 2</strong></td>
<td><strong>Citronella</strong></td>
</tr>
<tr>
<td>ΔT_{decomposition}</td>
<td>233 - 503 °C</td>
</tr>
<tr>
<td>T_{Max}</td>
<td>347 °C</td>
</tr>
<tr>
<td>Mass Loss</td>
<td>44%</td>
</tr>
<tr>
<td>Residual</td>
<td>16%</td>
</tr>
</tbody>
</table>

4. SUMMARY

Citronella oil was successfully encapsulated by complex coacervation. The morphology shows that microcapsules were obtained with almost perfectly spherical shape. The particle size for these microcapsules is at an average of 288 µm and they are at acceptable range. Thermal analysis revealed that microencapsulation of oil improved its characteristic, making it less volatile and suitable for applied in higher temperature.

REFERENCES

Characterization of Activated Carbon Produced from *Leucaena leucocephala* Biomass as Heavy Metal Adsorbent: Adsorption of Cadmium from Aqueous Solution

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ABSTRACT. Activated carbon (ACs) of *Leucaena leucocephala* biomass was produced by NaOH activation at impregnation ratios NaOH:char (w/w) of 1:1 (AC1), 2:1 (AC2) and 3:1 (AC3). ACs was prepared under activation temperature 750 ºC. The properties of these activated carbons which are BET surface area was analyzed. It was found that the ACs BET surface area was in order of 140 m²g⁻¹ for AC1, 531 m²g⁻¹ for AC2 and 735 m²g⁻¹ for AC3. Batch adsorption experiment was conducted for the adsorption of cadmium (Cd) from aqueous solution. The ACs samples were tested for adsorption capacity. Batch adsorption was studied in different parameters which were the contact time, effect of pH, initial concentration of cadmium (Cd) and temperature. The results show that the adsorption of Cd was reaching equilibrium within 40 min of contact time for metal ions at initial concentrations of 30 mg/l. Higher pH (>7.0) was found to be favorable for the adsorption of cadmium removal.

Keywords: Activated carbon, *Leucaena leucocephala*, *Petai belalang*, Cadmium, Adsorption;

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1. INTRODUCTION

For the last few decades, phenomenal economic development has been observed throughout Malaysia. Urbanization, agricultural expansion and industrialization have resulted in increased usage of water and the use of different toxic chemicals. This rapid development has resulted in widespread contamination of soil, vegetables and above all fouling of water bodies up to a greater extent [1]. Water pollution is a very persistent problem. This situation has evolved gradually over time. Recognition of these sorts of problem usually takes a long time and application of necessary preventive measures takes even longer time [1]. Different reports and
complaints about industrial waste disposal, stinking water courses within overcrowded cities were an early manifestation of water pollution.

Momodu and Anyakora [2] reported that industries such as plating, ceramics, glass, mining and battery manufacturing are considered as the main sources of heavy metals in local water streams, which can cause the contamination of water with heavy metals. Excessive accumulation of these metals in water, soil, and plants may threaten the safety of ecosystems and also pose serious health risks to human. For example, long-term exposure to as from drinking water and food could cause various human health problems like skin lesions (e.g., hyperkeratosis and pigmentation changes), hypertension, cardiovascular disease, and cancers [3].

Among the techniques that had been developed in cleaning waste water from those dangerous materials are dialysis or electro dialysis, electrolyte extraction, chemical precipitation, solvent extraction, oxidation-reduction, reverse osmosis, ion exchange, evaporation, cementation, dilution, adsorption and filtration [4]. Adsorption is the most attractive option for heavy metal removal [5]. Adsorption is normally used in water treatment to remove dissolved contaminants by physical phase separation in either a steady-state (PAC) or a nonsteady-state (GAC) process [6]. Activated carbon is one of the materials used to remove impurities from solutions. It had been widely used to treat industrial and household water because of its excellent adsorption properties, characterized by a high specific surface area [7].

Generally, activated carbons derived from natural sources, such as coconut shells, wood, coal, and carbonization of synthetic polymers, have large pore volume and high surface area [8]. A number of researches had been reported using biomass as a raw material for producing activated carbon [9]. Most researchers are focusing on the best way on removing metal and dyes for their experiment. In Malaysia, there are many potential of raw material resources for the production of activated carbon. The concept of waste-to-wealth had been promoted and became popular widely in Malaysia where the unwanted wastes are converted into valuable materials [10]. Leucaena leucocephala which is petai belalang biomass is a suitable candidate to be used for producing activated carbon due to the availability and abundance of the species.

Therefore, this research utilizes Leucaena leucocephala biomass for the main material for producing activated carbon. Besides that, evaluation of heavy metal uptake from contaminated water using activated carbon made from Leucaena leucocephala biomass were also done to see their efficiency in service.

2. MATERIALS AND METHODS

2.1 Material preparation. Samples from wild Leucaena leucocephala were collected around Selangor, Malaysia. Stem of the Leucaena leucocephala were oven dried to a moisture content of around 10%. Samples were cut into smaller pieces and further grind to turn them into particles. Produced wood particles were sieved into 1 µm to 2 µm of size. Actual moisture content of the wood particles was determined using oven-dry method and the particles were kept in a closed container for further use.

The dried sample was prepared for pyrolysis to produce charcoal. Pyrolyzer is an old method used for producing charcoal. Pyrolyzer was chosen as the carbonization method as it can produce large amount of charcoal at faster rate. About 6 kg was placed inside the pyrolyzer and only 1.5 kg left after carbonization process.

2.2 Activated carbon preparation. Leucaena leucocephala biomass particles were activated using chemical means. Leucaena leucocephala char was impregnated with NaOH which is sodium hydroxide. This step was performed using impregnation ratio of NaOH:char at 3:1, 2:1 and 1:1. Next, 10 g of char were mixed with 30 g of NaOH and 100 mL distilled water in a vertical stainless steel reactor under magnetic stirring for 2 hours before placed in the oven at 105 ºC for 24 hours.

After 24 hours drying in the oven, the sample was place into the muffle furnace for activation process. The furnace was heated from the room temperature to 700 ºC, 750 ºC and 800 ºC for 90 min. The nitrogen gas
will be steam into the furnace at constant 150 cm$^3$/min flow rate. At the end of the activation time, heated sample will be left to cool down with nitrogen gas flow until room temperature to avoid sample to become ash.

2.3 Activated carbon surface area characterization. Surface analyser, Tri Star 3000 (Micromeritics, USA) was used to measure the surface area, determined by N$_2$ isotherms using the Brunauer-Emmett-Teller equation (BET). The sample was first degassed at 300 °C for 2 hours before analysis by nitrogen adsorption isotherm at 77 K in the range of relative pressure $10^{-6}$ to 1.

2.4 Activated carbon adsorption capacity. The adsorption capacity of activated carbon was measured under different conditions such as contact time, pH of solution, initial concentration of adsorbate and adsorption temperature. Approximately 0.5 g of the *Leucaena leucocephala* activated carbon was mixed with 50 ml of the aqueous solutions of cadmium ion in different conical flasks using a temperature-controlled water bath shaker. The mixtures were stirred for pre-determined contact time before filtered using filter paper to get the treated solution. Final solution was analysed using Inductively coupled plasma mass spectrometry, ICP-MS in triplicate to reduce error in experimental results [11].

3. RESULTS AND DISCUSSION

3.1 Properties of activated carbon

The pore size distributions of the prepared AC from *Leucaena leucocephala* biomass is 140.53 m$^2$/g, 531.19 m$^2$/g and 735.68 m$^2$/g for AC from chemical activation with NaOH:char ratio 1:1, 2:1 and 3:1, respectively. The data show that the BET of the AC increased as the NaOH:char ratio increased from 1 to 3. The differences between the BET values of AC-1 and AC-2, AC-2 and AC-3 were of approximately 600 m$^2$/g, showing a surface area increment with increasing of the NaOH:char ratio. As observed, the increase in the NaOH:char promotes an increase of the BET but showed a decrease in the AC yields.

The surface areas of activated carbon can be up to 3000 m$^2$/g. The surface area of commonly available activated carbon is about 1000 m$^2$/g. These high surface area results from development of mainly micro- and meso pores of different size and shape. Macro pores have little contribution to the development of surface area [12]. The adsorption capacity of an activated carbon for a specific adsorbate is dependent on its physico-chemical properties such as effective surface area, pore volume and pore size distribution and surface functional groups. The development of micropores and mesopores is vital as they entrap and retain various types of adsorbate either from gas or liquid phases [13].

3.2 Batch adsorption study

**Effect of contact time on the cadmium adsorption.** The adsorption contact time is an important parameter to an effective interaction between adsorbate-adsorbent. This data is important because equilibrium time is one of the parameters for the economic wastewater treatment plant application [14]. Experimental studies were carried out with contact time 10 min until 160 min with initial metal ion concentrations used were 30 mg/l of Cd (II) using 0.5 g/l of adsorbent dosage at pH 7.0. Fig. 1 shows the contact time effect on the percentage removal of Cd (II). Equilibrium adsorption was established within 40 min for metal ions at initial concentrations of 30 mg/l.

The highest ratio of NaOH:char resulted in higher adsorption for removal Cd (II) due to higher surface area for adsorption. It is very clear from the results that the agitation time required for maximum uptake of metal ions by activated carbon was dependent on the initial metal ion concentration. Obviously, the initial high adsorption rate is due to the abundance of free binding sites. The meso-pores become almost saturated with Cd (II) ions during the initial stage of the adsorption process. Thereafter, the Cd (II) ions have to traverse farther and deeper into the micro-pores encountering much larger resistance, thus leading to
decreased driving force and adsorption rate. Additionally, with the process of adsorption, desorption rate increased, adsorption-desorption equilibrium is also affected around equilibrium [15].

Fig. 1 Effect of contact time on removal cadmium

3.3 Effect of pH on the cadmium adsorption. Fig. 2 shows that with an increase in pH, the residual of Cd (II) decreased and adsorbents are effective for the quantitative removal of Cd (II) ions at pH = 8.0. A sudden change occurred at pH ranging from 7.0 to 8.0. At higher pH (> 7.0), the adsorption of Cd (II) ions is nearly constant. The maximum removal and adsorption capacity of *Leucaena leucocephala* AC occurred at the pH 8.0. Almost 100% cadmium were removed at the pH 8.0.

Similar results with pH have been reported by many studies that adsorption capacity of adsorbents is low at acidic pH while increases at higher pH values. When the pH is < 6.0, the surface charge on the surface of *Leucaena leucocephala* AC is positive. A significant electrostatic repulsion exists between the positively charged surface and the cationic Cd (II) ions, which inhibits the adsorption of Cd (II). Besides, a higher concentration of H+ in the solution competes with Cd (II) ions for the adsorption sites, resulting in the reduced uptake. The increase in adsorption with the increase in pH can be attributed to the fact that the positively charged metal cations are repulsed less by the oxide surfaces at higher pH values. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases on the surface of adsorbents. Obviously, a negatively charged surface site favors the adsorption of cationic Cd (II) ions due to electrostatic attraction [15].

Fig. 2 Effect of pH on removal cadmium

3.4 Effect of concentration on the cadmium adsorption. The effect of initial concentration on the adsorption of cadmium by *Leucaena leucocephala* activated carbon was investigated with varying solution concentrations (10, 20, 30, 40 and 50 mg/L) using 0.5 g adsorbent dose and pH 7.0. Lower initial concentration resulted in highly adsorption percentage for cadmium removal. However, for highly
concentrated initial solution resulted in lower adsorption percentage. This can be conclude that, at low initial solution concentration, the surface area and the availability of adsorption sites were relatively high, and the cadmium were easily adsorbed and removed [16]. At higher initial solution concentration, the total available adsorption sites are limited, thus resulting in a decrease in percentage removal of cadmium. Fig. 3 shows the different adsorption curve for the ratio 1:1, 2:1 and 3:1. The ratio 1:1 is the lowest adsorption percentage between 2:1 and 3:1. It is because of the different surface area of activated carbon.

![Fig. 3 Effect of concentration on removal cadmium](image)

3.5 Effect of temperature on the cadmium removal. The effect of temperature on the adsorption of cadmium by Leucaena leucocephala activated carbon examine with different temperature from 30 °C to 70 °C using 0.5 g adsorbent dose, pH 7.0 and with initial concentration 40 mg/l. Based on the results in Fig. 4, adsorption percentage were increase on temperature 30 °C and started to decrease on temperature 40 to 70 °C for both ratio. However, the ratio for 3:1 resulted in higher adsorption rate. It can be conclude that the percentage of adsorption for cadmium is decrease when the temperature is increase. So, temperature 30 °C is equilibrium point for the temperature parameter. This result has a similarity from the previous studies that has been reported from Kumar, Ramakrishnan, Kirupha and Sivanesan [17], the decreasing of adsorption rate from 86.87 to 76.25% for 50 mg/L concentration of the cadmium with an increase in temperature from 25 to 55 °C.

![Fig. 4 Effect of temperature on removal cadmium](image)
4. SUMMARY

In the present study, batch adsorption of cadmium removal from aqueous solution had been carried out using *Leucaena leucocephala* biomass as an adsorbent. The adsorption characteristic had been examined at a different contact time and pH values. For the contact time, the equilibrium adsorption was established within 40 min for metal ions at initial concentrations of 30 mg/l. The highest adsorption percentage for contact time is by ratio 3:1 which is NaOH:char. It is very clear from the result that, longer time required for maximum uptake of metal ions by activated carbon was dependent on the initial metal ion concentration. Generally, adsorption capacity of cadmium ions by *Leucaena leucocephala* AC increased with an increase in the pH of the adsorbate solution. The optimum pH for cadmium removal is 8.0. Based on the obtained results, activated carbon from *Leucaena leucocephala* biomass would be useful for the economic water treatment that containing cadmium metals.

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REFERENCES


Comparison of HPOM and TiO₂ as Photocatalyst for Degradation of Methylene Blue in Aqueous Solution

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ABSTRACT. In this work, the hybrid polyoxometalates (HPOM) (Na₂[PW₁₂O₄₀]ₙH₂O) photocatalyst has been synthesized by precipitation method and was characterized by SEM and ATR-FTIR techniques. Photocatalytic activity of HPOM was compared with TiO₂ for the photocatalytic degradation of methylene blue (MB) dye. The effect of initial concentration of MB, catalyst dosage and temperature were studied in details. The study found that the HPOM showed the highest photocatalytic activity under UV-vis irradiation and also exhibited remarkable ability to remove MB, suggesting they are promising photocatalyst for wastewater treatment.

Keywords: Polyoxometalates, Photocatalyst, Photodegradation, Methylene blue;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Currently, environmental pollution is the serious problems for human life [1]. The harmful organic pollutants have become one of the major sources of environmental pollution. Therefore, the advancement of economical and green method to treat and purify contamination water has been in the central subject in the technological developments. The conventional treatment methods are physical and chemical methods, such as absorption, oxidation, and so on [2]. Among many methods, photocatalysis is most practicable one, especially for treatment of contaminations, due to its usage of sunlight to decompose organic pollutants [3]. Titanium dioxide (TiO₂) is the most active semiconductor photocatalyst because of its strong oxidizing, long-term thermodynamic stability and relative nontoxicity [4]. Even though TiO₂ with regards to photocatalysis has high band gap energy 3.2 eV, but it has its own limitations which are critical to photocatalytic technology [5], such as: i) recombination of photo-generated electron/hole pairs, ii) fast backward reaction and iii) inefficient visible light utilization. Therefore, studies of new high efficiency photocatalyst are significant.

The syntheses of organic-inorganic hybrid material based on polyoxometalates (POMs) have been paid great attention in the last two decades. Hybrid-POM (HPOM) is a material consisting of three major components, namely POMs, metal ions and organic ligands [6]. HPOM has some potential as a photocatalyst. Generally, HPOM is photo-sensitive activity, which similar to TiO₂. Under UV irradiation, these materials can generate electrons to activate the hydroxyl radicals in water and then degrade the organic dye molecules [7]. Moreover, the diversified structures and topologies of HPOM can be control through different coordination modes and configurations of organic ligands. These make them attractive in applications as diverse as
catalysis, magnetism, photoelectron chemistry, medicine and selective active photocatalyst for the dye degradation [8]. However, the synthesis of HPOM and the research of their photocatalytic performance have seldom been reported so far. So, the study provided a method for the synthesis of HPOM (Na2[PW12O40].nH2O) by nitro aromatic fragments as a ligand. The methylene blue (MB) was used as organic compound to evaluate its photocatalytic activity under UV irradiation in batch photoreactor. Then, the results were compared with the well-known P-25 TiO2.

2. MATERIALS AND METHODS

2.1 Materials. Sodium tungstate dihydrate, Na2WO4·6H2O, p-nitrophenyl phosphate disodium salt hexahydrate, C6H4NO6P·2Na·6H2O and MB were purchased from Merck, Germany (EMD Millipore Corporation). TiO2 (99.5%) samples was obtained from Degussa (P-25 TiO2) Sigma Aldrich. All chemicals used were reagent grade without further purification. Synthesis of HPOM photocatalyst. Na2WO4·6H2O was dissolved in distilled water. Then C6H4NO6P·2Na·6H2O was added to the solution. The reaction was stirred up to dissolution of solids. After that, concentrated H2SO4 was added drop wise into the constantly stirring reaction mixture. After some time a yellow precipitate began to form. The solution was kept in dark for 3 days at room temperature. The precipitate was filtered and dried in dark at room temperature for a day. After that, the product was dissolved in ethyl alcohol. The alcohol was evaporated in the oven, and grey-green precipitate is formed. Then, the precipitate was washed with water and dried in the oven at 70 °C.

Characterization. The morphology of the samples was observed by using a Scanning Electron Microscope (SEM) on a Zeiss SUPRA 35VP. The elemental content from the samples were observed by using ATR-FTIR. The spectra were obtained on a PIKE MIRacle transform instrument from Perkin Elmer and recorded using a horizontal ATR cell covering the 650-4000 cm⁻¹ spectral range. The ultraviolet-visible (UV-vis) diffuse reflectance spectra were carried out using a spectrophotometer (Shimadzu, Japan/UV-1800 Plus).

2.2 Photocatalytic Experiments. Photocatalytic Reactor. The experiments were performed in a batch photoreactor. Light source was offered by a Pen-Ray® Light Source PS-4 (26mA) with emission λ = 254 nm. Photoreactor was set-up as shown in Fig. 1.

![Schematic diagram of batch photoreactor](image.png)

Fig. 1 Schematic diagram of batch photoreactor

2.3 Operating Parameters. Effects of Initial Dye Concentration. In order to investigate the effect of initial MB concentration, various dye concentrations such as 5, 10, 15, 20 and 25 ppm were prepared. 5 ppm MB solution mixed with 0.3 g/L HPOM in the batch reactor and reaction mixture stirred continuously using
magnetic stirrer, at a constant stirring speed of 120 rpm. The temperature of reaction kept constant at 25 °C. After that, 3 ml of sample withdrawn from the flask after the UV light switched on and the absorbance using UV-VIS spectrometer at 664 nm for reaction time at 0, 20, 40, 60, 80, 100 and 120 min. The same procedure were repeated for other initial concentrations and TiO₂ catalyst.

2.4 Effect of Catalyst Dosage. The effect of photocatalyst dosage on photocatalytic degradation of MB using HPOM and TiO₂ were carried out at 0.10, 0.20, 0.30, 0.40, 0.50 g in a room temperature (25 °C). 0.10 g/L of HPOM of 15 ppm of MB solution were added in batch photoreactor. The solution was stirred using magnetic stirrer at constant stirring. 3 ml of reaction mixture drawn after the UV light illuminated to test the absorbance rate at 664 nm in UV-vis spectrophotometer at fixed time interval 0, 20, 40, 60, 80, 100 and 120 min. Later, the experiment were repeated as stated above using different HPOM and TiO₂ dosage.

2.5 Effect of Temperature. 0.3 g of HPOM was added to 15 ppm of dye solution. The temperature of MB solution is varied at 15, 25, 35, 45, and 55 °C using water bath, the solution were stirred at constant stirring speed. The temperature of the reaction mixture was measured using digital thermometer throughout the experiment to ensure the temperature of reaction mixture constant from beginning to end of illumination session. However, for temperature that lower than room temperature (25 °C), ice cubes were used to reduce the temperature of reaction mixture. This method is used to let the temperature of reaction mixture reduced in short period of time. Later, 3 ml of sample withdrawn from the flask and absorbance was tested. The experiment were repeated as stated above for TiO₂.

2.6 Analytical Measurement of MB Dye Concentration. The photocatalytic activity of HPOM and TiO₂ samples were evaluated by photocatalytic degradation of MB under UV-vis irradiation (λ = 254 nm). The samples were analysed after centrifugation (3000 rpm for 3 min). The concentration change of MB determined by the absorbance of the solution at 664 nm, was evaluated with a UV-vis spectrophotometer. Percentage degradation of MB was defined as in Eq. 1.

\[
\text{Degradation\%} = \left[\frac{(C_0-C)}{C_0}\right] \times 100
\]

where C₀ is the initial concentration of MB and C is the concentration of MB after photocatalytic reaction.

3. RESULTS AND DISCUSSION

3.1 SEM Analysis. Material morphology was obtained and the micrographs are shown in Fig. 2. SEM micrographs of the HPOM photocatalyst (a) showed large aggregated particles, whereas the TiO₂ (b) particles appeared to be smaller aggregated particles. This results in a high porous volume due to aggregation among tiny particles [9]. Generally, photocatalytic activity of photocatalyst is strongly dependent on its phase structure, crystallize size, surface area, and pore structure. Larger specific area allows more organic reactants to be absorbed onto the surface of the catalyst, while high pore volume results in an improved diffusion of various inorganic products during photocatalytic reaction.

3.2 ATR-FTIR Analysis. Infrared spectroscopy was used to detect the presence of functional groups adsorbed on the surface of the photocatalyst. Fig. 3 represents the FT-IR spectra of TiO₂ and HPOM photocatalyst. The infrared band around 3353 cm⁻¹ and 2866 cm⁻¹ are assigned to the stretching and bending vibrations of O-H of TiO₂ and HPOM, respectively. According to Yu and co-researchers [10]. The hydroxyl groups on the surface of samples contribute to enhancement of the photocatalytic activity. This is because O-H can interact with photogenerated holes, which give better charge transfer and inhibit the recombination of electron-hole pairs [11].
Fig. 2 SEM micrographs of (a) HPOM and (b) TiO₂ photocatalyst

3.3 Photodegradation Study. Effect of Initial MB Concentration. The effect of initial concentration of MB solutions on the percentage removal was investigated at catalyst dosage of 0.3 g and the reaction time of 120 min. Fig. 4 shows the effects of initial concentration of MB from 5 ppm to 25 ppm on percentage degradation of MB. From the result, the percentage of degradation decreased with an increase in the initial concentration of MB. As the concentration increases, more dye molecules are absorbed on the catalyst surface [12]. It causes the penetration of light to the surface of catalyst decreases. Since, the active sites was occupied by dye molecules, the generation of OH⁻ and OH₂⁺ decreased [13]. Moreover, increase in dye concentration shields the UV light. The path length of the photons entering the solution reduced [14]. High concentration requires increment in catalyst surface which needed for degradation. However, the illumination time and the dosage of catalyst are constant in this experiment. Therefore, the relative number of free radicals attacking the dye molecules decreases with increasing amount of dye [15]. At low initial concentration (5 ppm), the MB dye by HPOM giving the highest value of percentage degradation (86.11%) compared to TiO₂ (79.42%) while the percentage was 54.94% by HPOM and 40.56% by TiO₂ for high concentration (25 ppm). This indicates that the photocatalytic activity of HPOM is effective compared to TiO₂.
3.4 Effect of Catalyst Dosage. Fig. 5 shows the degradation of MB in the range of 0.1-0.5 g/L catalyst dosage. From this figure, it is confirm that for HPOM by increasing the dosages, the percentage of MB removal is increase to 81%. Initially, when the catalyst dosages increase, it will increase the number of active sites on the photocatalyst. This will increase the number of hydroxyl and superoxide radical [16] and the amount of photons accelerated become larger in this the process [17]. Thus, it lead to higher degree of degradation of MB was observed.

In contrast, this not happened to TiO2 when excessive the catalyst dosage. Some of the catalyst effect the solution opacity (transparency or translucency) when the catalyst dosage increased and it causes the reduction in the photon flux in the reaction mixture [18]. Thereby, it decreases the photocatalytic degradation rate. Moreover, increment of catalyst dosage beyond the optimum may also results a loss in surface area by agglomeration (particle-particle interaction) of catalyst particles, hence the part of catalyst surface become unavailable for photon absorption and the rate of degradation decrease [14]. The suspended particles in the reaction mixture cause the excessive light scattering which also progressively reduces the rate of degradation [19]. Therefore, degradation of MB by TiO2 was reduce after exceed 0.3 g.

Fig. 4 The effect of initial concentration on the photocatalytic activity of MB dye at 120 min. Photocatalyst dosages: 0.3 g, reaction temperature: 25 °C.

Fig. 5 The effect of catalyst dosage on the photocatalytic activity of MB dye at 120 min. Reaction conditions: MB Concentration: 15 ppm, photocatalyst dosage: 0.3 g, reaction temperature: 25 °C.

Fig. 6 The effect of temperature on the photocatalytic activity of MB dye at 120 min. Reaction conditions: MB concentration: 15 ppm, photocatalyst dosage: 0.3 g.
temperature: 25 °C

3.5 Effect of Temperature. Fig. 6 illustrates the effects of temperature by reaction mixture of MB from 15 °C to 55 °C while other parameters were fixed at 0.3 g catalyst dosage and 15 ppm of MB concentration. HPOM shows the highest degradation rate compared to TiO2. The percentage degradation of reaction mixture for HPOM and TiO2 at 55 °C is 81% and 72% respectively. The overall results show that, the increase in the reaction temperature results in an increase in the photodegradation rate. The enhancement of the photoxidation is probably due to the increasing collision frequency of molecules [20].

4. SUMMARY

The HPOM was synthesized by precipitation method with nitro aromatic fragments as a ligand. The degradation behavior of the MB dye under UV-vis light irradiation was studied. Multiple factor affect the degradation rate of the photocatalyst on the MB removal. High MB removal is achievable with HPOM compared to TiO2.

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Comparison Study of Magnesium Anodizing by using Alternating Current (AC) and Direct Current (DC)
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ABSTRACT. The corrosion behavior of a AZ80 Magnesium alloy which anodized using a different power source AC and DC up to 30 V in an alkaline silicate solution containing 60 g/L sodium hydroxide, 10 g/L sodium silicate and 40 g/L sodium phosphate has been investigated using linear polarization method. The change of the oxide film morphology both of anodized sample also examined using scanning electron microscopy. Anodization of the AZ80 Mg alloy significantly improves its corrosion resistance for both power source as the potential applied up to 30 V. The Tafel polarization method result demonstrated that corrosion resistant was also increased by voltage applied which also lead to better corrosion resistant. Sample that been anodized with AC power source has more compact surface with pores structure compared to the sample anodized with DC power source. The anodic film is mainly composed of MgO, Mg2SiO4 and Mg3(PO4)2.

Keywords: Anodizing, Magnesium AZ80, Corrosion, Characterization;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION
Magnesium alloys have many outstanding properties relative to other engineering materials such as low density, high strength, great damping capability, excellent fluidity for casting, high temperature conductivity, low heat capacity, less negative electrochemical potential, suitable for recyclability, and non-toxicity. These properties make magnesium alloys attractive to many industries especially in the automotive and aerospace sectors where the strength/weight ratio is main concern. Magnesium (Mg) alloys have been seen as a promising alternative to aluminum alloy [1, 2].

However, despite all of the advantages of the Mg alloy, their poor corrosion and wear resistance limits their usage specifically in harsh environments [3]. Proper surface treatment such as anodizing is vital further to produce protective film which can help in corrosion protection of magnesium.

Anodizing is an electrolytic oxidation process where the surface of the metal is converted into a thick and stable oxide film. Making an anodizing under high voltage using DC current has attracted many researchers due to excellent adherence between the coating and substrate [4-6]. Higher voltage oxidation film is generally porous and brittle and sparking might occur at higher potential hence reduce the mechanical properties of magnesium alloys [7]. However, a limited study is found on comparing between both anodizing process using different power sources which are alternating current (AC) and direct current (DC) at low potential. This research aims to compare the different of both power sources to oxide film formed on the surface of magnesium alloy.
2. MATERIALS AND METHODS

Rectangular shape (15 mm×15 mm×3 mm) of magnesium alloy AZ80 (Al 7.5 wt.%, Zn 0.22 wt. %, Mn <0.51 wt.%, Si <0.01 wt. %, others <0.01 wt.% balance Mg) were used as substrates in this study. All samples were prepared from the same area of a cast ingot in order to minimize the differences in composition and microstructure. After grinding up to 1200 grit paper, the samples were first cleaned with acetone and then ultrasonically cleaned in distilled water. Electrolytes were prepared from solutions of 60 g/L sodium hydroxide, 10 g/L sodium silicate and 40 g/L sodium phosphate.

During anodizing process, the samples to be coated and a platinum electrode used as a cathode were connected to a DC and AC power source. The electrolyte was stirred by magnetic stirring equipment in order to maintain a uniform distribution of solution concentration and temperature. Microstructure analysis performed using JOEL-JSM-6460LA Instrument to characterize the surface morphology of the samples before and after anodizing process with different power source. X-ray diffraction (XRD) analysis performed using a Shimadzu XRD 6000 diffractometer at 2θ values of 20-80° with Cu Kα radiation to determine the phases of the anodic film and later analyzed by X’Pert High Score Plus software.

Polarization measurements were conducted using a custom three electrode flat corrosion cell system which has a 1 cm² exposed area for a working electrode to expose its flat surface to the electrolyte in the cell. The working electrode specimen in a slot holder outside the cell was attached tightly to the window by a steel screw bolt through the holder. The bolt pushed the specimen firmly against the window, and also acted as an electrical conductor to connect the working electrode specimen to an electrochemical measurement system. Platinum plate was used as counter electrode and saturated calomel electrode (SCE) were used as reference electrode in 3.5 wt.% NaCl solution. The measurement was performed using AUTOLAB PGSTAT 204 and analyzed using NOVA software. The scanning rate for potentiodynamic polarization was 1 mVs⁻¹ and the scan potential range used was -2.0 to 1.5 V Vs SCE.

3. RESULTS AND DISCUSSION

3.1 Polarization Measurement. The results of linear polarization experiments at different voltages and power source was summarized in Table 1. The anodic behavior of Mg alloys is strongly influenced by the voltage applied [8]. The corrosion resistance of AZ80 magnesium alloys is enhanced significantly as the anodizing potential applied is increased. This is notable by the decrease in Corrosion current (Icorr) and shift of Corrosion potential (Ecorr) in the noble direction (more positive values) for both anodized sample in comparison with AZ80 substrate. The corrosion rate drops from 0.689 mm/year to 0.571, 0.236, 0.211 and 0.112 mm/year for DC power source and drops from 0.883 mm/year, 0.3987, 0.2867, 0.1263 and 0.0579 mm/year. Different passive and active states were found, depending on the applied voltage and power source on the substrate. At different anodizing voltage, the anodized coatings have different formation processes.

<table>
<thead>
<tr>
<th>Power Source</th>
<th>Sample</th>
<th>Icorr(µA)</th>
<th>icorr(µA/cm²)</th>
<th>Ecorr (V)</th>
<th>Corrosion rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>10V</td>
<td>25.266</td>
<td>32.186</td>
<td>-1.4507</td>
<td>0.68861</td>
</tr>
<tr>
<td></td>
<td>15V</td>
<td>13.255</td>
<td>16.885</td>
<td>-1.0175</td>
<td>0.571</td>
</tr>
<tr>
<td></td>
<td>20V</td>
<td>8.4337</td>
<td>10.744</td>
<td>-1.2768</td>
<td>0.23607</td>
</tr>
<tr>
<td></td>
<td>25V</td>
<td>7.6186</td>
<td>9.7052</td>
<td>-1.4121</td>
<td>0.21325</td>
</tr>
<tr>
<td></td>
<td>30V</td>
<td>4.0149</td>
<td>5.1145</td>
<td>-1.2529</td>
<td>0.11238</td>
</tr>
<tr>
<td>AC</td>
<td>10V</td>
<td>31.57</td>
<td>40.217</td>
<td>-1.1394</td>
<td>0.88369</td>
</tr>
<tr>
<td></td>
<td>15V</td>
<td>14.245</td>
<td>18.146</td>
<td>-1.2323</td>
<td>0.39873</td>
</tr>
</tbody>
</table>
Fig. 1 shows potentiodynamic curves tested on AZ80 magnesium alloys before and after anodizing processes by using different power source at 30 V. Corrosion potential for both anodized sample are shifted in the more positive electropositive value compared to AZ80 substrate. Its is shows these both sample indicate a higher corrosion resistance [9].

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Current Density 10^(-6) A/cm²</th>
<th>Corrosion Potential (V)</th>
<th>Coefficient of Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>20V</td>
<td>10.241</td>
<td>-1.0608</td>
<td>0.28666</td>
</tr>
<tr>
<td>25V</td>
<td>4.5116</td>
<td>-1.1259</td>
<td>0.12628</td>
</tr>
<tr>
<td>30V</td>
<td>2.6387</td>
<td>-1.344</td>
<td>0.057981</td>
</tr>
</tbody>
</table>

3.2 Surface morphology analysis. The microstructures of anodic films on AZ80 magnesium alloys show in Fig. 2. Both samples has a granular rough surface with microcracks. However, sample that been anodized with AC power source has more compact surface with pores structure compared to the sample anodized with DC power source that show non-uniformity of coating. The coating on DC power source form with island like shape compared to AC power source that is more uniform. Micro cracks are noticeable on the coated surface (Fig. 2). The formation of cracks caused by thermal stresses resulted from rapid cooling of the oxides by the electrolyte. The electrolyte act as a coolant agent in the anodizing process. This is agreed by El Mahallawy et. al that studied on AZ91 magnesium alloy [9]. These differences on surface result from the differences of spark behavior and evolution of gases, as in AC power source the spark phenomena was stronger and accompanied with higher evolution of gases and generation of heat compared to DC power sources.

3.3 Phase Composition. The XRD pattern of the anodized film is shown in Fig. 3. The XRD pattern shows that both of the anodized sample is mainly composed of MgO, Mg₂SiO₄ and Mg₃(PO₄)₂. This shows the components
of the electrolyte which is Silicon (Si) and Phosphorus (P) and the AZ80 substrate (Mg) participate in the anodic film formation during anodizing process. The XRD spectrum of AC anodized sample exhibit more Mg$_2$SiO$_4$ phase compared to DC sample. Silicate medium (Mg$_2$SiO$_4$) contributed to the better corrosion resistant where the silicate medium function as a seal to porosity of the anodic coating [10].

![Surface morphology of the anodized AZ80 Mg Alloy with a different power source (a) DC and (b) AC at 30V](image)

**Fig. 2** Surface morphology of the anodized AZ80 Mg Alloy with a different power source (a) DC and (b) AC at 30V

This is accordance with the tafel polarization curve result presented in the Fig. 1. The formation mechanism of MgO can be shown by the following reactions [11]:

\[
\text{Mg} = \text{Mg}^{2+} + 2e \quad (1)
\]

\[
\text{Mg}^{2+} + 2\text{OH} = \text{Mg(OH)}_2 = \text{MgO} + \text{H}_2\text{O} \quad (2)
\]

\[
4\text{OH} = 2\text{H}_2\text{O} + \text{O}_2 + 4e \quad (3)
\]

\[
2\text{Mg} + \text{O}_2 = 2\text{MgO} \quad (4)
\]

A high temperature phase transformation occurs between SiO$_2$ and MgO at sparking areas, and finally transforms into Mg$_2$SiO$_4$:

\[
\text{SiO}_2 + 2\text{MgO} = \text{Mg}_2\text{SiO}_4 \quad (5)
\]
SUMMARY

In this work, anodizing completed at different potential in order to access the effect power source on the surface morphology and the anodic behavior. This study found that the increased of the anodizing potential up to 30 V will enhance the corrosion resistance of AZ80 magnesium alloys significantly for both power source AC and DC. However, the sample that anodized with 30 V AC power source is much more compact than the basic film, which results in better corrosion resistance compared to the sample anodized with DC which is 0.0579 mm/year and 0.11238 mm/year respectively. The anodized film for both power source basically has granular rough surface with some microcracks. The anodic film is mainly composed of MgO, Mg₂SiO₄ and Mg₃(PO₄)₂.

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Compression Behaviour of Pseudowollastonite-Mullite Biocomposite

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ABSTRACT. In this work, the mechanical properties of pseudowollastonite-mullite (PSW-M) composite were investigated over a range of sintering temperature. The amount of mullite was varied at different percentage 10, 20 and 30 wt.% relative to the composite content to assess the optimum amount of compressive strength. The pseudowollastonite was produced by sol gel method using calcium oxide from limestone and silica from the raw rice husk ash as a precursor. Next, pseudowollastonite and mullite was ball milled for 15 min with acetone. All different composition of PSW-M was sintered at 800 ºC, 1000 ºC, and 1150 ºC to examine the sintering effect. The phase composition of the pellet was analysed using XRD and the compression strength was measured through the universal material testing machine INSTRON 8874. It was found that, the sintering temperature had the greatest influence on the compressibility when measured over a range of mullite composition during compression test. PSW-M sample with 20 wt.% of mullite addition and sintered at temperature 1150 ºC was found to be the highest compressive strength, 30 MPa.

Keywords: Compression, Pseudowollastonite, Mullite;

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1. INTRODUCTION

In the quest of ideal bioactive bone implant material, significant efforts have been devoted entirely to produce bioceramic composites with better mechanical strength as well as biocompatible with the human body. Several biomaterials that were commonly used in biomedical applications as scaffold are hydroxyapatite (HA), calcium phosphate (CaP), and calcium silicate (CaSiO3) based composites. Over the past few years, a stable forms of calcium silicate which also known as pseudowollastonite above temperature ~1125 ºC (α-CaSiO3) has been proved as bioactive and has an excellent osteogenic properties which has been considered for dental and load bearing applications [1,2]. One of the biggest features that indicate the excellent bioactivity of the material is the ability to have a quick direct integration with bone [3]. Several study reported that, pseudowollastonite was able to stimulate the apatite formation on their surface within short induction period [4,5]. However, calcium silicate ceramics has a low mechanical strength such as fracture toughness, low compressibility and hardness which has become one of the biggest challenges [6]. Therefore, it is sensible to modify the calcium silicate in order to enhance the mechanical strength and realise
the full potential of the composite. Numerous types of polymer [7,8], metal [9], and ceramics reinforcement such as alumina [10] and zirconia [11] has been used as reinforcement to form a better mechanical strength of the biocomposite. In this study, mullite 3Al2O3·2SiO2 was selected as the reinforcing phase to enhance the mechanical properties of calcium silicate. Mullite is the refractory material that commonly used for high temperature applications which consists of alumina and silica. Mullite has much lower density (3.05 g/cm³) than zirconia (6.1 g/cm³) and alumina (3.95 g/cm³), but higher hardness (15 GPa) than ZrO2 (12 GPa), with tolerable fracture toughness (3 MPa.m0.5). Thus, a new combination of pseudowollastonite with a high strength potential of mullite was prepared to enhance the compressibility property of the biocomposite. Besides compression test, the phase composition and morphology of the composite were examined using X-ray diffraction (XRD, D8 Advance Bruker, Germany) and field emission scanning electron microscopy (FESEM, Gemini, Zeiss Supra Series, Germany).

2. MATERIALS AND METHOD

In this study, pseudowollastonite was synthesized from the rice husk ash and limestone using the sol gel method with the ratio of CaO: SiO2 45:55. The CaO and SiO2 powder were mixed in distilled water and autoclaved at 135 °C for 8 hours, dried in the oven, and the powder was sintered at temperature 1250 °C for 1 hour to produce pseudowollastonite phase. The detail procedure of synthesizing wollastonite has been described in the previous work [12]. Mullite was simply synthesized by the calcination of the andalusite at the temperature 1450 °C for 4 hours. The synthesized pseudowollastonite was ball milled at 400 rpm with mullite powder at 10, 20 and 30 wt.% composition for 15 min with acetone. Then, a cylindrical pellet was formed by mixing the composite powder with phosphate buffer as a lubricant using magnetic stirrer and pressed manually with the dimension of 12.5 mm height and 6 mm diameter. Next, for densification purposes, all samples were sintered at varied temperature 800, 1000 and 1150 °C. The uniaxial compression strength of the composite was determined using 5 kN load cell of the universal material testing machine Instron 8874 at a crosshead speed of 0.5 mm min⁻¹. At least 7 specimens were tested on each group. The compressive strength was obtained using Eq. 1.

\[
\sigma = \frac{F}{A} \quad (1)
\]

Where F is the maximum load at failure (N) and A is the pressure area (mm²)

3. RESULTS AND DISCUSSION

XRD analyses of the pseudowollastonite-mullite (PSW-M) system were carried out to compare the phases after sintering at different temperature (Fig. 1). Based on the XRD patterns, the sintered sample for 20 wt.% of mullite additions into pseudowollastonite identified the main crystalline phase of mullite at peak angle 26.2 and pseudowollastonite at (2θ = 27.5°, 45.6°, and 32°). However, XRD indicates the presence of gehlenite when sintered at 800 °C and 1000 °C. Nath et al. [13] found that the presence of gehlenite (Ca2Al2SiO7) and CaO will cause reduction of calcium phosphate-mullite composite hardness and young modulus. Based on the XRD spectra in Fig. 1, gehlenite phase were presented at 800 °C and 1000 °C. Nevertheless, at 1150 °C, only mullite and pseudowollastonite phase was present. Sintering at 1150 °C is the maximum temperature for PSW-M composite since sintering over 1150 °C will results in the melting and crystallizations of the composite.

The result of average compressive strength measured over a range of composition (10, 20, 30 wt.% of mullite) sintered at (800, 1000, 1150 °C) respectively is depicted in Fig. 2. Samples sintered at temperature 800 °C have the lowest compressive strength with only in range of 0.2-3.3 MPa across all different composition. A slight increase on the strength could be seen for PSW/M composite when sintered at 1000 °C. However, when sintered at 1150 °C, the obvious changes in strength could be observed for 20 and 30 wt.% of
mullite addition which abruptly increases the compressive strength up to 30 MPa and elastic modulus of 4.37 GPa.

![XRD patterns of pseudowollastonite-20% mullite pellet sintered at (a) 800 ºC, (b) 1000 ºC, and (c) 1150 ºC](image)

**Fig. 1** XRD patterns of pseudowollastonite-20% mullite pellet sintered at (a) 800 ºC, (b) 1000 ºC, and (c) 1150 ºC

The results revealed that PSW-20M composite sintered at temperature 1150 ºC with about 92.74% of the theoretical density has the highest compression strength. Mullite has turned out to be the strengthening agent to improve the mechanical properties of the pseudowollastonite. Besides, a similar trend could be observed in other study on calcium phosphate-mullite composite whereby 30% of mullite additions has far better compressive strength compared to the pure hydroxyapatite [14]. Fig. 3 displays the agglomerated microstructure of the PSW-20% mullite pellet sintered at 800 ºC, 1000 ºC and 1150 ºC. Fig. 3 reveals that, at 800 ºC sintering, abundant of micro-porosities could be seen which were considerably reduced after sintered at higher temperature. Based on the FESEM image, the dominant process that occurred after sintering over 1000 ºC was the coarsening of particle.

![Compressive strength of sintered pseudowollastonite-mullite (PSW-M) composite plotted against different compositions](image)

**Fig. 2** Compressive strength of sintered pseudowollastonite-mullite (PSW-M) composite plotted against different compositions The density was measured using Archimedes principle (Table 1). As the sintering
Table 1 Densification and elastic modulus of biocomposites at different sintering temperature

<table>
<thead>
<tr>
<th>Sample/ Sintering temperature (Time: 2 h)</th>
<th>Densification (%)</th>
<th>E.Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSW, 1150 ºC</td>
<td>89</td>
<td>150.40</td>
</tr>
<tr>
<td>800 ºC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSW10M</td>
<td>78.7</td>
<td>16.03</td>
</tr>
<tr>
<td>PSW20M</td>
<td>82.8</td>
<td>25.02</td>
</tr>
<tr>
<td>PSW30M</td>
<td>81</td>
<td>20.75</td>
</tr>
<tr>
<td>1000 ºC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSW10M</td>
<td>79.34</td>
<td>160.17</td>
</tr>
<tr>
<td>PSW20M</td>
<td>84.94</td>
<td>330.21</td>
</tr>
<tr>
<td>PSW30M</td>
<td>85.5</td>
<td>179.86</td>
</tr>
<tr>
<td>1150 ºC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSW10M</td>
<td>85.06</td>
<td>407.74</td>
</tr>
<tr>
<td>PSW20M</td>
<td>92.74</td>
<td>4370.00</td>
</tr>
<tr>
<td>PSW30M</td>
<td>90.04</td>
<td>2870.00</td>
</tr>
</tbody>
</table>

Fig. 3 The SEM micrographs and EDAX Spectrum of PSW20M sintered at temperature (a) 800 ºC, (b) 1000 ºC and (c) 1150 ºC
temperature increases, the density also increases due to the shrinkage that occur thus reduced porosity. Theoretically, as the porosity decrease, the mechanical property increases. Some research reported on the correlation of porosity rate, grain arrangement and the mechanical strength which supports this theory. The grain coarsening happen and at the meantime, the porosity rate were reduced [15]. Based on table 1, each sample represents relatively low dense. The maximum achievable density was only 92% $\rho_{th}$ for sample P20M sintered at temperature 1150 °C. This could be one of the possible reasons that lead to a moderately low compressive strength compared to other sintered ceramics (up to 350 MPa) [14]. Nevertheless, a great sudden increased in compressive strength after been sintered at 1150 °C proves that porosities and densification after sintering has some influence on the mechanical properties. Thus, the optimization of sintering parameters and phases existed after sintering was part of the major concern that may affect the mechanical strength of the composite.

4. SUMMARY

The compressive strength of the developed biocomposite PSW-M has been evaluated. The increments of sintering temperature for different compositions enhance the compressive strength. The addition of 20% of pseudowollastonite-mullite composite mixture sintered at temperature 1150 °C lead to the highest strength of biocomposite.

ACKNOWLEDGEMENT

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Effect of Acidic and Alkaline Treatments to Methylene Blue Adsorption from Aqueous Solution by Coconut Shell Activated Carbon

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ABSTRACT. In recent years, pollution from dye wastewater becomes a serious environmental problem due to the high demand and the increment of dye application in textile industry. The purpose of this study was to investigate the potential application of coconut shell activated carbon as methylene blue (MB) removal from aqueous solution. The carbonization process was conducted in temperature range from 300 to 500 °C. For the activation process, two different activating agents namely phosphoric acid, H3PO4 (acid activating agent) and sodium hydroxide, NaOH (basic activating agent) were used. Physical characterization of coconut shell activated carbon (CSAC) was realized by using X-ray diffraction (XRD) for phase identification. After that, the percentage of dye removal was investigated in order to determine the adsorption capacity of the prepared activated carbon. It can be concluded that when the dosage of CSAC increased, the amount of dye removal would also be increased. The results indicated that the coconut shell activated carbon could be employed as a low cost alternative in controlling wide range of sorption processes.

Keywords: Activated carbon, Coconut shell, Acidic, Alkaline, Methylene blue;

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1. INTRODUCTION

In recent years, contamination of the industrial waters with the organic based creates a serious environmental problem. Synthetic dye is a group of organic pollutants that are extensively used in several industries that can cause hazardous effect once introduced to aqueous solution [1]. Reactive dyes pose the
greatest problem in terms of colour, which is released by the textile industry [2]. Due to their chemical structures, dyes are resistant to light, water and many chemicals. Therefore, dyes are difficult to treat once they are released to the aquatic environment [3]. There are several approaches to remove the organic pollutants from wastewaters such as chemical oxidation, physicochemical and biological processes. Among these, adsorption is considered one of the most promising alternatives for the removal of organic pollutants from wastewater because of its simplicity, ease of operation, high removal efficiency and regeneration capacity [4]. Activated carbon is a well-known adsorbent that has been used effectively for the removal of organic pollutants, because it is a highly porous material and possesses an extensive surface area [5, 6].

Activated carbon could be produced from different raw carbon resources like lignite, peat, coal, as well as biomass resources namely wood, sawdust, bagasse, and coconut shells [7-9]. By reusing and recycling the agriculture waste like coconut shell into activated carbon, it provides another eco-friendly alternative to dispose the waste and reduce the impact of waste to the environment [10-12]. Activation process of native carbon into activated carbon could be realized by two different processes namely physical activation and chemical activation [13,14]. Chemical activation by using acid and alkali treatments could functionalize the surface of native carbon into activated carbon where the surface modification happens at the molecular level [15,16].

In this paper, activated carbon was produced from coconut shell with different activating agents namely H₃PO₄ and NaOH. Physical characterization was realized by XRD. Subsequently, the adsorption study of methylene blue removal from aqueous solution onto activated carbon was conducted using batch and dialysis tube adsorption methods to determine the adsorption capacity of the prepared activated carbon. It is expected that the active surface of CSAC would be able to remove the methylene blue from aqueous solution via adsorption process.

2. MATERIALS AND METHODS

2.1 Preparation of raw material. The coconut shell (CS) was washed repeatedly with tap water and crushed into smaller pieces. Then, the CS was dried in oven for 3 hours at 105 ºC to remove the moisture content. Next, the CS was ground and sieved by using 300 µm siever.

2.2 Adsorbent preparation using phosphoric acid (H₃PO₄). 85% of orthophosphoric acid was diluted into 40% of phosphoric acid. Then, the CS was soaked in heated solution of 40% phosphoric acid for 1 hour. Then, the CS was placed in furnace at 300 ºC for 1 hour for further activation process. Next, the CS was washed and filtered with hot and cold deionized water copiously until the pH reached to neutral. Finally, the CS was dried in oven at 120 ºC for 2 hours and stored in the airtight lid container prior to further analysis.

2.3 Adsorbent preparation using sodium hydroxide (NaOH). NaOH pellet was mixed with distilled water and stirred until it was fully dissolved. The CS was soaked in 4% of NaOH for 1 hour (CS:NaOH;1:20). Next, the CS was kept overnight before dried in oven at 105 ºC for 3 hours followed by the carbonization process in furnace at 200 ºC for 60 min for further activation process. After that, the CS was washed by 0.5 M HCl solution and hot deionized water to neutralize the pH. Later, the CS was rewashed with cold deionized water and dried in oven at 105 ºC for 2 hours and subsequently stored in airtight lid container.

2.4 X-ray diffraction (XRD) measurement. Phase identification of activated CSAC (XRD) was recorded on a Bruker D2 Phaser X-ray diffractometer with monochromatized Cu Kα radiation (λ=1.5418 Å).

2.5 Adsorption studies. 0.15 g of methylene blue (MB) powder was weighed and diluted with 20 ml of distilled water in 250 ml beaker. Then, the solution was stirred and added to the 100 ml volumetric flask followed by adding distilled water. Next, the dye solution was filtered by using 0.45 µm Whatman filter paper. Lastly, the prepared dye was stored in the polypropylene bottle. For batch adsorption study, 1 to 5 g of CSAC were weighed and distributed into 5 beakers containing 50 ml of MB with concentration of 50 mg/ml, respectively. Then, the mixture were stirred for 2 hours at 150 rpm and was left in room temperature for 24
hours. After that, the mixture was filtered with 0.45 μm Whatman filter paper. Subsequently, 1.5 ml was taken from MB solution and put the into cuvette followed by measurement with UV-VIS spectrophotometer at wavelength of 668 nm.

For adsorption study by dialysis tube, 1 to 5 g of CSAC were filled into 10 cm dialysis tube and tightly tied up. Then, the 1 to 5 g of CSAC were immersed in 5 beakers containing 50 mg/ml of MB each and were left in room temperature for 24 hours. After 24 hours, 1.5 ml was taken from each beaker and put into the cuvette followed by measurement with UV-VIS spectrophotometer at wavelength of 668 nm.

For kinetic study, 5 g of CSAC was weighed and was filled into 10 cm dialysis tube and tightly tied up. The dialysis tube with CSAC inside was immersed in 50 ml and 100 ml of MB with concentration of 100 mg/ml both with continuos stirring. Decolorization of MB was measured by taking 1.5 ml of MB solution in cuvette and observed by using UV-VIS spectrophotometer for each hour in 6 hours. Percentage of dye removal was calculated by using Eq. (1).

\[
\text{Percentage of dye removal (\%)} = \left(1 - \frac{C_i}{C_0}\right) \times 100
\]

where \(C_0\) is the initial concentration of dye while \(C_i\) is the concentration of dye at \(i\)-th hour.

3. RESULTS AND DISCUSSION

3.1 Characterization of the activated carbon. XRD analysis of coconut shell activated carbon as depicted in Fig. 1. Fig. 1(a) showed there were three sharp peaks obtained at the angle of 25°, 45° and 55° respectively which revealed the crystalline carbonaceous structure. The percentage of crystallinity for untreated carbon was 32.6% with percentages of amorphous of 67.4% [17]. For CSAC with NaOH activation, the crystalline peak can be seen at 65° followed by three sharp peaks at the angle of 25°, 45° and 55° for amorphous peaks as depicted in Fig. 1(b). The percentage of crystallinity was 29.4% with percentages of amorphous was 70.6%. While for CSAC with \(\text{H}_3\text{PO}_4\) activation revealed the highest crystalline peaks started at 20°, 30° and 50° followed by three sharp peaks at the angle of 17°, 22° and 18° for amorphous peak as shown in Fig. 1(b). The percentage of crystallinity was 35.2% with amorphous peak was 64.8%. Previous study revealed that the synthesized activated carbons in the form of high amorphous state with low crystallinity [14].

![Fig. 1 XRD profile of coconut shell (a) native carbon, (b) activated carbon with NaOH as activating agent and (c) activated carbon with \(\text{H}_3\text{PO}_4\) as activating agent](image-url)
3.2 Batch adsorption study. Generally, activated carbon could adsorb the organic material due to the attractive forces between the CSAC surface (non-polar) and the contaminant or adsorbate (MB) which is also non-polar. The attractive force between CSAC surface and the contaminant are found to be stronger than the attractive force of the contaminant with polar solvent (water) [18]. The adsorption rate increased with the increment of adsorbent dosage for 1 to 5 g of CSAC as illustrated in Fig. 2. When the active sites on the adsorbent were fully occupied with adsorbate (MB) molecules, it would be impossible for other adsorbate molecules to bind into the active site [19]. The adsorptive forces can only occur when the organic molecules are closed to the carbon surface.

![Fig. 2 Adsorption rate of methylene blue is directly proportional to coconut shell activated carbon (CSAC) dosage. (blue: CSAC basic activation with dialysis tube adsorption method, green: CSAC acid activation with batch adsorption method, red: CSAC acid activation with dialysis tube adsorption method)](image)

Investigation of dye removal percentage for 5 g/L of CSAC in 100 ml of 100 mg/L of MB and 50 of 100 mg/L of MB as illustrated in Fig. 3. The dosage of 5 g of CSAC was chosen in this kinetic study because the optimum dye removal could be achieved with this amount of activated carbon.

![Fig. 3 Comparison of decolorization percentage of methylene blue (%)](image)
It can be seen that the percentages of decolorization of MB increased with the increment of measurement time. The percentages of decolorization of 5 g CSAC in 100 ml of 100 mg/L of MB rose from 27.6 to 60.1% while the percentages of decolorization of 5 g CSAC in 50 ml of 100 mg/L of MB showed an increment from 43.3 to 71.1%. These results proved that the adsorption rate of 5 g CSAC in 50 ml of 100 mg/L of MB was better compared to 100 ml of 100 mg/L MB.

4. SUMMARY

The present study proved that the activated carbon prepared from coconut shell by acid and basic activation agents could be an excellent adsorbent for dye removal from aqueous solution. Characterizations of the prepared activated carbon by XRD revealed the presence of significantly different peaks of CSAC before and after activation process. The adsorption study of methylene blue removal from aqueous solution onto activated carbon was conducted using batch and dialysis tube adsorption methods. It can be concluded that when the dosage of CSAC increased, the amount of dye removal would also be increased. The adsorption rate will reach at the saturation point where the dye molecules will completely bind into CSAC pore and there were no longer molecules could be adsorbed on the CSAC surface. The results indicated that the coconut shell activated carbon could be employed as a low cost alternative in controlling wide range of sorption processes.

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Effect of Molarity of HCl on Production of Silica (SiO$_2$) From Palm Oil Fuel Ash (POFA)

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ABSTRACT. Palm oil fuels ash (POFA) is a by-product from palm oil industries that constitutes of different compounds such as silica (SiO$_2$), alumina (Al$_2$O$_3$) and many others, its abundances and improper disposal in waterways and as a landfill cause environmental pollution and hence need for its modification and usage. This paper presents an alternative way of producing silica from POFA. Untreated POFA was dried in an oven for 24 hours at a temperature of 110 °C and ground in a ball mill machine for 12 hours at a speed of 250 rev/s. After sieving, the powder was dispersed in 1 mole, 2 mole and 3 mole of HCl. An increase in the composition of SiO$_2$ was observed using X-ray Fluorescence (XRF) analysis due to the increase in the molarity of acid, X-ray Diffraction analysis (XRD) and Scanning Electron Microscopy (SEM) shows that POFA has a crystalline and porous cellular structure. This shows that acidic wash treatment is good and an improved method for the production of silica from POFA.

Keywords: Silica, POFA, Effect of molarity, Acidic wash treatment, Microstructure;

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1. INTRODUCTION

In countries like Malaysia and Thailand palm oil industries are some of the major agro-industries. To extract crude palm oil, the industries uses waste removed from fresh fruit of palm oil such as fiber, shell and empty fruit bunches to heat up the turbine and generate electricity for palm oil extraction [1]. After extracting crude palm oil, Palm oil fuel ash (POFA) is produced and disposed in waterways and as landfill of no economic value and causes environmentally unfriendly situation [2-6].

POFA has a pozzolanic properties therefore can be used as partial cement replacement without sacrificing for either the mechanical or physical properties of cement [4,7,8]. The only feasible solution to reduce future environmental problems that may be caused by disposal of POFA is to use it as replacement of cement in concrete or quartz in ceramic industry [9]. Malaysia is among the largest producers of palm oil, thus, facing environmental problems by disposing palm oil fuel ash. In 2007, it was estimated that 3 million tons of POFA was produced and this figures are expected to increase annually as the palm oil plantations increased [10]. Research by Altwair [11] shows that, to lower the cost of production of Portland cement and also improve the durability and engineering properties of concrete, partial replacement of cement with POFA...
is necessary. Use of POFA not only contribute to a healthier and sustainable environment but also increasing the ecological properties of concrete.

Waste by-products such as fly ash, rice husk ash, silica fume and POFA were used by several researchers as either replacement or filler to produce concretes due to their potentials [12] but only few used these wastes as replacement of quartz, feldspar or clay. This paper aimed at presenting a different method of POFA treatment using hydrochloric acid (HCl) for the optimum production of silica.

2. MATERIALS AND METHODS

POFA usually contained unburnt materials; therefore removal of these excess carbons is necessary as to increase its reactivity. Raw POFA was dried in an oven for 24 hours at a temperature of 110 °C, to obtain a fineness material the powder was then grounded in a ball mill machine for 12 hours at a speed of 250 rev/s. The powder is then sieved with a set of sieve for particle size less than 50 µm. The powder undergoes different types of acidic treatment in order to have an optimum amount of silica from the upcoming characterization. POFA powder was then divided into 3 and was dispersed in 1 mole, 2 moles and 3 mole of HCl and an electric shaker was used to shake it for 30 minute. A Whatman ashless filter paper was used to filter the solution and separate the treated POFA from the acidic solution. The powder was then dried again to remove the acid moisture in an oven for 24 hours at temperature of 110 °C and then grind using ball mill machine for 90 min and then sieve to remove the agglomeration and obtain a fine powder. Energy dispersive X-ray and X-ray florescence analysis (XRF) were used to analyze the elemental and chemical compositions of POFA, to determine the morphology and phase of the POFA powder scanning electron microscopy and X-ray diffraction analysis were used.

3. RESULTS AND DISCUSSION

The chemical composition of POFA was determined using XRF, the machine was operated at 60 KVP and 50 mA. The result shows the presence of SiO₂ and many other compounds, it is clear that SiO₂ is the major composition then followed by other compounds such as CaO, K₂O, P₂O₅, Fe₂O₃ and Al₂O₃ as seen in Table 1.

The result also shows that acidic wash treatment is efficient and enhances the production of silica from POFA as the amount of silica increased from 54.33 wt.%, 56.17 wt.% and 59.77 wt.% by 1 mole, 2 mole and 3 mole acid treatment, respectively as shown in Table 1. This shows that acidic wash treatment is a good treatment for the optimum production of silica (SiO₂) from POFA. Table 1 below shows chemical composition of POFA using XRF.

The morphological structure was analyzed using JOEL-JSM 6380 Scanning Electron Microscopy (SEM) operated at 15 KV. A 1000X magnification was used to capture the image of the POFA powder, from Fig. 1 it can be deduce that POFA has spongy and porous nature with irregular shapes. It can be seen clearly from the micrographs that due to the acidic wash treatment the powder agglomerates and form porous structure and become irregular. After the acidic wash treatment, the particle compacted together and form amorphous-like structure, the picture revealed that POFA treated with 2 mole and 3 mole of HCl become more stacked and packed together than that treated with 1mole of HCl acid and this may be as a result of the reaction between acid and chemical compounds present in palm oil fuel ash (POFA).

Fig. 3 shows the XRD patterns of 1 mole, 2 mole and 3 mole HCl acid treatment, respectively. The result indicates the presence of quartz (Q) as the major phase and calcium silicide (CS) = aluminum phosphate (A) and manganese oxide (M) as minor phase for 1 mole HCl treatment. After the molarity of acid was increased to 2 mole the crystalline phases determined are Q as major phase and other minor phases. Similarly, for 3 mole the peak increase and the crystalline phase detected are Q as major phase and magnesium silicate as minor.
Table 1 Chemical composition of POFA

<table>
<thead>
<tr>
<th>Composition of POFA</th>
<th>Different molarities of acid (HCl) (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 mole</td>
</tr>
<tr>
<td>SiO₂</td>
<td>54.33</td>
</tr>
<tr>
<td>C</td>
<td>6.22</td>
</tr>
<tr>
<td>CaO</td>
<td>5.63</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.63</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>6.65</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.20</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.74</td>
</tr>
<tr>
<td>Cl</td>
<td>8.25</td>
</tr>
<tr>
<td>MgO</td>
<td>1.88</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.91</td>
</tr>
<tr>
<td>TiO₂</td>
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</tr>
<tr>
<td>MnO</td>
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<tr>
<td>Cr₂O₃</td>
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</tr>
<tr>
<td>ZrO₂</td>
<td>0.03</td>
</tr>
<tr>
<td>CuO</td>
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<tr>
<td>SrO</td>
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</tr>
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<td>ZnO</td>
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<tr>
<td>Na₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>Rb₂O</td>
<td>0.02</td>
</tr>
<tr>
<td>NiO</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Fig. 1 SEM micrographs of (a) 1 mole (b) 2 mole and (c) 3 mole HCl acid treatment

Non-carbon EDX analysis of POFA treated with 1 mole, 2 mole and 3 mole of HCl acid reveals that (with assumption that all Si come in form of SiO₂ as reported by Kalapathy et al. [13] SiO₂ has the highest elemental composition then the remaining elements. Fig. 2 shows the EDX of (a) 1 mole, (b) 2 mole and (c) 3 mole HCl acid treatment.
Fig. 2 EDX of (a) 1 mole, (b) 2 mole and (c) 3 mole HCl acid treatment

Fig. 3 XRD Pattern of 1mole, 2mole and 3mole HCl acid treatment
4. SUMMARY

The amount of silica increased as the molarity of acid wash increased, the XRF result indicated that acidic wash treatment is good for the production of silica (SiO\textsubscript{2}) from palm oil fuel ash (POFA). The SiO\textsubscript{2} peaks show an incredible increase from 1 mole to 3 mole with increase from 54.33 wt.% to 59.77 wt.% This study proved that HCl wash treatment is suitable for the optimization of silica production.

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REFERENCES

Effect of Solid Loading on Fabrication of Porous Cordierite
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ABSTRACT. The cordierite powder was synthesized through glass melting method using silica, magnesia and alumina as raw materials. The cordierite powder was used to fabricate porous cordierite. The porous cordierite was fabricated through gelcasting method. The cordierite powder, polyethylenimine and distilled water was mixed together for 2 hours. The solid loading of cordierite slurry were varied to get the best properties of porous cordierite (62 - 72 wt.% solid loading). The foaming agent was added to be the cordierite foam, the green body was sintered at 1350 °C. The porosity of porous cordierite show when solid loading increase, the porosity decrease. The compressive strength also increase when solid loading increase.

Keywords: Porous ceramic, Solid loading, Cordierite;

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1. INTRODUCTION
Cordierite (Mg2Al4Si5O18) is a magnesium-aluminium-silicate mineral. There are great deal of intension since it has a lot of excellent properties of cordierite ceramics such as low thermal expansion coefficient, excellent thermal shock resistance, low dielectric constant, high resistivity, high chemical durability, high refractoriness and high mechanical strength [1]. These excellent properties contribute to wide application such as electrical porcelains, catalytic converter substrates for exhaust gas control in automobiles, heat exchanger for gas turbine engines, industrial furnaces, packing materials in electronic packing, refractory coating on metals and integrated circuit substrates [2].

Porous cordierite is one of the great interest in porous ceramics due to its demand for wide application such as filters, membranes, catalytic substrates, thermal insulation, gas burner media, and as refractory material [3]. Porous cordierite has become the new development of cordierite materials [4]. In porous ceramics, the pore structure influenced the mechanical properties of porous ceramic [5] while the solid landing will influence the pore structure of porous ceramic. The aim of this study is to investigate the effect of solid loading on fabrication of porous cordierite.

2. MATERIALS AND METHODS
2.1 Synthesis of cordierite powder. A mixture of alumina (Al2O3), silica (SiO2) and magnesia (MgO) was dry mixed together for 6 hours using polyethylene bottle. The homogeneous mixture powder was put into alumina crucible and melted at 1550°C for 4 hours soaking time in Elevator Hearth, Lenton EHF 1700. Then, the melted powder was quenched in the water to get frit. The frit was dried for 24 hours at 80°C. The frit was crushed to the small size and milled for 5 hours (D50=7.39 μm) using Planetary Mill. After that, the milled powder was used for fabrication of porous cordierite using gelcasting method.
2.2 Fabrication of porous cordierite. The cordierite powder (62.0, 67.1, 72.0 wt.%), distilled water (28.8 wt.%) and polyethyleneimine (4.1 wt.%) as dispersant was mixed together for 2 hours at 600 rpm. After mixing, the sodium dodecyl sulfate (SDS) as foaming agent was added while the cordierite slurries were vigorously mixed at a rate of 1000 rpm to the mixture for expand the mixture 4 times from original volume. Then, 1.4 wt.% of gelation agent, Denacol-EX614B (Nagase Chemical Co. Ltd., Japan) was added to maintain the bubble shapes of slurry. Immediately after the SDS as foaming process, the bubbled cordierite slurries was moulded. The moulded cordierite slurries was sealed for 1 hour at room temperature. The wet green bodies were demoulded and immediately moved to a drying oven at 80°C. After 24 hours drying using drying oven and sintering was performed using Lenton Furnace at 1350°C for 2 hours using heating rate 100°C/hour up to 600°C and the 200°C/hour up to 1350°C. The slower heating rate was used until 600°C due to decomposition of polymer in the green body.

2.3 Characterization. The purity of cordierite was characterized using X-ray diffraction analysis. The porosity of porous cordierite was measure using Archimedes Method, the morphology of porous cordierite was observed using Scanning Electron Microscope (SEM) and the compressive strength was measured using Instron Machine.

3. RESULTS AND DISCUSSION

3.1 Glass produced after quenching. Fig. 1 shows the glass produced after melting. The glass was placed on white paper and the transparency was observed using the naked eye. Based on Fig. 1, all of the glasses produced are transparent. These glasses were produced after rapid cooling from molten state that is fast enough to avoid crystallisation. This result was in agreement with the previous study by Banjuraizah et al. (2011), which used the glass melting method to produce cordierite and they found that a transparent glass was in an amorphous phase. This is due to the molecules in the glass being stacked randomly. Random organisation of molecules in glass caused the formation of such gap and will be filled with air and as a scattering point for light penetration [6].

![Glass produced after quenching](image-url)
3.2 X-ray diffraction of glass. XRD analysis was conducted to confirm that the glass produced after quenching. Fig. 2 shows the XRD pattern of the glass powder. A large amorphous hump and no crystalline peaks were detected in the diffraction pattern of the sample melted at 1550 °C.

![X-ray diffraction pattern of glass](image)

**Fig. 2** X-ray diffraction pattern of glass

The absence of peaks in the XRD pattern indicated that the compound was completely transformed into amorphous or glassy phase. Atoms in the glass were randomly moved during melting [7], producing an amorphous hump in the XRD pattern. The amorphous phase of the glass was proven by the transparent appearance shown in Fig. 1.

3.3 X-ray diffraction of porous cordierite. Fig. 3 shows the X-ray diffraction pattern of the sintered porous cordierite. The main component of the powder was 98.9% cordierite, plus small amount of cristabolite low, 1.1%. The high purity of cordierite powder was successful produced. The melting temperature, 1550°C will produced high purity of cordierite powder. The high purity of cordierite powder needed to ensure the properties of porous cordierite maximized. The raw materials was melted in high temperature (above 1550°C).

The amount of cristabolite lower, the so the high purity of cordierite will obtained [4]. Any molten substance will form a glass if it was cooled fast enough. Therefore, melting at a much lower temperature requires the molten glass to be cooled at a sufficiently high rate to avoid a significant degree of crystallization so that the ‘disordered’ atomic configuration of the liquid state is frozen in, thus avoiding the formation and growth of crystal [6].

The 62 and 67.1 wt.% solid loading samples was fabricated but 72 wt.% solid loading sample was fail to fabricate because the cordierite slurry too viscous. The bubble unable to form when foaming agent were added. Table 1 shows the porosity of porous cordierite using 62 wt. % and 67.1 wt. % solid loading of cordierite powder.
According to the results, the porosity was decreased from 79.83% to 60.58% by increasing solid loading from 62 wt.% to 67.1 wt.%. Results obtained were in agreement with Le Huec et al. (1995) and Jamaludin et al. (2014). They stated that when the solid loading increases, the solid content in the slurry increases, which creates low porosity of porous ceramic [8,9].

**Fig.3** X-ray diffraction pattern of porous cordierite

**Table 1** Porosity of porous cordierite at different solid loading

<table>
<thead>
<tr>
<th>Solid loading (wt. %)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.0</td>
<td>79.83</td>
</tr>
<tr>
<td>67.1</td>
<td>60.58</td>
</tr>
</tbody>
</table>

Pore size and pore distribution for porous cordierite produced using 62 wt.% and 67.1 wt.% solid loading were observed through SEM and are presented in Fig.4.
Both samples in Fig.4 contained interconnected open pore structure with non-uniform distribution. However, a lot of broken struts were found on 62% solid loading sample (Fig.4(a)), which almost collapsed the structure. Meanwhile, no cracks were observed in the 67.1% solid loading sample (Fig.4(b)). It is strongly believed that the failure in the lower content of solid loading sample was due to insufficient solid content to strengthen the wall to prevent it from collapsing. The smoother surface structure were also observed in sample with higher solid loading (67.1 wt.%). Meanwhile, irregular shape and the present of cracks on the struts were observed in the 62% solid loading sample. In order to support the previous result, strength determination through compressive strength were completed on the sample produced using different amounts of solid loading. Table 2 shows the strength of porous cordierite at different solid loading.

**Table 2** Strength of porous cordierite at different of solid loading

<table>
<thead>
<tr>
<th>Solid loading (wt.%)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.0</td>
<td>1.59</td>
</tr>
<tr>
<td>67.1</td>
<td>5.43</td>
</tr>
</tbody>
</table>

Result showed that compressive strength increased from 1.59 to 5.43 MPa by increasing solid loading from 62 to 67.1 wt.% . According to Macchetta et al. [10], the strength of porous ceramic strongly depended on the porosity, where the porosity decreased as the solid loading of the slurry decreased. The less solid proportion will cause low strength due to the fewer obstacles on external force [8].

4. **SUMMARY**

The cordierite powder was successful synthesized through glass melting method. The porous cordierite were successful fabricated with different solid loading. The higher solid loading resulted lower porosity and high compressive strength. 67.1 wt.% sample show better structure compare to 62 wt.%.

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Effect of Urea Formaldehyde to the Mechanical Properties of Particleboard from Neolamarckia Cadamba and Endospermum Diadenum

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ABSTRACT. The demand and trend uses wood panel such as particleboard is increasing. It cause faced problem in shortage of raw material sources. This research was carried out to investigate the mechanical properties of particleboard (PB) by using two different wood waste of neolamarckia cadamba (NC) and endospermum diadenum (ED). NC and ED are fast growing species available in Peninsular Malaysia. A single layer particleboard was fabricated with 0.8 mm particle size with density 650 kg/m³ and bonded with urea formaldehyde (UF) as binder. NC and ED species based of oven-dry weight and amount of adhesive which are 8%, 10% and 12%. The mechanical properties in bending strength modulus of rupture (MOR) and modulus of elasticity (MOE) and internal bond (IB) were determined. The morphological observation on PB was conducted using light microscopy and field emission scanning electron microscopy. The results of morphological properties of ED species shows were less adhesion between fiber and UF in the structure. The results of mechanical properties shows MOR testing of NC wood species at 12% had the highest values which are 25.20 N/mm² compared to ED species of 24.07 N/mm². However, the results of MOE and IB testing shows the samples of ED had the highest values which is 3303.32 and 1.29 N/mm² compared to NC wood species has 3226.07 and 1.12 N/mm². Thus, NC and ED particles can be used as a raw materials to wood-based PB for general purpose application.

Keywords: Particle board, Urea formaldehyde, Neolamarckia cadamba, Endospermum diadenum;

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1. INTRODUCTION

The alternative of natural woody species have been declining, causing the search for new lignocellulosic materials that may efficiently meet the demand. Due to the rise in wood consumption, this issue makes the researcher identify regarding a new products and better utilization of the new raw material available. The main materials use nowadays to produce furniture is using engineered wood as known as wood composite. The production of wood composite is widely commercial around the world due to its applications, advantages, cost and multifunction [1-3]. Furthermore, by used wood waste materials in producing wood composite might profitable and might reduce the wood waste through reuse to maintain the ecosystem in the future.
Recently, many different lignocellulosic woods were used in particleboard production; such as coconut chips [4], waste tea leaves [5] and wheat straw [6]. The reason of using those materials because to utilize the waste become new materials in PB production. Particleboard is a wood based composite come up with any shapes and sizes of wood particles of lignocelluloses materials which is bonded together with an adhesive and associated under heat and pressure [7].

Utilization of wood chips can be one of the factor in varying more types of composite panel products. Wood chips can be utilized to produces any types of wood composite as main materials in wood composite manufacturing. Furthermore, the wood composite can be engineered to various specifications and applications.

NC is fast-growing tree species which is being advanced for its physical and mechanical properties in order to assess its potential for future utilization [8]. NC species can be commercialized as raw material for PB industry [7]. Thus, NC and ED have many benefits and can be modified for wood chips, veneer and wood composites. ED is one of the good alternative timber for furniture industry [9]. This species also can be considerable portion of the supply for raw materials. In this work, the morphology of NC and ED in wood composite for particleboard application was carried out by FESEM.

2. MATERIALS AND METHODS

The main materials to produce particleboard is from wood waste of NC and ED. Wood waste is obtained from Forest Research Institute Malaysia (FRIM). The wood excessive in the form of wood end cut, wood chips and sawn timber. A single layer particleboard was fabricated with 0.8 mm particle size with density 650 kg/m³ and bonded with UF as binder. NC and ED species based of oven-dry weight and amount of adhesive which are 8%, 10% and 12% was applied, respectively. The board were evaluated to determine its mechanical properties which is MOR, MOE and IB based on British European Standard (BS EN 310, 319-1993). The sample proceeded to examine the surface of sample by using light microscopy model Jenoptik Progres Capture Pro 21001 magnification applied were 20x each sample. The morphologies analysis of PB composites was conducted using (FESEM) Zeiss Supra 40-VP used to identify clearer image on the surface morphology of the board composite samples.

3. RESULTS AND DISCUSSION

3.1 Bending Strength. Bending strength test was carried out to determine the MOR and MOE of single layer particleboard composite. MOR applied to determine the suitability of materials for structural application and specifies the ability of a sample to bear a transverse (bending) force perpendicular to its longitudinal axis [10]. Table 1 shows the MOR and MOE of single layer particleboard composite with different resin content which is 8%, 10%, 12% at same density of 650 kg/m³ with two different wood species. From the results obtained, NC species shows improvement compare to ED species. Whereas the MOR values increased from 20.73 N/mm² to 25.20 N/mm² as shown in Table 1. Besides that, ED species also has improvement MOR values which is increased from 20.60 N/mm² to 24.07 N/mm². The MOR values increase with the increasing amount of resin content of each panel. According to the British European Standard the MOR requirement is 14 N/mm² EN310-1993. Most of the values is passed.

Table 1 shows the results of MOE for both species. Overall, ED species has better strength compared to NC species in terms of MOE testing. The MOE values of ED has increased from 2591.37 N/mm² to 3303.32 N/mm². As well, MOE values for NC species also has increased from 2985.55 to 3226.08 N/mm². It proved that the increasing of resin addition increasing the MOR values was obtain. Similar results had been observed by [11, 12] who reported that the urea UF could effectively be useful as binder for the manufacturing of
particleboard. Previous study [13] who stated that different wood species used in producing particleboard would effect to the properties of particleboard because it related to the sorption properties and chemical composition of wood itself. Based on the MOE (EN310-1993) requirement is 11800 N/mm², MOE value is met the requirement.

3.2 Internal Bonding Strength. Table 1 show the IB values of single layer particleboard composite were produced. This test was used to determine the resistance to tension perpendicular to the plane of the particleboard. From the results obtained, ED species shows the improvement compared to NC species. The IB values increased from 0.65 N/mm² to 1.29 N/mm². The amount of resin used had effects the internal bond strength of the panel due to the excessive amount of resin would reduce the wettability properties of the particles [14-15]. These indicated that higher amount of resins boosts up strength of interfacial bonding between fibers in the boards panel, thus could extend the ability for the boards to withstand the pulling force created through the test. According to the BS EN the IB requirement is 0.40 N/mm² EN310-1993. Mostly all the IB value is met the requirement.

### Table 1 Mechanical testing of particleboard panel bonded with different species ratio and resin content

<table>
<thead>
<tr>
<th>Species Ratio</th>
<th>Resin Content (%)</th>
<th>Mechanical Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MOR (N/mm²)</td>
<td>MOE (N/mm²)</td>
</tr>
<tr>
<td>NC</td>
<td>8</td>
<td>20.73</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>23.03</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>25.20</td>
</tr>
<tr>
<td>ED</td>
<td>8</td>
<td>20.60</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>23.82</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>24.07</td>
</tr>
</tbody>
</table>

3.3 Morphology observation. Fig. 1 shows the images of ED board panel with different resin content using light microscopy with 20x magnification. It can be seen the surface of panel has glue spot and uneven distribution of glue as marked with red circles shown in Fig. 1 (a) and (b). It occurred during the preparation in mixing process of panel board between fiber and UF. The distribution of UF in uneven condition caused glue spot on the surface of board. This is because the panel ED wood species did not give better performance. Thus, can be proven according to the previous test evaluation results which is has lowest values.

![Fig. 1 Surface morphology ED species of 8%, 10%, and 12% UF](image-url)
Thus, the good spreading of binder will increase the properties of panel board. It might improve the mechanical properties of panel. Therefore, it can be proven according to the previous test evaluation results which is has higher values.

![Fig. 2] Surface morphology panel NC species of (a) 8%, (b) 10%, and (c) 12% of UF

Fig. 2 shows the surface morphology of NC board panel with different resin content using light microscopy with 20x magnification. Refer to the Fig. 2 (c) it can be seen clearly the surface of panel board is in good condition without any glue spot on the surface. Besides, the arrangement of wood particles in uniform arrangement as marked with red arrow. The glue with uniform distribution along the wood particles made the binder easy to penetrate between UF and NC fiber. As more glue penetrate into the wood fiber might improve the strength properties.

The effect of different species and UF resin as a binder in manufactured particleboard panel was observed by FESEM analysis. The FESEM micrograph of the particle board are shown in Fig. 3. From the Fig. 3 (a) it can be observed that, the particle of the NC species shows better structure between fiber and UF in the structure due to the different species of the particleboard panels as mark with red arrow compared to Fig. 3 (b) shows a poor properties. The macrostructural of ED species revealed uneven distribution of UF on the surface as mark with red arrow. The condition of ED species cause the panel has lower properties in terms of MOR, MOE and IB.

![Fig. 3] FESEM image of panel (a) NC and (b) ED wood species at 8% UF

This can see more clearly on the panel produced with NC and ED wood species. Therefore, the mechanical strength of the panels also improve especially for panel manufactured using NC species. UF resin at 8% did not give better bonding between wood particles and binder. The microstructure shows as 8% of UF contribute poorest bonding particles was obtained as shown in Fig. 3a. In addition, used of more resin content increased the bonding hence improved the interfacial bonding between fiber in boards as shown in Table 1.
This can be proven through mechanical properties testing whereas the NC species showed the highest strength properties of particleboard panel compared to ED species as shown in Table 1.

4. SUMMARY

The objective of this study was to investigate the mechanical properties of particle board by using two different wood waste of NC and ED. The panel made of NC shows highest values of MOR which are 25.20 N/mm² compared to ED which is 24.07N/mm². IB board made of ED showed high value compared to NC which is 1.29N/mm². Different wood species and different amount of resin content are affects the strength properties of particleboard. Hence, NC and ED particles can be used as a raw materials to wood composite particleboard for product applications in order to sustain the resource for wood-based industry in the future.

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Elucidation of Morphological Behavior on the Samarium Strontium Cobaltite Carbonate Composite Cathode for LT-SOFC

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ABSTRACT. Samarium strontium cobaltite, Sm0.5Sr0.5CoO3-δ (SSC) and samarium doped ceria, Sm0.2Ce0.8O1.9 (SDC) carbonate or (SDCC) was used as the new composite cathode powder materials. Composites cathode powder samples with different weight percentages, 50:50 wt.% of SSC:SDCC, 60:40 wt.% of SSC:SDCC and 70:30 wt.% of SSC:SDCC were chosen to be use in this research work. The prepared samples of composite cathode powders were characterized by using high energy ball milling (HEBM) techniques for LT-SOFC application. Characterizations of the composite cathode were performed through energy dispersion spectroscopy (EDS) and field emission scanning electron microscopy (FESEM) analysis. From EDS analysis shows SSC-SDCC composite cathode powders produced via high energy ball milling techniques (HEBM) or mechanochemical activation indicated that all major elements such as sodium, cobalt, samarium, cerium and strontium were well distributed among the composite cathode powders. Nonetheless, the FESEM images revealed HEBM technique can be used to prepare composite cathode powders with high homogeneity. These results showed that SSC-SDCC composite cathode powders, content with 50 wt.% of SDCC revealed a smallest of particle size with good homogeneity of particle to be used as cathode materials for LT-SOFC applications.

Keywords: SSC, SOFC, Carbonate composite electrolyte, High Energy Ball Milling;

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1. INTRODUCTION

The demand for secure, sustainable and clean energy sources has stimulated countless interests in the electrochemical energy storage and conversion technologies such as fuel cells, batteries and super capacitors. Solid oxide fuel cells (SOFCs) are considered as one of the most promising energy exchange devices which show advantages of high efficiency, fuel flexible and low emission. Development of SOFCs which devoted on issues associated with reduced operational temperature and presents significant solutions regarding (anode, cathode and electrolyte) material selection, synthesis, and processing. Due to reliability issues at high operating temperature, currently, SOFCs research have been motivated towards the cell development of low temperature (LT) to intermediate temperature (IT) [1,2]. The stability of the LT-SOFC performance with excellent of power density is the main key with operating temperature within the range of 400 °C to 600 °C (Morandi, 2013). However, the cathode has been the center of the focus in the electrode development largely. In order to maintain sufficient high electrochemical activity to enable SOFC operating at lower temperatures, it is also critically important to have new cathode materials with low polarization loss [4]. Rare earth cobalt...
oxide such as samarium strontium cobalt oxide, Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (SSC) has attracted much attention as cathode due to high mixed ionic and electronic conductivities at low temperature that can improve the cell durability and stability issues. This promising material been revealed as a potential cathode material reveals a good electro-catalyst for oxygen reduction compared to BSCF and particularly compatible with the ceria carbonate based electrolytes [5,6]. Unfortunately, SSC itself is having high reactivity with some electrolytes when operating at high temperature [7,8]. Previous author had proven this disadvantage can be diminish with incorporation samarium doped ceria (SDC) electrolyte with pure of SSC (H Lv, Wu, Huang, Zhao, & Hu, 2006). The introduction of certain amount from alkaline salts into samarium cerium oxide or SDC in order to develop new SDC-ceramic (SDCC) were improve the electrical performances and stability of the chemical part compared with pristine of SDC. Currently, there has no reported regarding study on the preparation of SSC-SDCC composite cathodes. Furthermore, the electrical properties might be improves with this new composite cathode by expecting the increase in triple phase boundary value (TPB) [9,10].

Beside the selection of cathode materials used, the processing of starting composite powder with, such as milling process strongly influence the composite cathode powder properties and subsequently the cell performance. Preparation of composite cathode powders with high energy ball milling (HEBM) or mechanochemical activation oriented technique potentially produces a fine and well distributed powder (Gao, Zhao, Zhou, Ran, & Shao, 2011). Furthermore, the information regarding preparation of SSC-SDCC by using this technique is still rare. Homogenous and fine powders might be obtained from this new SSC-SDCC composite cathode which prepared using this outstanding HEBM technique [12,13]. In the present study, morphological studies of new composite cathode powder microstructure will be investigated. These characterizations will be done by EDS analysis and FESEM.

2. MATERIALS AND METHODS

2.1 Powder preparation. In this study, three groups of samples were prepared. Began with producing composite electrolyte which has been prepared by employing suitable amounts of 20 wt.% from the binary carbonates (67 mole.% lithium carbonate, Li$_2$CO$_3$: 33 mole% sodium carbonate Na$_2$CO$_3$) and 80 wt.% from the Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ powders. The mixed electrolyte powder was milled together by employing wet ball milling technique (Fritsch Pulveristte, Germany) with low speed of rpm in ethanol for 1 day. After a complete mixed, the powders were further dried in an oven. This process was done in order to eliminate excess ethanol with temperature at 100 °C for 1 day. After the composite electrolyte powder produced, it was grounded using agate mortar and followed by calcinations process in a furnace with temperature at 680 °C for 1 hour. In order to prepare composite cathode powders, the commercial Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ raw powder (Kceracell, Korea) containing different weight percentages of Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ and Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ carbonate as presented in Table 1 were then mixed together followed with milling process. HEBM from Fritsch Pulveristte 6, was applied in order to obtain SSC based composite cathode powders using of bowl from zirconium oxide, in an ethanol as the milling medium at high speed of rpm for 2 hours. Finally the similar procedure was employed until all the composite cathode powder was grounded, before it will be used for further characterization as mention in the next section.

Table 1 List of composite cathode powders

<table>
<thead>
<tr>
<th>Sample recognition</th>
<th>SSC (wt.%)</th>
<th>SDCC (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC-CE55</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>SSC-CE64</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>SSC-CE73</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

2.2 Characterization. For investigating the nature of all the samples, EDS analysis of SSC-SDCC powders were
analyzed using scanning electron microscopy-energy dispersion spectroscopy mapping (SEM-EDS mapping) (JEOL-JSM 6380LA, Japan). While FESEM image has been conducted via field emission scanning electron microscopy, (JEOL, JSM-7600F, Japan) The average composite particle size was attained by measuring of 50 particles via Image J 1.48 software, while

3. RESULTS AND DISCUSSION

Morphology at Fig. 1 shows the elements distributions and EDS spectrum of SSC-CE55, SSC-CE64 and SSC-CE73 composite cathode powders after high energy ball milling process. All of SSC based composite cathode powders indicated that all major elements such as sodium (Na), samarium (Sm), strontium (Sr), cobalt (Co) and cerium (Ce) were homogenously and well distributed among the composite cathode powders [14]. However, for lithium (Li) was not detected from EDS due to its low atomic mass. The implementation of HEBM with high speed method able to disperse the elements homogeneously [13]. From EDS spectrum shows the intensity of the elements which has been contained in the SSC-SDCC composite cathode powder. Quantitative results revealed the amount of each element is given in percentages atom. SSC-CE55 display highest atomic percentage for Na elements followed by SSC-CE64 and SSC-CE73. However, for SSC cathode powders, SSC-CE73 gives a highest atomic percentage compared with SSC-CE64 and SSC-CE55. This phenomenal illustrations that the amount for carbonate content and the cathode content is in line with the carbonate compositions. The homogeneity of particle distributions of each element was very crucial in order to provide each of the elements optimize functioning during oxidation reduction process as well as increased the effectiveness of electrochemical reactions that takes part in cathode [15].

![Fig. 1 EDS spectrum of SSC-CE55 composite cathode powder](image)

The FESEM morphologies of the SSC-SDCC composite cathode powders for all samples were in nano-submicron size, as shown in Fig. 2. The powder morphology of the raw commercial SSC, calcined SDCC, and uncalcined SSC-CE55, SSC-CE64 and SSC-CE73 composite cathode powders, are in nano-scale. All the samples of SSC based composite cathode powders prepared via HEBM at different SSC loadings (50 wt.% to 70 wt.%)
display a good powder distribution and fine equiaxed agglomerates (Fig. 2) [15]. The particles of the composite cathode powders obtained were suggestively tiny compared to the starting raw powder of pure SSC. This changes in the particles size as compared to the initial value, can be a measure of the HEBM effectiveness. Analysis of data obtainable in Table 2, allows us to conclude that reduction in particles size as evidenced by the reduction of average composite cathode powders particle size. The mechanical energy created during the ball milling process occurred possible to break particles into tiny pieces. This observation will promote an enlargement on surface area of SSC based composite cathode powders within a shorter processing time. The increased surface area indicates good porosity behaviour and remarkable the expansion of TPB area which subsequently magnify the cell performance of SSC-SDCC composite cathode [16,17,18].

![Fig. 2 FESEM micrograph of SSC, calcined SDCC and SSC-SDCC composite cathode powders](image)

**Table 2** Mean value of particle size for raw and composite cathode powders

<table>
<thead>
<tr>
<th>Sample recognition</th>
<th>Mean value of composite particle size ($D_{\text{FESEM}}$, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SSC</td>
<td>89.01</td>
</tr>
<tr>
<td>Calcined SDCC</td>
<td>226.66</td>
</tr>
<tr>
<td>SSC-CE55</td>
<td>72.10</td>
</tr>
<tr>
<td>SSC-CE64</td>
<td>77.30</td>
</tr>
<tr>
<td>SSC-CE73</td>
<td>78.00</td>
</tr>
</tbody>
</table>

4. **SUMMARY**

Preparation of SSC based composite cathode powder with incorporation of carbonate were optimized using HEBM technique. EDS analysis display SSC based composite cathode powders produced via ball milling
demonstrations all major elements such as sodium, cobalt, samarium, cerium and strontium were distributed in good manner. FESEM images were confirmed that HEBM can be used to prepare composite cathode powders with high homogeneity. HEBM technique dramatically influenced the particle size and morphology of the composite cathode powders and has been revealed that SSC with 50% of Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ carbonate content has high potential to be used as cathode powder materials for LTSOFC applications. However, further detailed analysis will be accomplished in future to determine the effects of carbonate content based on the calcination process, sintering, porosity, thermal expansion coefficients, electrochemical characterization and single cell performance testing.

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Enhancement of K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN) Properties through Optimization of Pressure Applied during Sintering Process via HIP Methods

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ABSTRACT. KNN ceramics were synthesized by solid state reaction method. This investigation was focused on the influence of pressure applied during sintering process via HIP technique to the phase formation, microstructure, density, piezoelectric and dielectric properties of KNN where argon gas pressure applied were varied (2900, 7257 and 14504 psi, respectively). The increment of pressure caused broadening of peak of XRD pattern, increase in peak intensity, density, grain size, and dielectric properties up to 7257 psi. However, at 14504 psi, the grain size start to drop and slightly decrease in dielectric properties.

Keywords: KNN, HIP, Piezoelectric, Dielectric;

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1. INTRODUCTION

Lead Zirconate Titanate (PZT) was being used frequently as piezoelectric ceramics as actuators and sensors because of their superior piezoelectric and electrical properties [1]. But, the lead based ceramics will cause a serious environmental issue because of their high toxicity of lead and easily to vapourize when exposed to a high sintering temperature [2]. Several works have been done by other researcher in order to develop lead-free piezoelectric ceramics with excellent piezoelectric properties besides replacing the lead based materials in various application. There are several example of lead free piezoelectric ceramic such as Bi$_{0.5}$Na$_{0.5}$TiO$_3$-based materials, Tungsten bronze type materials and alkaline niobate based materials have been investigated.

Among them, perovskite based lead-free alkali niobates, potassium sodium niobate (KNN) have attracted much attention. K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN) is considered as one of the most promising candidates for lead free piezoelectric ceramics because of its very high Curie temperature (above 400 °C), good ferroelectric properties ($P_r = 33 \ \mu \text{C/cm}^2$) and large electromechanical coupling factors [3]. The major drawbacks associated with KNN lies in its poor densification and volatilization of Na which results in non-stoichiometry of the composition thus changing the morphotropic phase boundary (MPB). The addition of excess alkaline oxides to compensate the loss leads to hygroscopic nature of the samples [4]. A numbers of studies have been carried out to improve the properties of KNN ceramics includes the formation of solid solution KNN with other ferroelectric or non-ferroelectric, e.g., KNN-LiNbO$_3$, KNN-BaTiO$_3$, KNN-SrTiO$_3$ as well as the use of sintering aids.
In order to improve the density and piezoelectric of KNN ceramics, advance processing method like hot isostatic pressing have been used in order to established the ~99% density and $d_{33}$ as high as 150 pC/N like reported by [5]. In this research, the pressure of argon gas applied during sintering process the samples using HIP method have been varying in order to determine the most suitable pressure should be used in order to achieve the highest density body of KNN sample.

2. MATERIALS AND METHODS

$K_{0.5}Na_{0.5}NbO_3$ was synthesized via solid state reaction method using hot isostatic pressing (HIP) technique. A mixture of $K_2CO_3$ (Merck, 99%), $Na_2CO_3$ (Merck, 99.9%), and $Nb_2O_5$ (Merck, 99%) were used as starting raw materials. The raw materials were dried at 200°C for 1 hour in an oven to remove any moisture due to hygroscopic nature of the powders. The raw materials were then weighed and mixed in a ball mill using ZrO$_2$ balls in ethanol medium for 24 hours, then dried and calcined at 850 °C for 4 hours with a heating rate of 3 °C/min. The calcined powder was ground and mixed with 6 wt.% of polyvinyl alcohol (PVA) binder solution before pressed into disks with 13 mm diameter and 2.5 mm thickness at 300 MPa. The pellets were finally sintered by using Hot Isostatic Pressing technique on three different pressure of argon gas applied (2900, 7252 and 14504 psi) at 1080 °C for 30 min. The KNN samples have been labelled as KNN2900, KNN7252 and KNN1450, respectively. The densities of the sintered pellets were measured using gas pycnometer (Micromeritics Accupyc II 1340). X-Ray diffraction (XRD) (Bruker AXS D8 Advance) analysis was carried out to check the phase composition and structure. The microstructure of the samples was observed by using Field Emission Scanning Electron Microscope (FESEM) (Zeiss SUPRA 35VP). The samples were coated by using silver paste on both sides, and then heat treated at 143 °C for 30 min for the dielectric measurement. The relative permittivity ($\varepsilon_r$) and tangent loss (tan $\delta$) have been measured using impedance analyzer (RF Impedance/Material Analyzer 4291B Hewlett Packard) from 1 MHz to 1 GHz.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of KNN sample sintered by hot isostatic pressing technique and being applied at three different pressure of argon gas. In all samples, it shows an identical peak position and peak shape besides no secondary phase is observed. The cells possessed orthorhombic symmetry which is similar to our previous reported [6]. Besides that, the XRD patterns show that as the pressure of argon gas applied increase, the peak intensity becomes larger also exhibits little bit broadening. This is due to average particle size effect as reported by Ghosh et al. [7] and Theivasanthi et al. [8] where the peaks broaden and the widths becomes larger as the particle size become smaller.

Fig. 2 shows FESEM micrograph of KNN pallets sintered at 1080 °C for 30 min using HIP technique on three different pressure of argon gas that applied during sintering process. HIP technique improved the sinterability of KNN ceramic body where creating liquid phase during sintering process which the particles hold strongly between each others. The statement can be support from the fracture surface image which shows that there are many fracture formed on the grains of the KNN fracture sample compared to fracture occur on the grain boundary. On the other hand, increasing the argon gas pressure will improve the relative density of KNN sample near 99% and hence will improve the electrical properties of KNN sample.argon gas applied (2900, 7257 and 14504 psi) via hot isostatic pressing technique as the pressure during sintering was increased, the grain microstructure become finer compared to conventional sintering similar as reported by Egerton and Jaeger [5]. The grain size of sample been applied pressure 14504 psi are substantially smaller than those of lower pressure applied which is 2900 psi due to HIP technique can consolidate ceramic powders into highly dense microstructure without inducing exaggerated grain growth [9].
Fig. 1 The XRD pattern of the KKNN samples after prepared under different sintering pressure of

Fig. 2 The FESEM micrograph of KNN samples after applied 3 different pressure during sintering process by HIP (a) 2900, (b) 5257 and (c) 14504 psi
KNN exhibits good densification behavior and cuboid morphology was observed under hot isostatic pressure sintering condition which typical for KNN-based ceramic. The density results for KNN samples are shown in Table 1. It can be seen that with increasing the pressure of argon gas during sintering process, the densification of sample improves.

**Table 1** Densities of KNN samples fabricated under different pressure of argon gas during sintering process by HIP technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNN 2900</td>
<td>4.4850</td>
</tr>
<tr>
<td>KNN 7252</td>
<td>4.5011</td>
</tr>
<tr>
<td>KNN 14504</td>
<td>4.6102</td>
</tr>
</tbody>
</table>

Fig. 3 shows the result of dielectric permittivity ($\varepsilon_r$) for KNN sample. The KNN 7252 sample experience the highest $\varepsilon_r$ properties compared to the others sample. The $\varepsilon_r$ increase as the density increase. We previously reported [6] that dielectric permittivity value will be increased as density of the sample increased. It is due to more space for holding larger quantity of charge at longer period of time [10-13]. Therefore, sample sintered at highest pressure (14705 psi) shows a little bit decrease of dielectric permittivity value due to decreasing in grain size. The decreasing in grain size make the grain difficult to spin during poling process due to pinning effect of the small grain.

**Fig. 3** The relative permittivity of KNN samples after applied 3 different pressure during sintering process (2900, 5257 and 14504 psi)
Fig. 4 shown the variations of piezoelectric properties ($d_{33}$ and $k_p$ value) with pressure applied during sintering process for the KNN sample. The observed $d_{33}$ increases significantly from 155 to 183 pC/N as pressure arises from 2900 to 7257 psi, then decreases at pressure 14505 psi. The observed $k_p$ value also shows significant increase with increasing pressure up to 7257 psi, giving maximum values (0.523) before reduce at 14504 psi (0.4296). The improvement in densification [Fig. 2 and Table 2] may lead to the enhancement in piezoelectric properties [14]. However, at the highest pressure applied (14504 psi), the grain size start to reduce. So, it will disturb the domain from align easily during poling process which lead to the difficulties to align the domain which cause the reducing in piezoelectric properties of sample KNN 14504 psi [6].

Fig. 4 The variations of piezoelectric properties ($d_{33}$ and $k_p$ value) of KNN samples after being applied 3 different pressure during sintering process by HIP technique (2900, 5257 and 14504 psi)

4. SUMMARY

The effect of different pressure of argon gas applied during sintering process using HIP technique on the phases, structure, microstructure, density and dielectric properties of KNN ceramics was investigated. The increment of pressure caused broadening of peak, increase in peak intensity, density, grain size, and dielectric properties up to 7257 psi. However, at 14504 psi, the grain sizes start to drop and reduce the dielectric properties.
REFERENCES


Failure Analysis on Stud Bolts of Chock Valve

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ABSTRACT. Laboratory investigation was performed on the damaged stud bolts of choke valve which has been installed on offshore platforms. The used and keep stud bolt of the same production batch were also examined as a reference. The damaged sample was found badly corroded and parted in a brittle manner. The fracture surface of damaged stud bolt was found has a sign of excessive torsional stress. The chemical composition of keep and used samples proven that stud bolts were in compliance to ASTM A320 grade L7 specification. The coating thickness analysis was conducted on keep and used sample by scanning electron microscope using backscattered signal. A significant depletion occurred on the top coat. Metallographic analysis shows the presence of branched cracking on a damaged stud bolt. It proves that there was a slightly residual stress suffered by the damaged sample. The microstructure for keep and damaged sample were tempered martensite whereas the microstructure of used sample was characterized as fine grained ferritic-bainitic microstructure. The laboratory analysis revealed that the root cause of failure was primarily as a result of overtightened of the stud bolts to choke valve during installation. The hardened steel in form of tempered martensite structure is indeed brittle and easily cracked by means of slightly overloaded stress. Another factor was a depletion problem of top coating creates exposure of underneath the metal to corrosive environment.

Keywords: Failure Analysis, Stud bolts, Hardened steel, Over-tightened, Tempered martensite, Ferritic-bainitic steel;

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1. INTRODUCTION

Stud bolt is a threaded rod with 2 hexagon nuts for assembly of the choke valve. In particular, stud bolts can be a major source of concern engineers. Frequently, assumptions are made to assess whether the assemble parts are capable of sustaining the force applied upon it. Failure of stud bolts can have disastrous consequences for the reliability and safety of assembling parts. Stud bolts are typically made from high strength steels, which when fully tightened, exert high clamp force onto assemble area [1]. The area directly under the stud bolts head or but face sustains the high bearing stress. If the maximum stress limit of the joint material is exceeded, then deformation occurs over a period of time. This leads to the extension being lost in the stud bolts, resulting in the clamp for subsequently being reduced [2].

Before this, the stud bolt failure has occurred during drilling operations in the Gulf of Mexico (GOM). Leakage was detected as a cause of failure due to severe stress-corrosion cracking fracture of the bolts on the valve. The failure of the GE H4 connector bolts at the same place was primarily caused by due to hydrogen embrittlement. It was found out that the material hardness and strength were not in compliance with the
recommended specification [3]. Due to that, almost 10,000 bolts were replaced over a relatively long time frame and long-term disruption of offshore activities and cost more than billions [4].

Over torqueing is another cause of failure. Overtightened after the bolt fails is difficult, but would be a significant help in determining the circumstances leading to failure. The intergranular fracture mode was also suggestive of an environmental cause [5]. One case was examined in which slew ring bolts on an offshore crane were twisting off when tightening with a calibrated system to the specified torque. The torque specified was for dry threads; however Loctite had been applied to the threads prior to torqueing. Calculations showed that lubricity from the Loctite increased bolt stresses to failure levels at the specified torque points [6].

In this case, an investigation has been carried out for stud bolts installed at a choke valve in one of the Malaysia's offshore platforms. The damaged bolts were assembling the body and bonnet parts of a chock valve. According to valve general drawing (Fig.1), body and bonnet material was duplex stainless steel (ASTM A995 4A), while bolt and nut materials were ASTM A320 grade L7 and ASTM A194 grade 4 respectively. General drawing has specified fluorocarbon coating for bolts and nuts. The coating systems include a cermet basecoat, which provides the corrosion resistance, and a fluoropolymer topcoat, which is intended to reduce torque-up friction. According to the client, stud bolts had been assembled in vertical position and had been in service for less than two years. This paper reports the failure investigation of damage stud bolts of choke valve. Some materials characterization of keep and used stud bolts was also reported as a reference.

![Fig. 1 Assembly drawing of choke valve. The stud bolt was marked in yellow color](image)

2. MATERIALS AND METHODS

The material characterization was carried out on two types of stud bolt samples, i.e. keep and used stud bolts. The keep the stud bolt is the same production batch, which was actually keeping by the manufacturer. The used stud bolt is the different production batch and it has been operated to the platform for two years. The used sample did not suffer any abnormal failure and visibly there were some scratches on the top coat and rusty threads. The damage stud bolts were parted and badly corroded.

Firstly, the chemical composition analysis was carried out on keep and used samples. It was done by using the optical emission spectrometer (Q8 Magellan, Bruker) to ascertain the compliance of stud bolt material to the ASTM A320 Gr. L7 specification. The damaged stud bolts were electrostatically cleaned by chemical solution. Visual inspection was documented by using digital DSLR camera (D3100, Nikon) to record the original condition before and after the cleaning process (Fig. 2). The closed-up photographs were zooming by stereo-
microscope (SZX16, Olympus) on damaged sample. Then all the specimens were grounded up to 1200 SiC grit paper and polished using 6 µm and 1 µm diamond solution. The metallographic analysis was examined by metallurgical microscope (BX41, Olympus) on the keep, used and damaged samples. The samples were then etched by using 2% nital solution to figure out the microstructure. The coating thickness of fresh and used specimen was analyzed by means of field emission scanning electron microscope (Nova NanoSEM™450, FEI) using backscattered detector.

3. RESULTS AND DISCUSSION

The visual inspection found that the keep stud bolt appeared as a dark-blue coated color. The used stud bolt sample was worn and faded to be light-blue, there were some light scratches on the surface and rusty threads. Although it has been used for 2 years on the choke valve on the same platform, but this sample still looks good and can be operated in service again. The damage sample was catastrophically parted and appeared as badly corroded stud bolt (Fig. 2a). Some coating layer was observed still remain on the surface. It shows the uniform corrosion was penetrated under coating layer. Fig. 2(b) shows the as-cleaned of damage sample. When the rust was cleaned, then it was obvious that bolt studs were mainly suffered by uniform corrosion and some wide and shallow type pitting in several areas. Visibly, the stud bolts were parted with no visible distortion. All of the stud bolts were fractured in the brittle manner and this normally happens to hardened steel which known has brittle properties.

(a)  
(b)  

Fig. 2 Camera photographs of (a) as-received damaged and (b) as-cleaned of damaged stud bolt samples

The steel composition of the keep and used stud bolts shown in Table 1. The analysis result was compared the material classification of the American Society for Testing and Material (ASTM). It was observed the chemical composition of both stud bolts were within the specification of ASTM A320 grade L7. Therefore, a failure due to chemical composition can be neglected.

<table>
<thead>
<tr>
<th>Element</th>
<th>ASTM A320 grade L7</th>
<th>Keep</th>
<th>Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.38 - 0.48</td>
<td>0.385</td>
<td>0.378</td>
</tr>
<tr>
<td>Si</td>
<td>0.15 - 0.35</td>
<td>0.313</td>
<td>0.283</td>
</tr>
<tr>
<td>Mn</td>
<td>0.75 - 1.00</td>
<td>0.785</td>
<td>0.827</td>
</tr>
<tr>
<td>P</td>
<td>0.035 max</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>S</td>
<td>0.04 max</td>
<td>0.0061</td>
<td>0.0059</td>
</tr>
<tr>
<td>Cr</td>
<td>0.8 - 1.10</td>
<td>1.072</td>
<td>0.982</td>
</tr>
<tr>
<td>Mo</td>
<td>0.15 - 0.25</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>Fe</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>
The closed-up photographs by stereo-microscope on damaged specimen were displayed in Fig. 3. As referred to Fig. 3(a), the excessive transverse cracked occurred at 30° to 40° direction which indicates that there was a torsional stress effect. The pitting corrosion marks on the stud bolt surface were seen. Fig. 3(b) shows the fracture surface of the parted stud bolts. Generally, the fracture looks like a torsional fatigue failure. This photographic image illustrates the fault that begins on the outer surface and ended at the center of the stud bolt bar. It was not very clear due to rust effect, nonetheless there were some multiple crack nucleation sites around the outer surface. With residual stress together with the vibrations inherent as the operation of the choke valve, the stud bolt finally cracked, propagated inward and finally breakdown at the center.

![Crack](image)

(a) ![Fracture](image)
(b)

**Fig. 3** Stereo microscope image on as-cleaned failed stud bolts focusing on (a) side and (b) top of the fractured area

Metallographic analysis was carried on keep, used and damaged stud bolt samples. The keep sample consists of some ferrite (white) in fine tempered martensite (Fig. 4a) whereas the structure of the used sample was ferrite (white) and carbide (black) constituents in fine grained ferritic-bainitic microstructure (Fig. 4b). Microscopically, the damaged stud bolt structure consisted of largely tempered martensite with the formation of cementite particles at the martensite lath boundaries and within the laths (Figs. 4(c,d)). The cracks occurred transgranularly (Fig. 4(b,c)) and branched (Fig. 4d). The transgranular crack proved the fractured was caused by overloading stress, whereas the branched crack demonstrated the stud bolts was suffered by the residual stress during the installation works. As the used sample exhibits a different microstructures than others, it was thus clear that there is an inconsistent pattern of microstructure pattern among the different manufacturing batch of stud bolts. This may happen coincidentally or might be due to a mistook that occurs during the manufacturing process level. However, in the choke valve operation condition at offshore platform, this type of fine grained ferritic-bainitic microstructure have proven that it has a better toughness than tempered-martensite structure. It did not fail under torsional residual stress.

The coating layer thickness was measured by means of scanning electron microstructure as displayed Fig. 5. The thickness of top and base coat for keep sample was approximately 30 µm and 20 µm respectively (Fig. 5a). On the other hand, the damaged specimen meanwhile, suffers depletion problem by time where the top coat decrease to 10 µm (Fig. 5b). The depletion of top coat was also believed to occur with the damaged
sample. The weakness of this top coat causes the exposure of underneath metal to corrosive environment resulted in the occurrence of under-coating corrosion leads to pitting and finally accelerates the crack propagation process of stud bolts.

Overall, out of all the analysis findings, it can be summarized that stud bolt bar failure was due to the hardening process of steel that forms a hardened and brittle martensite microstructure. The brittle metal materials are easily to crack or fracture. The probability for contractor worker to make a careless mistakes during stud bolt installation using the torque wrench is might be happened or maybe the installation is done manually. Based on the evidence that there were signs of torsional stress on the stud bolt studs, therefore one of these human errors is indeed true. Therefore, with the metal residual stress due to faulty during installation, coupled with the brittle metal and the vibration condition of choke valve service, then the cracking process has indeed occurred. In addition, the faulty process also occurs due to the depletion of top coat that leads to pitting problems on surfaces that are a factor to the occurrence of stress riser. With this pitting, the cracking propagation of stud bolts began started from this surface discontinuity.

Fig. 4 Optical metallographs on the etched cross-sectional surface of (a) keep, (b) used and damaged stud bolts shows (c) a transgranular and (d) branch cracking
The application of tempered martensite hardened steel as suggested by ASTM A320 grade L7 could be replaced by ferritic-bainitic steel. The microstructure of ferritic-bainitic steel consists of a softer ferrite matrix with fine bainite as second phase. The second hard-phase bainite and grain refinement make ferritic-bainitic steel a materials with excellent formability, improve stretchability of sheared edges [7]. Ferritic-bainitic steel provide higher strain hardening exponent at the same level of strength as reported by Pathak et al. [8]. They also good fatigue properties and crash performance, allowing a good performance under dynamic loading [9]. In order to overcome the top coating problems, the coating materials are recommended to replace by pure epoxy materials by electrostatic powder coating technology. The powder coating technology has been known producing a high corrosion resistance, robust and wear resistance.

4. SUMMARY

The failure of stud bolt was essentially due to the nature of the hardened steel containing tempered martensite structure which have hard and brittle properties. The existence of internal residual stress by reason of excessive torque resulted the stud studs metal has low ability to absorbed the stress attributed from overtightening. This condition become worsen when the stud bolt in which have been assembled on a choke valve that operates in vibration conditions. In addition, the depletion of top coat also contributes the the exposure of steel surface to corrosive environment to caused pitting corrosion which creates a starting point of crack propagation.

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Fourier Transform Infrared Spectroscopy of Porous Zinc with Different Concentration of Potassium Hydroxide in Agar Binder

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ABSTRACT. Fourier Transform Infrared (FTIR) is a method to identify the chemical bonding exists in materials. FTIR on porous Zn have been conducted with different concentration of potassium hydroxide solution. Bacto-agar and commercial agar were applied as binder in porous Zn. Both agars show the typical spectra of agar-like galactans under FTIR. The peaks in the range of 400 – 600 cm\(^{-1}\) were attributed to the Zn molecules. Applying different concentration of KOH on porous Zn gave different intensities to the spectra of FTIR for both agars. As KOH concentration increased, the amount of OH\(^-\) increased resulting the increasing of peak belong to OH\(^-\) and Zn bonding. Besides, addition of Zn and KOH in agar might not affect the bare Zn.

Keywords: FTIR, Porous zinc, Polysaccharide, Agar binder;

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1. INTRODUCTION

Agar is one of polysaccharides mixture that is recently getting attention in various applications because of gel strength, gelling and melting temperature as well as having great capability in adhesion with other materials. Properties of good mechanical and steel adhesion that possessed by some polysaccharides lead to the materials being processed in the film form. Moreover, agar is a natural, abundance in raw material and biodegradable sources that makes it easy to reach and safe for environment [1, 2].

This polysaccharide composes of two major fractions, agarose and agaropectin extracted from cell wall from certain seaweeds of the Rhodophyceae class. Agarose is the gelling fraction, composed of repeating alternate units of \(\beta-1,3\)-linked- D-galactose and \(\alpha-1,4\)-linked 3,6-anhydro-L-galactose [3]. Other than that, agaropectin is non-gelling fraction, composed of agarose within range 5% to 8% of sulphate, D-glucuronic acid and small quantities of pyruvic acid. Agarose normally represents bigger fraction than agaropectin in the natural agar.

The processes of polysaccharides modification through chemical reactions, such as etherification, esterification, cross-linking and grafting or physical modification has led to alteration of its gelatinization and pasting behaviour due to introduction of functional group into the polysaccharides molecules [4]. The structural differences between agarose and agaropectin are indicated by substitutions with various functional groups which polymerize into a long chain as Fig. 1 [5]. This situation has interrupted the molecular forces of hydrogen bonds, hence weakening the semi crystalline structure of materials. Besides, the motional freedom of polysaccharides chains in amorphous regions also increases due to poor inter and intra molecular reaction of hydrogen bonds. Previous study stated the morphological and structural properties of porous Zn in agar binder and additives but there is no study on chemical bonding exists after the materials corporation [6, 7]. In this study, porous zinc (Zn) mixed with two different agar (Bacto-agar and commercial agar) binder in
various concentration of potassium hydroxide (KOH) were analysed using FTIR to identify chemical bonds and molecular compositions presence in that materials.

![Diagram of agarose and agaropectin](image)

**Fig.1** Structure of agarose and agaropectin are indicated by substitutions with various functional groups at R1, R2 and R3

### 2. MATERIALS AND METHODS

Bacto-agar (Becton Dickinson, USA) commercial agar (BintangEmas), Zn powder (65.38 g/mol, Bendosen) and KOH pellets (ChemAR, System) are the main materials used. 0.3 g of agar was heated in 20 ml of distilled water at 90°C for 10 minutes. Then, the KOH pellets were balanced to get desired concentration as referred in Table 1 and the KOH solution was poured into the cool agar paste. 4.5 g of Zn powder were added into the agar paste. The preparation of porous Zn in agar binder with different concentration of KOH was following the composition as shown as Table 1.

FTIR spectra were evaluated by Thermo Fisher Scientific iZ10 FTIR Spectrometer. The spectrum was recorded between the wave number ranging from 4000 to 400 cm⁻¹ using 16 scans at a resolution of 4 cm⁻¹. The samples were tested by the transmission method. Then the spectra were analysed by using OMNIC software.

<table>
<thead>
<tr>
<th>KOH, [M]</th>
<th>KOH, [g]</th>
<th>Agar, [g]</th>
<th>Zn powder, [g]</th>
<th>Distilled water, [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.01</td>
<td>0.30</td>
<td>4.50</td>
<td>20</td>
</tr>
<tr>
<td>0.05</td>
<td>0.06</td>
<td>0.30</td>
<td>4.50</td>
<td>20</td>
</tr>
<tr>
<td>0.10</td>
<td>0.11</td>
<td>0.30</td>
<td>4.50</td>
<td>20</td>
</tr>
<tr>
<td>0.15</td>
<td>0.17</td>
<td>0.30</td>
<td>4.50</td>
<td>20</td>
</tr>
<tr>
<td>0.20</td>
<td>0.22</td>
<td>0.30</td>
<td>4.50</td>
<td>20</td>
</tr>
</tbody>
</table>

### 3. RESULTS AND DISCUSSION

Fig. 2 displays the spectra of commercial agar and Bacto-agar. Fig. 2(a) shows the FTIR spectrum for commercial agar powder. Broad band was observed at 3600 to 3050 cm⁻¹. Besides, the obvious sharp peak was indicated at signal 1040 cm⁻¹. These peaks are similar to the peaks of Bacto-agar spectrum in Fig. 2(b). The dominant bands appeared at 3600 to 3050 cm⁻¹ are attributed to stretching of hydroxyl (OH groups). There was a bump at 2925 cm⁻¹ is associated to chains of C-H bonding and 1350 cm⁻¹ are assigned to ester sulphate in both polysaccharide [8]. Sharp peak at 1050 cm⁻¹ of Bacto-agar spectrum also indicates the C-O
stretching group of 3,6-anhydro-galactose [9]. From these finding, both agar show the typical spectra of agar-like galactans [10].

![FTIR spectra of (a) commercial and (b) Bacto-agar](image)

**Fig. 2** FTIR spectra of (a) commercial and (b) Bacto-agar

In comparison between spectrum band 1040 cm⁻¹ of commercial agar and Bacto-agar, commercial agar displays lower intensity than Bacto-agar which indicates that C-O bonding in commercial agar is weaker than Bacto-agar. The spectra appeared at 1640 cm⁻¹ is due to the stretching vibration of the conjugated peptide bond formation by amide (NH) and acetone groups. In this wavelength, commercial agar gave lower intensity than Bacto-agar. On the other hand, the absorption band at 886 cm⁻¹ is due to C-H stretching residual carbon of β-galactose [8]. There were difference in intensity as Bacto-agar demonstrated higher intensity than commercial agar at peaks of 3600 – 3050, 2925, 1640 and 1040 cm⁻¹ that indicates a Bacto-agar as having stronger chemical bond. However, the spectra pattern of FTIR for commercial agar almost similar to the Bacto-agar suggesting that there is no significant chemical bond formed between commercial agar powders.

![FTIR spectrum of Bacto-agar containing Zn (a) 4000– 400 cm⁻¹ and (b) enlargement in range of 680– 400 cm⁻¹](image)

**Fig. 3** FTIR spectrum of Bacto-agar containing Zn (a) 4000– 400 cm⁻¹ and (b) enlargement in range of 680– 400 cm⁻¹

Bacto agar was mixed with Zn powder followed by the alteration of chemical bonding were performed on the spectra as Fig. 3. Based on Fig. 3(a), the broad peaks appear on wavenumbers of 3348.98, 2089.62 and 1489.13 cm⁻¹. While, the small peaks detected on wavenumbers of 832.71 cm⁻¹ and 687.12 cm⁻¹. In addition,
the sharp peaks were also detected on wavenumber in range of 400-500 cm\(^{-1}\). The most noticeable peaks in this range laid on 420.78 and 409.73 cm\(^{-1}\). The functional group possess on this spectrum are inorganic phosphates and aliphatic amino acids. The inorganic phosphates laid on wavenumber 1100–1000, 1500–1400, 3300–2600 cm\(^{-1}\) whereas aliphatic amino acids recorded at 1600 cm\(^{-1}\) and between 3200–2500 cm\(^{-1}\).

After the addition of Zn into Bacto-agar, the spectrum absorption changed, indicating the changes in structure and intermolecular interaction [11]. Changes of agar spectrum with the presence of Zn proved that the Zn\(^{2+}\) ions were successfully incorporated with the structure of agar [12]. The structures of Zn were always found in the range of 400 cm\(^{-1}\) – 600 cm\(^{-1}\) [11, 13]. The addition of Zn into Bacto-agar breakdown the O-H bonding then the Zn\(^{2+}\) replaced the H\(^+\) to make formation of ZnO bonding.

![Fig. 4 FTIR spectrum of commercial agar with Zn at (a) 4000–400 cm\(^{-1}\) and (b) enlargement in range of 650–400 cm\(^{-1}\)](image)

The spectra of commercial agar with addition of Zn powder is shown in Fig. 4. There was a hump peak calculated at 2098.45 cm\(^{-1}\) as Fig. 4(a). The rest of the peaks were laid between ranges 500–400 cm\(^{-1}\) due to ZnO existence. The sharpest peaks of ZnO detected at 417.82 and 410.03 cm\(^{-1}\) as Fig. 4(b). Similar pattern was observed on commercial agar and Bacto-agar with the presence of Zn. The peaks belong to aliphatic alcohol groups at 3358.30 and 1038.76 cm\(^{-1}\) decreased in intensity after the addition of Zn. These peaks experienced the weak molecular bonding between oxygen and hydrogen molecules due to the replacement of Zn.

The spectra of Bacto-Zn without and with different concentrations of KOH are shown as Fig. 5. The concentrations of KOH were increased up to 0.2 M. Compare to Bacto-Zn in absence of KOH, spectrum of Bacto-Zn with addition of KOH indicated the significant changes at wavenumber 575 cm\(^{-1}\). The peak was getting flatter for 0.01 M KOH that presumably due to the presence of KOH which altered the strong chemical bonding of O-H with the ZnO molecules. The area under bands 1100 – 1600 cm\(^{-1}\) can be explained by the Zn-OH bending mode. Some Zn\(^{2+}\) ions may be replaced with P\(^{5+}\) ions in inorganic phosphate or may distort P\(^{5+}\) ions and break the bonding between P\(^{5+}\) and O\(^{2-}\) in the range of 1100 – 1600 cm\(^{-1}\). As the concentration of KOH increased, the amount of OH\(^{-}\) also increased resulting the increasing of peak belong to OH\(^{-}\) and Zn bonding. However, the peaks refer to ZnO bonding were significant observed at range 450–400 cm\(^{-1}\). The changes in the transmission spectra indicate the changes in structure, conformation and intermolecular interaction. The most significant peaks observed in range 500 – 400 cm\(^{-1}\) indicated the presence of ZnO. Zn paste commercial agar-based with 0.01 M of KOH contains inorganic nitrites bonding associated at 1350 – 1200 and 850 cm\(^{-1}\). The peaks for Zn paste commercial agar-based in presence of 0.2 M of KOH was indicated at 1370.50 cm\(^{-1}\).
Fig. 5 FTIR spectra of Bacto-Agar-Zn (a) without KOH, and with different concentration of KOH (b) 0.01, (c) 0.05, (d) 0.10, (e) 0.15 and (f) 0.20

For spectrum in Fig. 5b, the hump peaks were recognized at 2092.56, 1370.50 and 826.82 cm\(^{-1}\). The paste contains inorganic nitrites stretching appeared at 1350–1200 and 850 cm\(^{-1}\). Among three Zn paste Bacto-agar, Bacto-agar in absence of KOH achieved the lowest intensity at peaks 1489.13 and 1391.99 cm\(^{-1}\). The decreasing of intensity for this spectrum are related to the weak chemical bonding for Bacto-agar and Zn until the existence of KOH strengthen the intermolecular bonding. Generally, almost all peaks showed increasing in intensity with the increases of concentration of KOH. This situation indicated the improvement in molecular strength with presence of potassium and hydroxyl molecules. All six spectra of commercial agar without KOH and different concentration of KOH as Fig. 6 show the similar pattern. In most cases, metal and its oxide can be observed by FTIR at lower wave number ranging from 400 to 800 cm\(^{-1}\). Since the presence of oxygen and existence of KOH that supplied oxygen initiate the chemical reaction thus lead to formation ZnO usually laid on range 400 to 500 cm\(^{-1}\) [14].

4. SUMMARY

Bacto-agar and commercial agar gave similar spectra to galactan-like spectra proving that both agars possess polysaccharides structures. However, the addition of Zn powderto agar has changed the spectra of agar. Several peaks between wavenumber of 400 – 500 cm\(^{-1}\) attributed to the ZnO molecules. Then, various concentration of KOH were applied on porous Zn gave small alteration to the spectra of agar which indicated
the changes of intermolecular reaction. This situation indicates the incorporation of Zn and KOH in agar might not affect the bare Zn. Difference in the intensities and the area under bands was strongly related with the concentration of the functional groups.

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Influence of Different Compositions of Fly Ash as Fluxing Agent in Porcelain

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ABSTRACT. Fly ash is alumina-silica waste products from the combustion of palm fiber and shells in the boiler which are collected at the multi-cyclone collectors where almost 3 million tonnes per annum being produced in palm oil industry in Malaysia. The aim of this paper is to investigate the replacement of feldspar by fly ash as potential fluxing agent in triaxial porcelain. Clay, feldspar, quartz and fly ash were mixed for 12 hours, pressed into pellets and sintered at 1250 ºC. The samples were measured according to the physical and mechanical properties. Microstructure study was done through SEM analysis. The optimum composition of fly ash was observed at 5 wt.% where the maximum compressive strength was achieved at 105.04 MPa and shows the decreasing results in volume shrinkage. SEM study shows intense interlocking between the primary and secondary mullite needles in glassy matrix which contribute in improving the strength of the porcelain at this composition. Therefore the substitution of fly ash is suitable as a fluxing agent in porcelain that improved its physical and mechanical properties.

Keywords: Fly ash, Porcelain, Fluxing agent, Physical, Mechanical;

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1. INTRODUCTION

Investigations of using fly ash in ceramics are widely reported over the decade ago. Fly ash is fine residue that has been produced from the combustion process of palm solid waste in the boiler where it can be an alternative source of alumina-silicate materials and has a good potential as raw materials of porcelain [1]. Porcelain is well-known as a type of ceramics which high in complexities in each aspect which start from its raw materials, forming and sintering, microstructure and phase formation [2]. Porcelain is comprised of three different raw materials which are clay, feldspar and quartz [2,3]. Clay are the main raw materials which provides plasticity and helps in giving strength at green state during forming process [2]. Feldspar as a fluxing agent in which it forming a viscous liquid at lower temperature where lead to a better vitrification and resulting to higher in densification. Quartz act as a filler where it has higher melting point which could reduce the shrinkage during firing [2,3].

Much work has been done by using fly ash as part of the raw materials in porcelain compositions. The replacements of quartz with fly ash are widely reported compared to feldspar due to higher of SiO₂ content which fulfill the essential criteria as filler in porcelain. Previous studies by Dana et al. [3], quartz has been progressively replaced by fly ash in triaxial porcelain compositions. They observed that the strength of the porcelain was increased with the increasing of fly ash due to higher presence of the mullite content. The maximum strength (70.5 MPa) has been achieved at 15 wt.% of fly ash content that sintered at 1300 ºC. Other
observation, the earlier formation of mullite and glassy phase in fly ash porcelain at 1200 ºC compared to normal porcelain at 1250 ºC where it was improved the microstructure and the strength of the porcelain at lower temperature [4]. Meanwhile, Kumar et al. [5] found that the strength of the tiles was decreased with the additions of fly ash greater than 25 wt.% due to higher content of glassy phases in fly ash porcelain. On the basis of literature, it was found that feldspar and quartz has been only partially and fully replaced with fly ash simultaneously in porcelain compositions by Mukhopadhyay et al. [6]. They obtained the optimum compositions were at 30 wt% of fly ash with the lowest apparent porosity and the highest strength achieved at 72.3 MPa. Therefore, it was found that the replacements of fly ash on feldspar are still not widely investigated in triaxial porcelain compositions.

This study involves triaxial porcelain compositions with substitution of fly ash progressively on feldspar. Thus, the aim of this study is to optimize the compositions of fly ash as fluxing agent with experienced the best physical and mechanical properties. Various compositions of fly ash were substitute on feldspar and the physical and mechanical properties and microstructure behavior were analyzed.

2. MATERIALS AND METHODS

Fly ash used in this study was collected from Bukit Lawiang Palm Oil Mill in Johor, Malaysia. Standard porcelain compositions used are 50 wt.% of Clay, 25 wt.% of quartz and 25 wt.% feldspar. Six different mixtures were prepared with various compositions of fly ash as shown in Table 1.

<p>| Table 1 Compositions of the mixture (wt%) |</p>
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Clay</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>Fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>A2</td>
<td>50</td>
<td>25</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>A3</td>
<td>50</td>
<td>25</td>
<td>15</td>
<td>10</td>
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<tr>
<td>A4</td>
<td>50</td>
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<td>10</td>
<td>15</td>
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<tr>
<td>A5</td>
<td>50</td>
<td>25</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>A6</td>
<td>50</td>
<td>25</td>
<td>0</td>
<td>25</td>
</tr>
</tbody>
</table>

Fly ash was dried in an oven at 110 ºC for 24 hours to remove the moisture content and then grounded for 12 hours using ball mill in order to reduce the particle size. After that, it was calcined at 800 ºC for 3 hours to remove the volatiles residue and excess unburned carbon. The porcelain powder and calcined fly ash powder were mixed together for 12 hours in order to obtain the homogenized mixture with additional of 2 wt.% PVA powder as a binder. Then, it was pressed into pellets under 3 tons pressure by using hydraulic press machine (Carver 3851-0). All the pellets were isostatically pressed at 100 MPa using cold isostatic pressing (CP360) for more compaction. Finally the samples were sintered using electrical protherm furnace at 1250 ºC for 2 hours. The physical and mechanical properties are measured. The bulk density testing was conducted based on Archimedes’ principle follow the standard of ASTM C373. The compressive strength was determined using universal testing machine (Testometric) as ASTM C773-88 and Vickers microhardness was determined by using Shimadzu (HMV-2 series). Characterization on the concentration of the crystalline phase was determined by using x-ray diffraction (Bruker D8 Advance) with Cu Kα radiation and analyzed by using X’Pert High Score Plus software (PANalytical). The sintered samples were polished and etched in 4% hydrofluoric acid for 3 min and the microstructure was observed using Scanning Electron Microscope (Hitachi-SU1310).

3. RESULTS AND DISCUSSION

Fig. 1(a) and Fig. 1(b) show the XRD results of the raw materials of porcelain and fly ash. Based on the XRD results, clay contains of kaolinite and quartz whereas feldspar contains of albite, quartz, microcline and muscovite. Fig. 1(b) indicates the presence of quartz, albite, mullite and cristobalite
in fly ash. It was observed that feldspar and fly ash have almost similar mineralogical compound where both of the materials was higher in quartz (SiO$_2$) and albite (NaAlSi$_3$O$_8$) content. The presence of quartz and albite as the main mineralogical compositions in fly ash is 56.6% and 21.2% whereas mullite and cristobalite is 19.2% and 3%. Albite are one of the feldspar mineral which is generally known as the pure sodium Na-feldspar [7]. The interesting fact was the presence of sodium-aluminium silicate (albite) in fly ash are suitable as a fluxing components where above 1100 °C, the albite will be dissolved in order to helps in the formation of glassy phase in the porcelain [8].

**Fig. 1** (a) XRD patterns of the raw materials of porcelain; (b) XRD pattern of fly ash

The apparent porosity and volume shrinkage of the samples is presented in Fig. 2(a). It may be observed that the shrinkage was decreased evenly with increasing in fly ash compositions due to the presence of fly ash. Fly ash was higher in SiO$_2$ content which leads to reduce the shrinkage in porcelain. Generally, volume shrinkage describes the reverse trend to the porosity. However, the porosity is much related to the bulk density of the samples. The apparent porosity was only increased at the substitution of 5 wt.% of fly ash and declined gradually afterwards. Dana and Das [4] reported that this behavior is cause by the higher formation of glassy phase due to the presence of excess amount of fluxing oxides from fly ash in porcelain compositions which is less viscosity and could fill up the open pores. According to the Yürüyen and Toplan [9], incorporation of 5 wt.% of fly ash in porcelain compositions increase the shrinkage compared to normal porcelain due to the formation of liquid phases from the melting process of fly ash.

The variation of bulk density and mass loss are shown in Fig. 2(b). The mass loss was increased with increasing in fly ash compositions. This result indicates that the additional of fly ash into the normal porcelain has a great potential of becoming lightweight porcelain. The bulk density plotted decreases with the increasing in fly ash compositions. The maximum bulk density, 2.40 g/cm$^3$ was obtained at 0 wt.% of fly ash and gradually decreased to the lowest bulk density, 2.12 g/cm$^3$ at 25 wt.% fly ash. These results are closely related to the apparent porosity where both of the results shows decreasing value in density and porosity with increasing in fly ash compositions. Mukhopadhyay et al. [6] reported that this behavior is due to the increasing in number or size of closed porosity caused by bloating formation due to the dissociation of oxygen (O$_2$) from the transformation of Fe$_2$O$_3$ to Fe$_3$O$_4$ and other possibilities is attributed to anisotropic grain growth in fly ash porcelain samples at a sintering temperature of 1250 °C [10].
The compressive strength and the Vickers microhardness of the porcelain samples were shown in Fig. 2(c). At the substitution of 5 wt.% of fly ash, the highest compressive strength was achieved with value of 105.04 MPa. The compressive strength was dropped dramatically at the composition of more than 10 wt.% due to increasing in closed porosity cause by the bloating pores in fly ash porcelain samples [6]. This behavior is also due to the increasing in glassy phase rather than crystallization of mullite which may be caused by the presence of alkali (K$_2$O + Na$_2$O) content in fly ash [5]. Meanwhile, there are difference trend observed in Vickers microhardness result shows a steady increase and obtained the maximum value, 819.1 HV at 20 wt% fly ash. As been reported by Kituoni et al. [10], different trend in both of the mechanical measurement is due to the appearance of different particle size of the materials between the raw materials of porcelain and fly ash. Zhang et al. [11] explained that the relationship between hardness and strength in ceramic could be influenced by the indentation of ‘sink-in’ morphology and different for coarse-grained since it only involves...
the surface of the samples. However, at the compositions of 5 wt.% of fly ash, the hardness could be consider higher since it shows an increasing value of 750.10 MPa compared to normal porcelain which is 733.40 MPa.

Fig. 3 SEM photomicrograph of the sample in different magnification (a-b) 5kx (d-f) 1kx (GP = glassy phase, PM = primary mullite, SM = secondary mullite, MC = microcrack, CP = closed pore)

The SEM photomicrographs of the samples were presented in Fig. 3 where it shows the presence of quartz and mullite in porcelain. According to Fig. 3(a), there are uneven surface structures in normal porcelain. It was observed that the extensive cracking occurred around the quartz grain at normal porcelain.
in Fig. 3(a) and at 15 wt.% fly ash in Fig. 3(c) due to the quartz conversion stress during cooling process [6]. However, at 5 wt.% of fly ash in Fig. 3(b) shows strong reinforcement and uniform distribution between fine primary mullite and secondary mullite needles in glassy matrix which probably lead to achieved higher compressive strength as reported by Dana et al. [3]. Fig. 3(f) shows higher formation of glassy phase which lead to increasing number of closed porosity where attributed to a reduction in strength of the fly ash porcelain.

4. SUMMARY

Replacement of fly ash on feldspar in the compositions of porcelain has a great effect to production of porcelain. The optimum compositions of fly ash were obtained at 5 wt.% according to the results of apparent porosity and compressive strength that shows the highest value respectively. The bulk density is obtained decreases as the increase in fly ash composition and contradict pattern with mass loss curve. The highest value of compressive strength and higher Vickers microhardness was achieved at composition of 5 wt.% fly ash with the value of 105.04 MPa and 750.10 HV respectively. Incorporation of porcelain with 5 wt.% of fly ash obtained intense interlocking of fine mullite needles in the glassy phase which contribute in achieving higher strength of porcelain.

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Influence of Slurry Rheology Behaviour for Fabricating Reticulated Macroporous Cordierite

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ABSTRACT. The reticulated macroporous cordierite body had been fabricated through polymeric replica template method by using different water content slurry. The rheology behavior of slurry study was performing by adjusting the degree of water content of slurry (45%, 50%, 55% and 60%). The viscosity and rheology behavior of different degree of water content's slurry was determined by using Viscometer at different shear rate. The viscosity profile indicated that, all the slurries was presented in pseudoplastic flow behaviour respectively. The SEM micrograph revealed that the macroporous cordierite prepared by using 50% water content slurry showed the bulky and mitigate flaws appearance with high porosity level (90.95±0.81%). However, the low solid content slurry resulted deficient in compressive strength (0.0306±0.012 MPa).

Keywords: Macroporous cordierite, Rheology behaviour of slurry, Water content;

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1. INTRODUCTION

Recently, porous ceramic was attracting the attention of industries such as automotive technologies, membrane application, medical (bone implantation) and catalyst supports application due to high melting point, good chemical, low density, high porosity, low thermal conductivity, high permeability and high specific surface area [1-5]. With the excellent properties, porous ceramic habitually applied as application where involved high temperatures and corrosion media atmosphere such as diesel particular filters (DPFs), water purification filters, metal molten filter and catalyst support [1-5].

Cordierite (2MgO.2Al2O3.5SiO2) has been found as alternative materials to fabricated as porous body instead of alumina (Al2O3) due to excellent properties, such as low thermal expansion coefficient (3.0 x 10-6/°C), excellent thermal shock resistance, good chemical durability, and mechanical properties [6-8]. Presently, the non-stoichiometric cordierite composition of 2.5MgO.1.8Al2O3.5SiO2 with 5 wt.% TiO2 has been discovered to give high purity (96.4 wt.%) of α-cordierite phase at sintering temperature of 1375 °C for 2 hours through solid state reaction method [9].

The final properties of porous ceramic were highly impacted by fabrication process route. The polymeric foam replica method is the most popular method to fabricate macroporous ceramic due to reproducibility and suitability of the process that allow the templates to hold its original shape [5,10]. The process involved impregnation the polymeric foam into a ceramic slurry and a layer of ceramic slurry coating over the strut of template. Followed, the dried green foam was undergoing the sintering process to an appropriate
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temperature to pyrolysis the template and crystallization the ceramic. During the sintering process, the pyrolysis of polymeric foam and organic content such as binder (PVA) contributed the formation of pore and longitudinal crack at edge of the struts. Thus, in this work, the porous cordierite prepared by using the slurry with different water content without any additives of deflocculants had been studied in order to mitigate the formation of flaws on the sintered porous cordierite.

2. MATERIALS AND METHOD

Cordierite with non-stoichiometric formulation of $2.5\text{MgO.1.8Al}_2\text{O}_3.5\text{SiO}_2$ with 5 wt% of TiO$_2$ as nucleating agent was used in this study for slurry preparation. The water content of the slurries was varied at 45%, 50%, 55% and 60% with 3 wt.% PVA binder (M.W 50000-85000) based on the total solid loading. The deionized water was heated to 60 °C to 70 °C to liquefy the binder. Subsequently, the cordierite powder was added based on the required amount of solid loading to the diluted solution. The replication route begins by fully immersed the PU foam (pore size range; 300-600 µm) into slurry to ensure the slurry get into and filled the cell of the template. The excess slurry was removed by squeezed with two parallel rollers with 5 mm gap. The immersion and squeezed procedure was repeated for four times for each sample. The green body coated PU templates was dried at room atmosphere for 48 hours. Followed, the dried green porous body were slowly sintered in a conventional high temperature furnace (MHI M18-40) in normal atmosphere. The sintering process was programmed as follows; the samples was sintered from room temperature to 575 °C at 2 °C/min for 1 hour and further sintered to 1375 °C for 2 hours at heating rate of 5 °C and furnace cooled to room temperature.

The rheology behavior of different water content slurry was determined by using viscometer (Brookfield DV-II+ Pro) at different shear rate respectively. The microstructure analysis of sintered porous cordierite was established using Hitachi TM3000 Tabletop Microscope. The bulk density and total porosity of sintered porous samples were determined by electronic densimeter (Hildebrand H-300S). The compressive strength test was carried out by using universal testing machine (Instron) at ambient temperature. The crosshead speed and load cell was 0.5 mm/min and 100 kN, respectively.

3. RESULTS AND DISCUSSION

3.1 Rheology behavior of slurries. The rheological behaviour of the slurry plays a key role in impregnation process. Fig. 1 shown the rheology profile of the slurries with different water content at various shear rate respectively. The slurries showed high viscosity at low shear rate and gradually decreased as increased in the shear rate, this rheology behaviour refer to as shear thinning or pseudoplastic flow and indicates a flocculated state of slurry. All slurries had shown the pseudoplastic flow behaviour as evidenced by the viscosity profile. The viscosity of slurry decreased as the solid content decreases and this result is similar to the work done by Jamaludin et al. [5] and Zhu et al. [11]. The flocculated ceramic slurry was greatly dependent on the solid loading as well as concentration of ions in the system. In water-solid system, the concentration of ions was dependent on the water and solid loading ratio. Hence, the association equilibrium in this work was expressed as.

$$2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+] \quad (1)$$

All the flocculated system required time to break and restructure and shear thinning behaviour was greatly related with flocculated suspension [11]. When force (shear) applied to the flocs system, the particles network in the suspension becomes unstable and lead the particles rebuild and form a new network structure in static equilibrium by Brownian motion driving force [12, 13]. The high solid loading slurry provided high concentration of bivalent ion in the association equilibrium system which reduce the repulsive inter particles force and the motion of particles was restricted by the consolidated layer and new incoming particles [13]. Therefore, the time allowed for particle rearrangement in freedom particle network in static condition is insufficient and resulted the slurry become viscous [11, 13]. Furthermore, $\text{H}_2\text{O}$ molecule in the flocculated system act as dipole and re-compensation the unsaturation bonding site of $\text{O}^2-$ at the outermost layer of pure
oxide particles by increasing the repulsive force between the particles in the aqueous system. Hence, the slurry with high water content (60%) obtained lower viscosity at low shear rate compared with high solid loading slurries.

![Viscosity profile of MAS slurries with different water content respectively](image)

**Fig. 1** Viscosity profile of MAS slurries with different water content respectively

### 3.2 Microstructure Analysis

Fig. 2 shown the SEM of sintered macroporous cordierite prepared from various water content slurries. All the samples were presented in three dimension interconnected open cell versatile pore structure with pore size range of 300 - 600 µm. As can been see in Fig. 2(a), the sintered cordierite foam prepared via 45% water content’s slurry shows a clear longitudinal crack along the edge of strut. Furthermore, the pore size in range of 3.53 - 8.44 µm was observed on the wall of the strut. This is due to the high flocculated slurry system leaded an uneven coating layer especially at the shape edge of template. As a result, formation of longitudinal crack along the edge of strut due to thermal stress and solid diffusion occur during sintering process. Besides, an inadequate thickness slurry coating layer also promoted the formation of flaws after sintering as evidenced in sintered the samples fabricated via 55% water content slurry (Fig. 2(c)) and 60% water content’s slurry (Fig. 2(d)) respectively. On the other hand, the sintered samples prepared from 50% water content’s slurry (Fig. 2(b)) obtained bulky and smooth appearance with minimized flaws compared with high solid loading slurry (60%). Due to the slurry with appropriate fluidity at high shear rate and sufficient viscosity recovering during impregnation process facilitated an uniform slurry layer coating over the template [11]. This mitigated the formation of flaws after sintering.

### 3.3 Physical properties

Fig. 3 illustrated the compressive strength of the samples fabricated from different water content slurries with corresponding total porosity and bulk density, respectively. Obviously, the compressive strength of sintered porous cordierite was directly proportional to bulk density and disproportional to total porosity. The high solid loading slurry (45% water content) attained higher compressive strength (0.0709 ± 0.0066 MPa). The high solid loading’s slurry promoted thicker coating layer during impregnation process resulted the higher bulk density (0.29 ± 0.017 g/cm³) after sintering. Conversely, the sintered samples fabricated from 50% water content’s slurry, the compressive strength (0.0306 ± 0.012 MPa) was dramatically decrease as well as bulk density (0.2157 ± 0.015 g/cm³), although the morphology analysis (Fig. 2(b)) revealed that the sintered body showed mitigated flaws structure.
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Fig. 2 The SEM micrographic of sintered porous cordierite prepared by (a) 45, (b) 50%, (c) 55% and (d) 60 % water content slurry

Fig. 3 The compressive strength of the samples with the bulk density accordingly

4. SUMMARY

The macroporous cordierite body with pore size range 300 - 600 µm was successful fabricated from different water content slurries. The slurry with 50% water content was found as appropriate rheology behaviour to reduce the defect of the strut of the porous body due to the adequate shear thinning effect at high shear rate resulted a uniform slurry coating on the sharp edge of template during impregnation route and regained the sufficient viscosity at static condition. Hence, the formation longitudinal cracks along the
strut were reduced after crystallization. However, the compressive strength of the sintered porous ceramic was highly dependent to the bulk density of samples.

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Influence of Water Molar Ratio on Fabrication of Silica Ceramic Membranes via Sol-Gel Dip-Coating Method

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ABSTRACT. Ceramic membranes are an inorganic membrane that received great attention as it overcome the limitation of polymeric membrane. The silica ceramic membrane can be used in gas separation as it able to work at elevated temperature and in chemically aggressive environment. This work is conducted to study the influence of the molar ratio of water (R) on the fabrication of silica ceramic membrane by sol-gel dip-coating method. Commercial support was dipped into the solutions consist of the mixture of tetraethylorthosilicate (TEOS), distilled water and ethanol with the addition of a small amount of acid as a catalyst. The molar ratio of TEOS to ethanol was fixed at 1 to 3.8 (TEOS:ethanol, 1:3.8). However, the molar ratio of water are varied at 2, 3, 4 and 4.7. FESEM (Field Emission Scanning Electron Microscope), XRD (X-ray Diffraction) and FTIR (Fourier Transform Infrared Spectroscopy) are utilized to determine the structural and chemical properties of silica ceramics that are fabricated with different R. FESEM images implied that the silica has been deposited on the surface of silica membrane and penetrate into the pore walls. XRD analysis of the fabricated silica ceramic membranes illustrated the existence of silicate hydrate. The fabricated silica ceramic membrane with silica sol molar ratio 1:3:3.8 gave the lowest intensity of XRD peak. FTIR analysis, it was observed that the presence of Si-O-Si functional group is in the range 1060 to 1080 cm⁻¹.

Keywords: Water molar ratio, Silica sol, Silica ceramic, Sol-gel, Dip-coating;

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1. INTRODUCTION

The membrane can be defined as a selective barrier between two phases [1], which are selective to one component and while rejecting the other. Type of membranes can be classified into three categories based on their materials, which are organic (polymeric), inorganic and mixed matrix [2]. Polymeric membranes have limitation in some application due to low chemical resistant and cannot work at high temperatures. Hence, inorganic membrane was used as a substitution of the polymeric membrane [3]. Inorganic membranes are used in many practical applications such as gas separation, water desalination, treatment of wastewater and ultra-filtration in food industries [4]. Ceramic inorganic membrane had received a great attention as it offers many advantages such as high chemical, thermal, mechanical and physical stability, outstanding separation...
characteristics, long working life and ecologically friendly [5]. Silica is one of the examples of ceramic membrane that received great attention compared to other type of ceramic membranes, especially for the removal of carbon dioxide at high temperature in chemically aggressive environment [6,7].

The silica ceramic membrane can be fabricated by the sol-gel method, as this technique has been used for a long time in the fabrication of glasses and ceramics [8]. The sol-gel technique has been used in the reproduction of new porous nanomaterial that possessed well-defined structures and complex shape [9]. Sol-gel process refers to a process where the transition from liquid (solution or colloidal solution) into a solid (di- or multiphase gel) is happening. The sol-gel technique has received great attention in the research field since the last two decades due to the benefit they are offering, including the production of high purity homogeneous materials, ability to control the reaction of the solution by using chemical techniques, low processing temperature requirement, and it allows the formation of new crystalline phase of the non-crystalline solid. One specific example of a sol-gel method to produce silica ceramic membrane is the polymerization of tetraethylorthosilicate (TEOS) in ethanol and water, which are then resulting in formation of Si-O-Si chemical linkage [10]. Prepared sol can be deposited onto a substrate in order to form a film by several methods, for example dip coating. Silica sol-gel dip-coating method can be used when reduction of pore size of fabricated membrane is desired [4].

There are several parameters involved in the sol-gel technique that will affect the structural and textural properties of the synthesized materials. The parameters that will influence the result of this method including the molar ratio of reactant, initial reaction condition (precursor, pH and temperature), aging and drying conditions, and solvent compositions. Hence, this study will focus only on the influence of the molar ratio of water (R) in silica solution on the fabrication of silica ceramic membranes by using sol-gel dip-coating techniques. The fabricated silica were then characterized in order to observe any changes in their physical and chemical characteristics.

2. MATERIALS AND METHODS

2.1 Silica sol preparation. Silica sols was prepared by mixing TEOS, water and ethanol together at 298K with vigorous stirring. The molar ratio of TEOS to ethanol is fixed at 1:3.8, while the molar ratio of water, were varied at 2, 3, 4 and 4.7, as shows in Table 1. Then, a small amount of acid was added to the solution as a catalyst.

<table>
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<tr>
<th>TEOS</th>
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2.2 Membranes Fabrication. Commercial ceramics (Fig. 1), 10 inch Doulton OBE Ceramic with 32 mm internal diameter, 48 mm outer diameter and length of 200 mm, were used as a substrate or support to the fabricated membranes. The commercial support was dipped into the prepared silica solutions, and then were dried at room temperature for 24 hours. After that, the samples were calcined at 773 K with holding time of three hours. The dipping, drying and calcine process was repeated for three times.

2.3 Membranes Characterization. X-ray diffraction (XRD) was used to determine the element of the fabricated membrane. The morphology of the membrane surface and support were determined using the field emission scanning electron microscope (FESEM) (JSM 6700F [EOL]). Fourier transform infrared spectroscopy (FTIR) analysis was performed in order to determine all the existed functional groups.
3. RESULTS AND DISCUSSION

Fig. 2 shows the XRD result of the fabricated silica ceramic membranes with different molar ratio of water (R). XRD analysis was performed in order to identify the compound that existed in materials. For this study, XRD is used to confirm the existence of silica if the fabricated ceramic membrane. The XRD pattern shows the existence of silicate hydrate element for fabricated silica ceramic membrane, which mean a trace on water still remain in the fabricated membrane. However, water has no substantial effect on the fabricated silica structure. The fabricated silica ceramic membrane with R=3 gave the lowest intensity which is 413.3 cps. This means that the membrane with this ratio is thicker among other membranes. Moreover, the highest peak, 22° (2θ) was appeared for all fabricated silica ceramic membrane indicates that there was the presence of the expected reaction, which is silica (SiO_2). This proof that silica ceramic had been successfully fabricated from the solution used.

Fig. 2 XRD pattern for fabricated silica ceramic membrane with different silica sol molar ratio (a) R=4.7, (b) R=4, (c) R=3, and (d) R=2

Fig. 3 presented the FESEM images of the fabricated silica ceramic membranes with different R. FESEM analysis was employed in order to study the surface morphology of the fabricated silica ceramic membranes. Fig. 4 shows the image of raw commercial support that had been used as a substrate, where silica sol will be deposited onto the support by sol-gel dip-coating method to produce silica membrane. From Fig. 4, the pore of the raw support is visible under the FESEM analysis, where the size of the pore ranges around 0.6 µm. However, in Fig. 3, no pore is observed on the fabricated silica, prove that the pore size had reduced after silica membrane has been fabricated.

Furthermore, before the coating, the image of the raw support in Fig. 4 shows a clear and clean surface without any foreign particle appear the surface. Conversely, after the silica ceramic membrane are fabricated,
the FESEM image in Fig. 3 shows some agglomeration of fine particle on the surface of the membranes. An agglomeration of particles resulting in particle aggregate formation as the particles adhere to each other. This leads to irregular arrangement on the surface of the fabricated membranes. Fine particle on the membrane surface indicate that the silica have already penetrated onto the surface of the raw support, creating silica ceramic membrane. Besides that, it is observed that, as the R is decreased, the surface of the membrane becoming more consolidated, and less particle aggregate appears on the membrane surface. Fig. 3 (c) illustrates that the surface of membrane fabricated is more consolidated than others, where R=2 is used.

At fixed concentration of TEOS, increasing of R in the solution leads to the increasing of the hydrolysis and rate of condensation. Solution with R=2 make the penetration of silica sol into pore membrane become difficult because the solution become more concentrated as the amount of water used is small, which is insufficient to complete the hydrolysis reaction of the sol. When a very low R is used in silica solution mixture, it will produce a matrix with a more open structure due to incomplete hydrolysis. Hence, there will be fewer cross linking in the sol-gel material. Moreover, a low water content in silica sol will produce a high content of oligomers, either volatile or soluble, and also resulting in reduction of silica generated. The homogeneity and composition of the fabricated silica membrane can be affected by the presence of those oligomers and also monomers that are only partially hydrolyzed.

**Fig. 3** FESEM images of fabricated silica ceramic membrane at different silica sol molar ratio (a) R=4.7, (b) R=4, (c) R=3, and (d) R=2
Fig. 4 FESEM image of raw support

Fig. 5 represents the FTIR result of the silica ceramics fabricated by various R. FTIR is used to determine the functional group of the fabricated ceramic, and also to analyze the bond existed. From the result illustrated, it displayed that all gels exist at the same absorption band. The band located at around 466 cm\(^{-1}\), 610 cm\(^{-1}\), 790 cm\(^{-1}\) and 1070 cm\(^{-1}\) are attributed to silica network. The major peak is around 1070 cm\(^{-1}\) due to the anti-symmetrical stretching vibration of Si-O-Si, are observed for all fabricated membrane. The strong vibration of silicon–oxygen covalent bonds occur mostly in the 1200-1000 cm\(^{-1}\) range exposing the existence of adense silica network. The oxygen atom acts as a bridge that connects the two silicon sites. Secondary bands around 790 cm\(^{-1}\) related to the symmetric stretching vibration are observed, while bending mode are detected around 466 cm\(^{-1}\) [11-13].

![FTIR resultof fabricated silica ceramic membrane at different silica sol molar ratio(a) R=4.7, (b) R=4, (c) R=3, and (d) R=2](image)

4. SUMMARY
Fabrication of the ceramic membrane via sol-gel dip coating, generate membrane with uniform pore size distribution, while a variation of R affected the physical and chemical characteristics of the fabricated silica ceramic membranes. From the results obtained, it can be concluded that the silica ceramic membrane via sol-gel dip-coating method is successfully fabricated. The fabricated silica ceramic membrane is characterized chemically and physically. Silica solution was prepared by varying the R, then the sol were deposited onto the commercial support as that acts as the substrate. According to FESEM analysis, it is discovered that as the molar ratio of deionized water is decreased, the surface of the membrane becomes more consolidated and pore size was reduced. From the XRD analysis, the result proved the existence silica compound in the fabricated membrane. In addition, FTIR analysis presents the Si-O-Si bond which strengthen the proof of the existence of the silica in the fabricated membrane. Hence, according to analysis result, all fabricated membrane showing the existence of silica.

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Measurement of Pipe Strain Using an Ultrasonic System

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ABSTRACT. Ultrasonic sensors can be used to measure strain occurring on an object. In this investigation, an ultrasonic signal utilized the reflected signal as a means of monitoring the condition of a pipe. This is an alternative to the strain gage which is commonly used but has a limited life span. The ultrasonic signal was transmitted to a specific location on the pipe, and then reflected by the pipe surface which experienced strain towards the ultrasonic receiver. Collimation of the transmitted and received signals is performed by aluminum probe cones attached to both ultrasonic transducers. Changes in the strain due to the pipe bending will result in changes in the electric signal due to the changes in the sound intensity. The received electric signal was processed by a signal conditioning circuit consisting of preamplifier, amplifier, band-pass filter and rectifier before being displayed. Two experiments were conducted to establish the relationship between strain on the pipe and the ultrasonic intensity. In order to verify the results, an experiment was conducted using a strain gage and the results were identical. The results show that the system is able to measure strain when the pipe bends.

Keywords: Deformation, Pipe, Sensor, Strain, Ultrasound;

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1. INTRODUCTION

Industries used pipes to convey substances such as liquids and gases, slurries, powders and masses of small solids [1]. The use of pipes provides the safest means of transporting oil, gases and other types of fluids [2]. To enable pipes to perform long distance transportation, the pipes must be able to fulfill the requirements of safety, reliability and efficiency [3]. It is vital to continuously monitor the condition of pipes in order to ensure that it is safe to be used. Industries made use of pipes to convey various types of flow such as high-temperature, high-pressure, inflammable gas/liquid flow. In order to extend the life span of pipes it is important that they are properly maintained. Pipe leakages are mainly as a result of damage from excavation equipment which is located nearby. Pipes which are not maintained properly can corrode gradually, especially at construction joints or at deformation on the pipe [4]. These defects or leaks must be identified as early as possible and corrected before they became serious [5]. Other causes of leaks or deformations include accidents, earth movement, or sabotage.

There are various ways of measuring pipe deformation. One of the common methods of doing it is by installing strain gages on the pipe's surface. When the pipe deformed, changes in the pipe strain resulted in the change in gage's resistance [6]. Nevertheless the use of strain gage has some limitations. Since the strain gage has a small and limited size it is capable of making point measurement only [7]. As such it does not give a wider picture of what actually happened to the pipe. Another disadvantage is that the electrical strain gage can only be utilized for a limited time especially after it has exceeded its elastic limit and after that it has to be disposed. The same thing does not happen to the ultrasonic system which can be used repeatedly and thus it
has a longer life span compared to strain gage [8]. Ultrasonic sensors are widely used in the industry due to its advantages such as non-destructive, accurate, reliable, easy to use, inexpensive, long term stability, low power consumption, and its capability in reproducing defects caused by strain [9].

2. MATERIALS AND METHODS

2.1 Pipe Deformation. Stress on a pipe can be investigated using a circular long pipe which bent at certain angles. When a pipe is subjected to a particular force, there will be a certain amount of strain. Besides the shape and size at certain parts of the pipe will change [10]. The size of the deformation maybe too small to be observed by the naked eye or the shape and the size of the whole body might change completely due to the existence of a large deformation. Temperature fluctuation can also cause the body to deform whereby an increase in temperature caused an expansion of the body and vice versa. The ultrasonic system was used with the aim of detecting a small range of deformation. Deformation due to bending happens when a force perpendicular to the longitudinal axis is imposed on a long solid body. By applying load at the other end of a pipe beam, the beam at the support or the pivot tries to firmly maintain its position whereas the force attempts to change the position of the extrude beam. As a result of the force being imposed on the pipe beam, shear stress will be exerted on the pipe.

There are two components of strains namely normal strain and shear strain. Normal strain represents the change in length along a particular direction. Shear strain is due to opposing forces acting in a direction parallel to to a surface [10]. Each material will experience different value of strain. If a metal is subjected to a deformation caused by a force or pressure of the same value, the value of deformation will not be as big as deformation experienced by a non-metallic material. Pressure and modulus of elasticity influence the value of strain on an object. It is difficult to deform an object if it possess a large value of elastic modulus and as such a large value of force is needed to cause the material to deform. The same applies to pressure. Each material has a limit on how much it can deform. When the yield limit of a material is exceeded, it will disobey Hooke’s law.

The fundamental concept governing strain that occurred on a pipe is based on the Hooke’s law which can be expressed as,

\[ \sigma = \varepsilon E \]  

(1)

in which stress, \( \sigma \), is proportional to strain, \( \varepsilon \), as well as the modulus of elasticity, \( E \). Changes in the structure of the pipe such as bending resulted in changes in stress which can be formulated as [10],

\[ \sigma = \frac{My}{I} \]  

(2)

in which \( M \) represents the moment, \( y \) is the distance from the neutral axis, and \( I \) is the moment of inertia.

Since (1) and (2) are the same parameter, by equating them the following can be obtained,

\[ \varepsilon = \frac{My}{EI} \]  

(3)

The relationship between moment and force, \( P \), and length of the pipe, \( l \), can be expressed as

\[ M = Pl \]  

(4)

By substituting (3) into (4) the following expression is obtained,

\[ \varepsilon = \frac{Py}{EI} \]  

(5)

When the pipe is bent, strain is generated and this parameter was investigated in this project.

2.2 The Ultrasonic System and the Experimental Work. The frequency of the ultrasonic sensor was 40 kHz. The receiver circuit comprised a pre-amplifier, an amplifier, a band-pass filter and a rectifier. The signals
from the ultrasonic transmitter dispersed at a wide angle [11]. In order to collimate the signals from the ultrasonic sensor several cones were constructed so that the ultrasonics can be directed towards the point of interest. Fig. 1 shows the design of the cone. The left-hand of the cone is the region where the ultrasonic transducer is attached whereas the right-hand part is region where the cone is directed towards the measurement point. In order to hold the ultrasonic sensors inside the cone, hot melt adhesive was used. The cone is made of aluminum. Both ultrasonic receiver and transmitter used cones which have identical dimensions. The acoustic impedance for aluminum is 17064000 kg/m²s.

![Fig. 1](image1.png)

**Fig. 1** The dimensions of the cone. The red and black lines are the wires to the ultrasonic transducer

The ultrasonic signal coming out of ultrasonic transmitting sensor is transmitted at a wide angle [12]. By using the cone as in Fig. 2, the ultrasonic wave can be confined to an acute angle which enabled it to be collimated towards the measurement point in which bending occurs. By doing this the signal can be fully optimized rather than the case where the signal is dispersed widely.

![Fig. 2](image2.png)

**Fig. 2** The propagation of ultrasonic signal in the cone

The experimental setup is shown in Fig. 3 where a load of 15 kg was placed at one of the pipe caused the pipe to bend. The load is placed at the right hand side of the pipe. The ultrasonic transmitter and receiver are placed at the left hand side of the pipe. The aluminum cone was placed in such a manner so that a maximum
strain was obtained when a load was placed at the other end of the pipe. A scale was placed at the right hand side in order to measure the deflection caused by the pipe bending. Initially a load of 1 kg is measured and the load was gradually increased. The maximum load being measured was 15 kg.

Fig. 3 Experimental setup

3. RESULTS AND DISCUSSION

Fig. 4 represents the graph of voltage versus strain when the pipe was subjected to a tensile strain. The graph has a regression coefficient of 0.99 which is almost linear and the voltage, $y$, is related to the strain, $x$, by $y = -0.003x + 186.6$. Increasing the strain caused a decrease in the output voltage. A further displacement in strain caused an increase in the range from transmitter to receiver but there is a decrease in the sound pressure level. This affects the receiver transducer reception against the voltage. It can be expected that if the pipe is subjected to compressive strain, the voltage will be proportional to strain.
Fig. 4 Graph of voltage versus strain

Fig. 5 shows two graphs representing the results from an experiment conducted using a strain gage and an ultrasonic system. There is only a slight difference between the graphs. Both graphs show that when the pipe is subjected to an increasing load, the value of strain increased. The graph obtained from the strain gage is a straight line whereas the graph representing the ultrasonic system is not as smooth as the strain gage. This can be probably be attributed to the fact the measurement area of the strain gage has a narrow boundary whereas in the case of the ultrasonic system, the angle of the ultrasonic receiver has a wider measurement area compared to the strain gage.

![Graph strain formation (µm/m) versus load (N) for strain gage and experimental Young Modulus value](image)

**Fig. 5** Results obtained using a strain gage and an ultrasonic system

4. **SUMMARY**

The investigation shows the capability of an ultrasonic system in measuring the performance of a pipe when it is subjected to a certain amount of strain. Results from the ultrasonic system are identical with that obtained using a strain gage. The output voltage is inversely proportional to strain. As such the change in the electrical signal represented by the output voltage can be used to indicate a change in the strain experienced by the pipe. Further experiments can be conducted using other ultrasonic frequencies. An improvement in the processing of the signal could enhance the system.

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Mechanical Properties of Mahang (Macaranga) Wood as a Core Material in Sandwich Composites

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ABSTRACT. In this study, mechanical properties from clear specimens of mahang wood were investigated to determine the congeniality of this species to be used as balsa alternative in the construction of sandwich composite. Several ASTM standards were adopted to establish valid procedures to conduct the experimental investigation. 3-point-bending, compression and tensile tests were executed by using universal testing machine (UTM). The results obtained were compared with balsa wood. It was found that mechanical properties of mahang wood are comparable to balsa except for compressive Young’s modulus where it exhibited slightly lower than balsa which signifies mahang wood has lesser elastic properties in compression. The most significant finding to emerge in this study is that mahang wood seems to be a viable alternative to be used as a core in sandwich composite as it possess almost similar mechanical properties as balsa wood.

Keywords: Mahang wood core, Fiberglass reinforced skin, Bending, Tensile, Compression;

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1. INTRODUCTION

Low weight structure with high bending stiffness is always desirable in structural construction. In transportation sector especially marine and aerospace, weight reduction means less fuel consumption which translates into cost saving. The most practical way of reducing weight without significantly affecting its bending stiffness is to adopt sandwich structure [1]. The ability to provide less weight structure while maintaining high strength property expand the demand for sandwich composite in the manufacturing industry. Utilization of composite during recent year has been driven by the fact that sandwich composite offers low weight structures with high flexural stiffness. High strength-to-weight ratio balsa wood is among the most widely desired core material of the sandwich structure. It has been extensively used in the most sandwich structure in recent times. Sandwich structure in marine has found its biggest application in the Skjold class vessel which had its body made entirely of sandwich composites [2]. Sandwich composites in Skjold not only contributes to its lightweight structure, it also provides excellent impact properties, low infrared and radar absorbent properties.

Environmental concern raises the urge for the utilization of eco-friendly materials. Natural based materials are always preferable to comply with this demand. Srivaro et al. [3] conducted a study to develop a
lightweight sandwich panel from natural resources. It has conclusively been shown that lightweight sandwich panel made from rubber wood veneer skins and oil palm wood exhibited superior dimensional stability and excellent mechanical strength. The study provides important insights into the potential of natural resources in the application of lightweight sandwich panel. In another similar series of study, Azmi et al. [4] have highlighted the relevance of coconut coir fibres in reinforcing polyurethane foam core of sandwich composites. Mechanical properties of sandwich composites with 5 wt% coconut coir fibres showed a significant improvement compared to 0 wt% of coconut coir. Malaysians are blessed with one of the oldest and most myriad biological species tropical rainforest in the world. Most of the high quality woods are being fully utilized in various applications ranging from building construction, furniture, tools and also paper products. However, lesser known wood species (LKS) are not being maximised in terms of utilization due to either lesser quality or lack of information regarding these species. Macaranga or locally known as mahang wood is a lesser known wood species that locally available in Malaysia. It is one of those fast growing pioneering trees that naturally grow naturally in the forest. Due to fast growth, the density is very low, typically varied from 270 to 495 kg/m³ [5]. Hence this paper aims to investigate the mechanical properties of mahang wood to determine the congeniality of this species to be used in the construction of sandwich composite by comparing the mechanical properties to balsa wood.

2. MATERIALS AND METHOD

A 10 m tall mahang tree with diameter at breast height (DBH, 1.3 m above the ground) of 78 cm was obtained from Agro Park of Universiti Malaysia Kelantan. The age was estimated to be about 8 years based on the periodic annual increment (PAI) of 1.5cm per year. All logs were marked and painted on both end of the cross section to prevent excessive water loss and fungal attack. The process of cutting the logs into small clear specimen was done by the Forest Research Institute Malaysia (FRIM). The logs were cut into lumbers. The lumbers were then cut into blocks for mahang core and also for tensile, compression and flexural specimens according to ASTM standards [6]. Lumbers were pre-dried in a force convection oven at 50 °C for 12 days until 12% moisture content attained.

Sandwich composites skin laminate were manufactured from plain woven E-glass fabric (0.166 kg/m³, Fibreglast Company) and epoxy resin (Fibreglast Company) using hand lay-up process. Resin was applied by using hand brush and roller was used to remove trapped air bubble and excess resin. 50:50 fibre-matrix volume ratios were used to impregnate the fabric. Individual blocks of mahang wood measure 100 × 100 mm were adhesively combined into panels of 300 × 300 mm for sandwich core. The core grains were aligned in the through-thickness direction. The core was bonded to the skin laminates using epoxy resin. The sandwich panel was then consolidated by using vacuum-bagging process. The consolidation process was left to run for 24 hours. Once consolidated, the sandwich panel was post-cured in an oven at temperature 80 °C for 2 hours.

![Fig.1](a) Mahang core of sandwich composite and (b) Sandwich composite with fibreglass face skin and mahang core

The specimens for mahang wood were prepared based on ASTM D-143: Standard Test Method for Small Clear Specimen of Timbers, section 16 which specifies the methods and procedures for handling tension parallel to grain test [6]. Specimens were tested by using UTM (Testometric M500-50CT). The machine was
set to elongate the specimen at a uniform rate of 1 mm/min. Samples for sandwich composite were prepared in accordance to ASTM D-3039: Standard Test Method for Tensile Properties of Polymer-Matrix Composite Materials [7]. The dimension measures 250 mm in length and 25 mm in width with thickness of 10 mm as required by the standard. A standard head-displacement rate of 2 mm/min was set to elongate the specimens.

Axial compression test were carried out using UTM as per ASTM D-143 section 9 for compression parallel to grain. The specimens measure 50 × 50 × 150 mm³. The tests were performed using UTM through a 5 kN load cell. Compression was continuously applied at crosshead speed of 0.305 mm/min. Sandwich composite were tested according to ASTM C-365: Standard Test Method for Flatwise Compressive Properties of Sandwich Cores [8]. The specimens were made into 90 × 90 × 45 mm³. The specimens were compressed at standard head-displacement rate of 0.5 mm/min.

Mahang beams with dimensions 25 × 25 × 410 mm were tested in static bending test. 3-point bending test was performed in accordance with ASTM D-143, section 8 which specifies the methods and procedures for conducting static bending test. Testing was conducted UTM with loading span of 360 mm equipped with 222 N load cell. The loads continuously applied at a rate of 1.3 mm/min. Specimens for sandwich composites were prepared and tested according to standard requirement of ASTM C-393: Standard Method for Core Shear Properties of Sandwich Construction by Beam Flexure [9]. The specimens measure 200 mm in length and 75 mm in width and thickness of 20 mm. The displacement rate was set at 6 mm/min to deflect the beam under load.

3. RESULTS AND DISCUSSIONS

Tensile test assessed the strength and stiffness of mahang wood and sandwich composite in breaking under tension. The results of tensile strength and tensile modulus for mahang wood and sandwich composite consisting mahang core and fibreglass face skins are shown in Fig. 2.

![Fig. 2 Results of (a) tensile strength and (b) young's modulus comparison for mahang wood and sandwich structure.](image)

The ultimate tensile strength (UTS) corresponds to the maximum tensile stress a material can sustain prior to failure is often referred as tensile strength. Tensile strength and young’s modulus of mahang wood obtained in this study are 371.31 MPa and 52.59 GPa respectively. Tensile properties of mahang wood in this experimental work is significantly higher than tensile properties of balsa wood as reported by Soden and McLeish [10]. They reported the value of 31.5 MPa for tensile strength and 5.17 GPa for tensile modulus. Mahang wood exhibited ten times stronger than balsa wood. Both tensile strength and tensile modulus of wood are slightly higher than sandwich structure. Although sandwich structure incorporating fibreglass face skins, the grain alignment in sandwich structure is perpendicular to the direction of tensile loading which make it weaker as it easily tearing apart the wood fibres. As for wood tensile tests, the grain aligned parallel to the direction of tensile loading. As a results, the wood cells working together in axial direction and act.
as tiny column or tubes to resist tensile loads. The load-elongation curve obtained from tensile test is presented in Fig. 3. The first part of the graph shows slightly linear elastic behavior before plastic deformation occurs which transform the linear graph to curvature. Finally, a sudden drop occurs to signify an almost brittle rupture [11].

![Fig. 3 Load-elongation curve for mahang wood specimen in tension](image)

Compression test was used to determine the reaction of mahang wood and sandwich structure under compressive loading. The compressive strength and compressive modulus for mahang wood and sandwich composite is presented in Fig. 4.

![Fig. 4 Result shows (a) compressive strength and (b) Young's modulus comparison for mahang wood and sandwich structure](image)

Compressive strength of mahang wood obtained in this study lies in the range of compressive strength of balsa wood established in previous research [10,12]. They reported minimum value of 14.7 MPa and maximum of 43 MPa while this study yield a value of 21.61 MPa. When load is subjected at axial direction or parallel to grain, the fibres can support load greater than their weight [13]. However, compressive modulus of mahang wood in this experimental work is lower than balsa. Da Silva and Kyriakides in their study revealed a value of 6.62 Gpa for balsa wood whereas mahang wood in this study has a maximum deflection at 1.62 Gpa. This result suggests that balsa wood has better elastic properties and better in resisting deformation than mahang wood. The graph in Fig. 4 shows that there has been a steep increase in the value of compression strength and modulus for sandwich structure in comparison to wood. Sandwich composites with mahang core offer ten times higher compression properties compared to mahang wood itself. Sandwich structure can support a distributed load up to 70.1 Mpa. Efficiency of sandwich structure to resist compression load is due to the fact that high strength fiberglass face skin act as protective shield to protect less strength core material. 3-point bending test was performed to evaluate the bending strength and stiffness of mahang wood
and sandwich structure. Fig. 5 shows the results of modulus of rupture (MOR) and modulus of elasticity (MOE) of mahang wood and sandwich structure.

![Graph showing MOR and MOE comparison for mahang wood and sandwich structure](image)

**Fig. 5** (a) MOR and (b) MOE comparison for balsa wood and sandwich structure

MOR is a measure of the maximum load a material can sustain in bending before rupture. The flexural stress at which fracture occur is corresponding to the MOR. It determines the maximum strength while MOE determines the stiffness of the wood whereby it measures the amount of deflection a load causes in a material. It can be seen from the graph in Fig. 5 that the results obtained for mahang wood are 34.62 MPa and 4.14 GPa. During bending, the wood fibres on the upper part experience compression and the wood fibres on the lower part experience tension. Fig. 6 depicts the crack propagation started from the bottom of the specimen due to fibres failure in tension rather than in compression.

![Image of wood specimen with crack](image)

**Fig. 6** The crack at the lower parts of the specimen that explains the wood fibres fails due to tension stress during bending

Such failure mode is termed as ‘cross-grain tension’ as specified by ASTM D-143. Previous studies on the bending properties of balsa wood has reported the strength of balsa is in the range of 21.6 to 70 MPa while MOE in their investigation yield a value of 3.4 to 8 GPa [12,14]. These results suggest that mahang and balsa wood are comparable in terms of bending strength. Bending properties of sandwich structure increase by 10 times compared to wood, similar to compression properties. This can be explained by the presence of core and skins in resisting buckling when subjected to load [15].

4. **SUMMARY**

The mechanical properties of mahang wood were investigated. Bending strength and stiffness of mahang wood are comparable with balsa as it lies in the range of strength and stiffness of balsa wood. The mechanical strength is considerably high that it yields high strength to weight ratio properties of mahang wood. Tensile strength in this study emerges substantially higher than balsa wood. This indicates the outstanding resistance of mahang wood in breaking under tension. However, young’s modulus in compression shows otherwise. The relevance of mahang wood in core of sandwich composite is clearly supported by the excellent mechanical properties. The findings of this investigation add to a growing body of literature on the potential of lesser known wood species as a core in sandwich composite. In general, therefore it seems that mahang wood can be considered as a practical applications for the construction of sandwich composite core.
REFERENCES


Morphological Analysis of Silica-Nickel Oxide Foam Fabricated by Replication Method

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ABSTRACT. Foam materials are very light, but compared with bulk materials, their strength is quite low because of their random structures. Natural lightweight materials such as bone, is a cellular solid with optimized structure. In this research, silica-nickel oxide (SiO₂-NiO) foams were fabricated by a well-known method which is replication method. The compositions of SiO₂-NiO foams consist of 55 wt.% of silica (SiO₂) powder and 10 wt.% of nickel oxide (NiO) powder. SiO₂ and NiO powders were mixed together with binders; polyethylene glycol (PEG) and carboxymethyl cellulose (CMC) to prepare slurry solution for replication of polyurethane (PU) sponge which functioned as the template. 10 wt.% of SiO₂-NiO foams sintered at different temperatures; 1000 °C, 1100 °C, 1200 °C and 1300 °C. Morphology of 10 wt.% of SiO₂-NiO foams such as the structure of foams and particles distribution were studied by using scanning electron microscopy (SEM).

Keywords: Slurry method, Catalytic, Gas Conversion, Methane reforming, Reticulated;

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1. INTRODUCTION

Porous materials show a dramatic development nowadays instead of solid materials in various applications such as catalysis, filtration, thermal insulation and performs for metal-ceramic composites, biomedical implants and high-efficiency combustion burners [1]. The advantages of using porous ceramics in these applications are high melting point, high corrosion, and wear resistance, low thermal mass, low thermal conductivity, controlled permeability, high surface area and low density [2]. In order to produce porous ceramics with controlled microstructure, there are many novel methods have been developed in response to the increasing number of new potential applications for cellular ceramics. The fabrication method chosen will determine the range of porosity, the pore size distribution, and the pore morphology [3]. It is well said that processing route or fabrication method for the production of porous material highly influences the microstructural features.

Several types of materials are identified as common support materials, for example, alumina (Al₂O₃), silica (SiO₂), magnesium oxide (MgO), zirconia oxide (ZrO₂) and olivine ((Mg, Fe)₂SiO₄) which have been investigated as catalyst support because the catalytic activity of nickel also influenced by its interaction with support materials [4]. In this study, SiO₂ was used as the support for the catalyst or additive that was nickel oxide (NiO). Majewski et al. [5] stated that SiO₂ has strong structural robustness which is stable even at elevated temperature and chemically inert. It makes SiO₂ attractive as a catalyst support and presents the advantage of mechanical strength and has a strong interaction with metal [5]. Besides that, the advantages of using SiO₂ as the support for NiO particles are because SiO₂ is active for methane reforming and more resistant towards carbon formation [6].
Additives play an important role in defining the rheological behaviour of suspensions and the mechanical properties of green and sintered bodies [7]. Nickel is considered a good replacement for noble metals instead of other noble metal-supported catalysts such as rhodium (Rh), ruthenium (Ru), palladium (Pd), platinum (Pt), iridium (Ir), due to its comparable catalytic performance and low cost [6,8].

2. MATERIALS AND METHODS

Silica (SiO$_2$) and nickel oxide (NiO) are two main raw materials in SiO$_2$-NiO foam fabrication. Replication method is used to fabricate SiO$_2$-NiO foam by using polyurethane (PU) sponge as template and it has been cut in cylindrical shape with dimension 26 mm height and 13 mm diameter. To fabricate SiO$_2$-NiO foam, 55 wt.% of SiO$_2$ and 10 wt.% of NiO were poured into distilled water and mixed with binders. The binders used in this method were 2.5 wt.% of polyethylene glycol (PEG) and 2.5 wt.% of carboxymethyl cellulose (CMC). The mixture of raw materials, binders and distilled water produced slurry solution for impregnation of PU sponge as a template in making porous material. The impregnated sponge was left for drying in oven for 24 hours at 80 °C before sintered at 1000 °C, 1100 °C, 1200 °C and 1300 °C with 2 °C/min heating and cooling rate in programmable furnace.

The morphological analysis for SiO$_2$-NiO foam was carried out by using scanning electron microscopy (SEM) and electron dispersive X-ray spectroscopy (EDS).

3. RESULTS AND DISCUSSION

The morphology of SiO$_2$-NiO foam with 10 wt.% of NiO composition was observed using SEM at different sintering temperatures of 1000 °C, 1100 °C, 1200 °C and 1300 °C as shown in Fig. 1 (a-d). From observation, SiO$_2$-NiO foams with 10 wt.% of NiO composition sintered at different sintering temperatures also consisted of open pore, close pore and interconnected window cells by struts. The open pore size of SiO$_2$-NiO foams observed was in the range of 130 µm up to 537 µm.

![Fig. 1 Morphology of the silica-nickel oxide foam sintered at (a) 1000 °C, (b)1100 °C, (c)1200 °C and (d)1300 °C. (OP=Open pore, CP=Close pore, S=Strut)](image_url)

Sintering temperature also affect the morphology of the foam as shown in the micrographs in Fig. 1 as the open pore distribution on SiO$_2$-NiO foam sintered decreased and the pore size became smaller as the
sintering temperature increased. Open pore distribution on SiO$_2$-NiO foams sintered decreased and the pore size became smaller as the sintering temperatures increased. This is due to the shrinkage and densification of the samples as the sintering temperature increased. The presence of closed cells on SiO$_2$-NiO foam sintered at 1200 °C and 1300 °C became dominant as marked in micrographs compared to SiO$_2$-NiO foam sintered at 1000 °C and 1100 °C. The decreasing of open cell window could be explained by the increasing difficulty for ceramic slick removal at higher solid loading during manufacturing, leading not only to a higher density, but also to a higher number of close pores, and strongly influencing the permeability of the foams [9].

Both of SiO$_2$-NiO foams sintered at 1200 °C and 1300 °C showed increasing size of struts as the NiO compositions and sintering temperatures increased. The strut size of SiO$_2$-NiO foams observed at 1200 °C was in the range 80 µm to 330 µm while the strut size of SiO$_2$-NiO foam at 1300 °C was in the range of 100 µm to 360 µm. Views from previous researchers, the pore size of porous foam for steam methane reforming was uncommon between researcher within the range 0.1 µm to 21 mm [5,10,11]. The open pore size observed of SiO$_2$-NiO foams was within the range and compatible to be used in steam methane reforming application.

Densification of SiO$_2$-NiO foams was observed as shown in Fig. 2 (a-d) at different sintering temperatures; 1000 °C, 1100 °C, 1200 °C and 1300 °C. The micrographs in Fig. 2 represented the morphology of SiO$_2$-NiO foam with 10 wt.% of NiO after sintered at different sintering temperatures. The morphology of SiO$_2$-NiO foams showed open pore distribution with micro meter size. White spot or powder-like in Fig. 2 (a-d) represented the distribution of NiO particles at different temperatures while the grey structure was the structure of SiO$_2$. The structure of SiO$_2$-NiO foams became denser as the sintering temperatures increased from 1000 °C to 1300 °C.

![Fig. 2](image_url)

**Fig. 2** Morphology of silica-nickel oxide foams at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C ( = NiO distribution)

Nickel oxide particles distribution were marked by yellow circle while SiO$_2$ particles distribution was the grey structure where NiO particles distributed on as shown in Fig. 2 (a-d). The distribution of NiO and SiO$_2$ particles were distinguished by elemental mapping as discussed at Fig. 3. As shown in Fig. 2 (a,b), the particles were initially packed loosely and started to approach and contact to each other as the sintering temperature increased. The growth of grain structure was observed under SEM as the SiO$_2$ particles and NiO particles started to bond with each other at higher sintering temperature in which denser grain structure was clearly seen at 1200 °C and 1300 °C.
Based on Fig. 2 (a-d), open pore distribution with irregular shape was observed with micro meter size within the range 3 µm up to 20 µm for SiO$_2$-NiO foams with 10 wt.% of NiO composition. Grano et al. [12] reported that, sintering of nickel crystallite at elevated temperature disrupted the mesoporous SiO$_2$ template that contributed to the irregular shape on the foam microstructure. The distribution of open pore observed on the surface of SiO$_2$-NiO foams decreased as the sintering temperature increased due to the increasing in grain size as seen in Fig. 2 (a-d). The larger grains were found to grow and densified, whilst smaller grains and pores that had been created at a lower temperature to accommodate the volume shrinkage associated with reduction were observed to disappear [13].

Elemental mapping was extremely useful for displaying element distributions in textural context, particularly for showing compositional zonation instead of figured out element and mass content. The elemental mapping result showed the particles distribution of elements which existed in SiO$_2$-NiO foams. The result of elements mapped for 10 wt.% of SiO$_2$-NiO foams was showed in Fig. 3 (a-d). There was nickel (Ni), silica (Si) and oxygen (O) distributions observed through elemental mapping analysis. The highest distribution of NiO particles was observed at 10 wt.% of NiO composition. This might be due to the excess NiO particles which cannot be mixed with the SiO$_2$ particles [14]. Fig. 3 shows the elemental mapping test for SiO$_2$-NiO foam using Electron Dispersive X-ray Spectroscopy (EDS).

![Elemental mapping for 10 wt.% NiO composition sintered at 1300 °C](image)

**Fig. 3** Element distribution by elemental mapping for 10 wt.% of nickel oxide composition sintered at 1300 °C

Element and phase map were collected automatically and simultaneously. This helped to observe how each element was distributed individually. Fig. 3 (a) was the original image of 10 wt.% of SiO$_2$-NiO foams. The distribution of Ni, Si and O were differentiated by red, blue and purple colour, respectively in Fig. 3 (b-d). Through the elemental mapping analysis, the white spot as marked in Fig. 2 (a-d) were clarified as Ni particles and the rest of dense structure were Si and O. The colour-image represented the distribution and increased the possibility distinguish the different elements. The distribution of Ni particles was the highest for SiO$_2$-NiO foams with 10 wt.% of NiO sintered at 1300 °C as proven by EDS result tabulated in Table 1. The purpose to carry out the elemental mapping analysis in this research study was to identify the element and
mass content that existed in SiO$_2$-NiO foams. A micrograph of 10 wt.% of SiO$_2$-NiO foams morphology was captured to determine the element and mass content.

The result tabulated in Table 1 showed the mass of different elements such as 20.49% of nickel (Ni), 17.82% of silica (Si) and 17.82% of oxygen (O). The differences in element mass affected the particle distribution. The highest mass of Ni represented the higher distribution of Ni particles on the SiO$_2$-NiO foams as shown in Fig. 4. This was because the distribution of particles on SiO$_2$-NiO foams was affected by the early composition of raw material during sample preparation. As the NiO sintering temperature increased, the Ni particles distribution after sintering observed by elemental mapping analysis was increased.

**Table 1** Element obtained for 10 wt.% of nickel oxide composition sintered at 1300 °C

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni K</td>
<td>61.69</td>
</tr>
<tr>
<td>Si K</td>
<td>20.49</td>
</tr>
<tr>
<td>O K</td>
<td>17.82</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Fig. 4 (a-d) showed the Ni particles distribution at different sintering temperatures at 1000 °C, 1100 °C, 1200 °C and 1300 °C, respectively.

![Fig. 4](image)

**Fig. 4** The distribution of nickel particles of 10 wt.% of silica-nickel oxide foams after sintered at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C and (d) 1300 °C

The distribution of Ni particles increased as the sintering temperatures increased as observed in Fig. 4 (a-d). The lowest Ni particles distribution of SiO$_2$-NiO foams was observed at temperature of 1000 °C. Lowest distribution observed at lowest sintering temperature due to presence of open pore with macro size and thin strut. At 1300 °C, the highest Ni particles distribution was observed due to the decrease in pore distribution and size, presence a number of close cells and bigger struts. The highest Ni particles indicated the domains contained higher NiO contents than the matrix, which attributed to the formation of NiO-enriched...
agglomerates. As sintering temperature increased, the particles gain more energy and collision rate increases [15].

Sintering effect was clearly visible in the SiO$_2$-NiO foams of the sintered at 1200 °C and 1300 °C as higher Ni particles distribution observed on SiO$_2$-NiO foams compared to the SiO$_2$-NiO foams sintered at 1000 °C and 1100 °C. Nickel particles distribution on the surface of SiO$_2$-NiO foams depended on the structure of SiO$_2$-NiO foams. Low number of open pore with the larger strut gave Ni particles to distribute more on SiO$_2$-NiO foams surface. Larger strut with denser structure associated with the grain growth as the sintering temperatures increased. The structure of materials sintered at high temperatures indicated signs of particle grain growth and also substantiated by the grain size distributions [16].

4. SUMMARY

The morphology of 10 wt.% of SiO$_2$-NiO foams was affected by the compositions and sintering temperatures. Both of them affected the open pore size and distribution, closed pore and strut size which connected the cell windows together. The open pore size and distribution decreased as the compositions and sintering temperature increased. The number of closed pore became dominant at high temperatures. The size of struts also bigger as densification occurred as sintering temperature increased. Thus, the highest of Ni particles distribution was observed at the highest sintering temperature which was 1300 °C.

REFERENCES


Morphological and Thermal Analysis of Retted Rattan Waste Fibers

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ABSTRACT. The aim of this paper is to study the effects of retting processes on rattan waste fibers, specifically on its morphological and thermal properties. The fibers were prepared for water and chemical retting processes, and were labelled as RF, WRF and CRF for untreated rattan, water-retted rattan and chemical-retted rattan, respectively. Then, these fibers were mixed and hot-pressed into composite boards, which were analyzed for their thermal, strength and morphology properties. Comparatively from Thermogravimetric Analysis (TGA), the WRF has higher thermal stability at lower decomposition temperature, yet the CRF has slightly lower thermal stability compared to RF. It also shows that the retting processes have reduced moisture content inside rattan waste fibers. All the fibers underwent an endothermic process in Differential Scanning Calorimetry (DSC) analysis, where it also displayed that the melting point of RWF, WRF and CRF were 177.80 °C, 183.43 °C, 187.27 °C, respectively. Tensile tests showed that the water retting process had improved the strength properties of WRF/PLA composite board compared other boards. It is supported through the morphological structures of boards. The RF/PLA and WRF/PLA displayed smooth board surfaces indicating the better bonding between fiber and matrix. The removal of certain components such as hemicellulose, lignin and other impurities, obviously can be seen from the morphology of WRF and CRF. It resulted in coarser and rougher fiber surfaces that facilitated good bonding between fibers and matrix as well as reasonable thermal stability. Thus, it is recommended to apply the water retting process before proceeding with fabrication of composite boards.

Keywords: Retting, Rattan fibers, Morphology, Thermal;

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1. INTRODUCTION

High demand of green products has motivated researchers to actively explore the potential of utilizing natural fibers. Natural fibers have good properties of being nontoxic, biodegradable, lightweight, superior performance with the addition of easy availability and is cheaper [1]. Thus, it is believed that there is vital need to exploit the agricultural wastes of sisal, banana, kenaf and many more to produce value-added composites for the construction and automotive industries. The exploration of rattan waste usage as filler or reinforcement in bio-composites has not been extensively studied yet. The structure of rattan fibers comprises of cellulose, hemicelluloses and lignin; featuring good properties such as low density, renewability, flexibility, versatility and low cost [2], to be upright substitution as a reinforcing agent in natural fiber composites. The notable drawback of natural fibers is incompatibility between hydrophilic fibers and hydrophobic matrices in the composite world [3], due to impurities in fibers which can result in poor interfacial bonding adhesion of composite, and poor resistance to moisture absorption. This has limited their potential and wide-ranging use. It is important to comprehend that this interfacial bonding plays a vital role in determining the mechanical and physical properties of composites.
Based on these factors, the performance of produced composites can be improved by surface modification of fibers, specifically through the retting process. The retting process dissolves or washes out the impurities of cellular tissues on fiber bundle surfaces such as pectin, lignin, cellulose and wax, by employing water or chemical action [1,4]. Water retting process commonly performed in aqueous environment, where the fibers are soaked in water for a certain period in between 7 to 14 days [5]. The soluble substances come out from the plants and promote the growth of microorganisms that produced specific enzymes as retting agent which eventually degrade the complex structure of fiber to simpler compound. This process generates more uniform and high-quality fibers, yet it changes the chemical composition and pH of water during retting process. While, chemical retting process are affected by few parameters such as type of alkali, chemical concentrations, temperature, solution acidity (pH) and duration of treatment, for its effectiveness. Previous studies [5-7] stated that chemical retting process is more efficient as it produces smoother fiber surfaces within short duration of retting that also improved the mechanical properties of fibers, compared to other retting processes. However, this process has changed the retted fibers into darker color and it consumes high cost of processing. Both these processes improve the stiffness, strength and dynamic flexural moduli of composites, resulting in an increase in interfacial bond strength and adhesion between matrix and fibers. The factors considered for the retting process amongst others are cost-effectiveness, efficiency, labor-friendly, environment-friendly, low cost, simple and easy handling, requiring less skill [5]. Hence, the objective of this paper is to study the effects of water and chemical retting process onto rattan fibers, in terms of its morphology and thermal analysis.

2. MATERIALS AND METHODS

The rattan fibers were sieved and oven-dried for 24 hours. The prepared fibers underwent the water retting and chemical retting process [5]. For water retting process, the rattan fibers were immersed in a beaker with tap water for 8 days at the room temperature, before being taken out. Meanwhile, for chemical treatment, the rattan fibers were placed in a continuously stirred beaker with 1% solution of sodium hydroxide (NaOH), at 25 ºC for 60 minutes. Then, the fibers were washed several times with tap water. The fibers used in this study were oven-dried at 35 °C for 48 hours and were labelled as RF, WRF and CRF for untreated rattan, water-rettet rattan and chemical-retted rattan, respectively.

After that, the composite boards were manufactured by using an internal mixer (Haake Polylab System Thermo) machine at fiber:matrix ratio of 30:70. The parameters used were heating temperature of 165 ºC, rotor speed of 50 rpm and mixing time of 12 minute, to produce the compound materials which were labelled as RF/PLA, WRF/PLA, CRF/PLA. These compound materials were crushed and used in hot-pressing process at pressing parameters of 160 ºC, 3 min and 147.5 kPa.

2.1 Thermogravimetric Analysis test. The thermogravimetric analysis (TGA) was conducted using a Perkin Elmer Thermogravimetric analyzer. The fiber samples were prepared in powder form, placed in a sample pan and inserted into the thermogravimetric furnace, which was heated at a heating rate of 20 ºC min⁻¹ from room temperature up to a final temperature of 800 ºC, under nitrogen flow.

2.2 Differential Scanning Calorimetry test. The differential scanning calorimetry (DSC) analysis was performed using a TA Instruments DSC analyzer. The fiber samples were placed into an aluminum pan covered with a lid and the sample cell was heated under a nitrogen purge at a heating rate of 10 ºC min⁻¹, from room temperature up to a final temperature of 500 ºC.

2.3 Tensile Strength test. The samples were prepared for tensile strength test according to ASTM D 638, using the Universal Machine (Autograph AGS-X), at loading load of 10 kN and loading speed of 50 mm/min.

2.4 Morphology test. The morphological structures of rattan fibers and composite boards was investigated using a scanning electron microscope (SEM) model Hitachi SU1510, operated at 15 kV at 250x and 1000x magnification, respectively. The samples were coated with a thin layer of gold to avoid the samples’ charging as these samples were non-conductive.
3. RESULTS AND DISCUSSION

The thermal analysis, tensile strength and morphology tests are significantly important to determine the necessity of doing retting process on rattan fibers, before proceeding into further steps to produce composite boards in larger scale. The analysis was done to see if the retting process could make any noteworthy differences on the boards’ properties.

3.1 Thermogravimetric Analysis. The differences of TGA curves for RF, WRF and CRF were demonstrated in Fig. 1, to observe specific process of weight loss of weight loss of rattan fibers. The first derivative peak of these fibers occurred in the same range of temperature between 50 ºC to 135 °C due to the reduction of moisture content in rattan fibers. The retted fibers which were WRF and CRF retained the same weight loss of 5%, while RF experienced higher weight loss of 8%. Thus, sit showed that the retting process had reduced the moisture content inside rattan fibers [8]. The second derivative peak fell in the temperature range of 135 ºC to 257 ºC, attributable to thermal degradation of cellulose and hemicellulose [9]. The RF has 62.5% of weight loss ratio, while WRF and CRF had weight loss ratio of 61.9% and 65.4%, respectively. The WRF had a higher decomposition temperature of 278.45 ºC indicating that the water retting process had improved the thermal stability of the rattan fibers. However, the low weight loss of WRF indicated a low degradation of cellulose and hemicellulose. Based on this, it shows that the water retting process had improved the thermal stability of the rattan fibers at a lower decomposition temperature compared to RF. At the same time, the low thermal stability after the chemical retting process was due to degradation of the cell walls of fibers which may reduce the thermal protection of the treated fibers. Moreover, the exposure of cellulose to direct heat from the cell walls and hemicelluloses may contribute to this lack in thermal stability [10].

![Fig. 1 TGA graphs of rattan fibers](image1)

![Fig. 2 DSC graphs of rattan fibers](image2)
3.2 Differential Scanning Calorimetry. The DSC curves of RF, WRF and CRF are illustrated in Fig. 2, to identify the chemical activity when heat is applied to rattan fibers. The first peak indicates an endothermic process where heat was absorbed by rattan fiber sample due to heat flow needed to reach equivalent temperature of the reference pan. The second peak shows the melting point at which it changes from solid state into liquid state at atmospheric temperature. Based on the curves, the melting point of RF is at 177.80 °C, with energy required of 129.0 J/g. Meanwhile, the melting point of WRF is 187.27 °C and temperature differences of 9.47 °C from RF. The energy needs to melt for WRF is 90.9 J/g, which is much lower as it involved the biochemical reaction through specific enzymes that are produced as retting agent to decompose. The melting point of CRF is increased to 183.43 °C with temperature differences of 5.63 °C from RF. In contradict, the CRF needs high energy of 179.6 J/g compared to RF and WRF, as alkaline treatment resulted in increase of cellulose crystallization.

The temperature difference between WRF and CRF is 3.84 °C, indicating an increase of 2.09%, due to higher content of moisture after water retting [8]. The retting processes have improved the thermal stability of the rattan fibers [1], and this data is important for subsequent incorporation into various purposes [10].

3.3 Tensile Strength. Fig. 3 shows the tensile behaviors and Fig. 4 demonstrated the morphological of failure structure of composite boards, which are the RWF/PLA, WRWF/PLA and CRWF/PLA. Generally, it is observed that the neat PLA nominated the highest tensile strength of 69.5 MPa. The addition 30% of rattan fibers content has dropped the tensile strength drastically about 53% into 32.5 MPa. This is due to incorporation between rattan fiber and PLA matrix, with some fiber pull out that can be seen in Fig. 4(a). Water retting process shown the positive effect on the tensile strength of WRF/PLA composite with increasing about 28% that give the value of 41.6 MPa. The morphological structure in Fig. 4(b) had supported this increment value, which showed that the small void occurrence as well as improved adhesion of PLA and rattan fibers that leads to better stress transfer. The chemical retting process, however, had caused reduction in tensile strength values to 40.6% compared to RF/PLA, gave the tensile strength value of 19.3 MPa for CRF/PLA composite. The big micro-void presence during the production of CRF/PLA composite, attributed to poor interfacial adhesion of fiber and matrix, as illustrated in Fig. 4(c).

![Fig. 3 The graph of tensile strength for PLA, composite boards and rattan fibers](image-url)
3.4 Morphological Analysis. Fig. 5 shows the morphological of surface structures of composite boards at 250x magnification, along with the rattan fiber structures at 1000x magnification (in inserted pictures) under SEM images. The surface of RF/PLA board in Fig. 5(a) is smooth, with compacted fibers bonding that contributed to better strength and dimensional stability of boards. The fiber surface of RF is rather smooth with the presence of impurities and other elements. Fig. 5(b) shows the fine surface of WRF/PLA board, with the rougher fiber surfaces and cleaner vascular bundles of WRF due to removal of certain components compared to RF/PLA. This revealed the tendency of the water retting process to wash out the impurities and cemented materials such as lignin hemicellulose, lignin, waxes, oils and pectin away from the fibers bundle into more structured fibers bundle with greater uniformity and higher quality \[5,7\]. Similar observations were found in previous studies \[1,4,7,9,11,12\]. On the other hand, Fig. 5(c) illustrates coarser surface of CRF/PLA board, with more separated fibers and collapsed cell walls compared to RF/PLA and WRF/PLA boards. The difference is due to the effective degradation of natural and artificial impurities \[9,13\], hence increasing the aspect ratio and improving the dimension of pore size of rattan fiber, and increasing the amount of exposed cellulose \[4,8\]. It should be noted that the removal of impurities leads to a less dense and less rigid interfibrillar region \[9,13\], hence allowing the fibrils some rearrangement among themselves. The rough surfaces produce after retting process, has facilitates both mechanical interlocking and bonding reaction due to the disruption of hydrogen bonding in the fiber surface and exposure of the hydroxyl groups to the matrix, thereby leading to better incorporation and interfacial adhesion the fiber–matrix bonding \[4,5,7\]. It also leads to reduction of fiber diameter that increases the aspect ratio.

Based on both observations in Fig. 5, the structured surface morphology shows that water retting process has improved surface roughness as expected, resulting in better mechanical interlocking as well as increasing the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites during the manufacturing process \[8,13,14\]. Thus, it resulted in better load stress transfer between the
matrix and the reinforcing fibers during production of the composite \cite{7,11,14}, by removing hydrophilic hydroxyl groups and improved moisture resistance property.

4. SUMMARY

Rattan fibers underwent water retting and chemical retting processes; and then were analyzed for thermal analysis, tensile strength properties and morphological structures through TGA, DSC, tensile test and SEM. The thermal analysis, strength values and morphological observation showed that these two retting processes had changed the thermal stability and modify the surfaces of rattan fibers. Coarser and rougher surfaces after the retting process facilitated good interfacial bonding between fibers and matrix, which is vital in producing good quality composite boards with considerable bond strength. In conclusion, the water retting process can be applied on fibers, before proceeding with further steps.

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REFERENCES

Physical Properties of Edible Films Based on Tapioca Starch as Affected by the Glycerol Concentration

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ABSTRACT. The aim of this work is to study the influence of different proportions of glycerol on the properties of tapioca starch films. The films were characterized to determine crystallinity by using X-ray diffraction (XRD), thermal property by differential scanning calorimetry (DSC) and mechanical property by tensile test. The DSC thermograms show a decrease in the melting temperature (T_{Peak}) with increase in the glycerol content. According to XRD diffractograms, pure starch exhibits crystallinity, but gelatinisation converts the starch film with 0 (w/w) % glycerol to amorphous, it gains back its crystallinity with the increase in the glycerol concentration. Mechanical properties were also influenced by variation of the percentage ratio of glycerol. The tensile strength was observed to decrease with increase in glycerol concentration whereas the elongation at break sharply increase with increase in glycerol concentration.

Keywords: Tapioca starch, Glycerol, DSC, XRD;

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1. INTRODUCTION

Packaging plays important function in maintaining and protecting organic composition of food, it is essential to have a packaging material that protects the value, wholesomeness and safety of the food product with minimum cost and environmental impact. The monumental increase in non-degradable organic solid waste worldwide is championed by synthetic packaging materials [1]. The greater proportion of solid waste goes to food packaging [2]. A rare opportunity to move away from depleting fossil fuel to a replenish-able, environmentally benign material source is found in biodegradable, renewable bio-plastics [3]. Biopolymer potentially used for the production of food package ranges from polysaccharides, protein, lipids, cellulose or combination of both. The most important of polysaccharides for the production of food packaging is starch [4]. This is as a result of its abundance, low cost and processibility [5]. Starch is hydrocolloid substance, produced agriculturally by plants in a granulated form. It consists of about 30% amylase (poly-\(\alpha\)-1,4 D-glucopyranoside), a crystalline component and 70% amylopectin (poly- \(\alpha\)-1,4- D glycopyranoside and \(\alpha\)-1,6-glucopyranoside), a branched of amorphous part of the starch [5].
The gelatinisation is a significant method in starch processing. It involves the breaking of intermolecular links of starch fragments in the presence of water and heat, freeing the hydroxyl groups to interact with more water molecules. The effect of the interaction results to irreversible dissolution of the starch particles in water [5]. The bioplastic starch, when cooled over a period, thickens (or gel) and reorganise its molecules to a more crystalline form [6]. Certain amount of heat will be required to melt the semi crystalline material formed [7].

A specific amount of natural and artificial additives are used to enhance the properties of starch based thermoplastics namely plasticizers [8], antimicrobials [9], stabilizers [10], and antioxidants [11]. The essential function of plasticizers is to increase the elasticity and workability of polymers. Due to the low molecular weight of plasticizers, they tend to dwell in the intermolecular spaces within the polymer chains, reducing stiffness and enhancing intra-molecular hydrogen bonding [12]. Therefore, amount of strength and elasticity of a polymer invariably depend on the nature of the plasticizer including its chemical composition, functional groups and reactivity [3]. Some researchers found that glycerol excellently serves as plasticizer for water soluble polymers [12, 13]. The functional groups in the glycerol promotes molecular hydrogen bonding which become incentive for flexibility and processibility [14].

The main drive of this research work is to evaluate the effect of percentage proportion of glycerol on the features of tapioca starch film by employing the use of tensile analysis, XRD and DSC.

2. MATERIAL AND METHODS

Tapioca starch, was supplied by THC Sdn Bhd, it has the following property [15]: moisture, 13%; amylose, 17%; lipids, 0.1%; phosphorus, 0.01%; soluble sugars, 0.24%; protein, 0.1% and ash, 0.2%. And the glycerol was supplied by R & M Chemicals [16].

Tape casting was the technique employed for preparation of the starch-based films [13]. The formulations were made by 10% (w/w) H$_2$O, (0, 5, 10, 15, or 20%) (w/w) glycerol and the remaining proportion of the final mixture of 15g was completed by the starch powder. The mixture was heated at 125 °C for 5 min at 50 rpm agitation using mechanical stirrer. The final product was spread on 15 cm x 15 cm glass plates using the doctor blade. Oven was used to dry the film with air circulation at 30 - 40 °C for 2 hours. Curing of the finished product takes place in an open air at 24 - 48 hours [16].

The tensile properties were evaluated using Instron 4302 series IX, according to ASTM D 882-02 standard. Five samples, 2.54 cm x 5 cm, were cut from each film. Initial grip separation and crosshead speed were set at 50 mm and 500 mm/min, respectively [16].

The melting temperatures (Tpeak) were found using Differential Scanning Calorimeter (DSC) (TA instrument Q20 V24.10 build 122). The samples were evaluated in triplicate, (± 0.01mg, Mettler Toledo XPE analytical balance). Aluminium pans where impermeably sealed and heated at amount of 10 °C/min. Moreover, an empty pan was used as a reference. DSC thermograms were presented as exo-up. Therefore, the downward absorption represent endothermic, positive reaction.

The crystallinity of the films and solid starch was examined empirically with an XRD (Bruker D8 Advance) machine. It was operated at 40 kV and 40 mA. Nickel-filtered Cu Kα radiation was used in the incident beam. The square (2mm x 2mm) samples were analysed between 2θ = 10° - 30° with a step size of 2θ = 4°, according to [10].

3. RESULTS AND DISCUSSIONS

The presence of glycerol as shown in Fig. 1, has a significant influence on mechanical property of the starch film. Curve (a) in Fig. 1 showed a sharp decrease in the tensile strength as the percentage
concentration of the glycerol increases. It has been reported by Bergo et al. [12] that the resistance of starch film reduces with increase in glycerol content. This could be due to less contact between the starch molecules as a result of a barrier created by the presence of glycerol.

Conversely, the elongation at break as shown in curve (b) in Fig. 1 presented a consistent increase as the glycerol content increases. The behaviour of mechanical properties of starch film is widely reported in the literature [4,8,12,17].

**Fig. 1** Effect of glycerol concentration on tensile strength and elongation at break of tapioca starch films

![Graph showing the effect of glycerol concentration on tensile strength and elongation at break of tapioca starch films.](image)

**Fig. 2** X-ray diffraction of Tapioca starch containing (a) 0, (b) 5, (c) 10, (d) 15, (e) 20% glycerol and (f) dry starch

![X-ray diffraction patterns of tapioca starch with varying glycerol concentrations.](image)
Fig. 2 shows the XRD patterns obtained in the starch films as curve (a) to (e) and solid starch as curve (f). The XRD diffractogram of the solid starch indicate peaks around $2\theta \approx 15^\circ$, $19^\circ$, $24^\circ$, which shows high tendency of crystallinity. Whereas, curve (a) for film with 0% glycerol depicted no presence of peak, presenting a fully amorphous characteristic. While, in curve (b) to (e) a crystalline tendency is shown by the presence of peak at $2\theta \approx 17^\circ$ for films with 5, 10, 15, and 20% glycerol. The peak becomes more conspicuous as the percentage of the glycerol increases. Showing that the crystallinity of the starch film increase with the increase in the glycerol content [17].

Fig. 3 illustrates the DSC thermograms of the films investigated, having different percentage of glycerol concentration. The graphs of all the films showed an endothermic reaction from 25 ºC to 173 ºC, which indicates the softening of various starch crystals developed during retrogradation [1]. For the different films in curve (a) - (e) in Fig. 3 the endotherms changes in ascending order as the concentration of glycerol increases. Curve (a) shows the highest $T_{peak}$ as 117.8 ºC and enthalpy +1.061 W/g and Curve (e) shows the least $T_{peak}$ as 93 ºC and enthalpy +0.918 W/g. The transition parameters are shown on Table 1. The change in transition enthalpy was due to the occupation of the interstices of the polymer matrix by glycerol keeping the adjacent polymer chains apart, thereby reducing the forces of attraction (i.e. van der Waal's and electrostatic) between the film molecules aiding the molecules glide across each other easily which increases the flexibility of the polymer matrix. This tendency was similarly reported by some other researchers [1,2,7].
Table 1. DSC transition parameters of tapioca starch films with different glycerol percentage concentration

<table>
<thead>
<tr>
<th>% Glycerol</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{peak}}$ (°C)</th>
<th>$T_{\text{offset}}$ (°C)</th>
<th>$\Delta H (T_{\text{offset}} - T_{\text{onset}})$ (°C)</th>
<th>$\Delta T$ (W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>117.8</td>
<td>172.5</td>
<td>147.5</td>
<td>+1.061</td>
</tr>
<tr>
<td>5</td>
<td>34</td>
<td>109.1</td>
<td>175.5</td>
<td>141.5</td>
<td>+1.039</td>
</tr>
<tr>
<td>10</td>
<td>27</td>
<td>106.0</td>
<td>136.6</td>
<td>136.6</td>
<td>+1.003</td>
</tr>
<tr>
<td>15</td>
<td>26</td>
<td>99.6</td>
<td>160.7</td>
<td>134.7</td>
<td>+0.963</td>
</tr>
<tr>
<td>20</td>
<td>25</td>
<td>96.3</td>
<td>158.5</td>
<td>133.5</td>
<td>+0.918</td>
</tr>
</tbody>
</table>

4. SUMMARY

The tensile strength of the tapioca starch film is reduced by the increase in the amount of glycerol, while elongation at break increases with increase in glycerol. The rigidity of TPS film softens with the increase of glycerol content. Thereby, the use of glycerol increases the workability of TPS for food packaging. Though, excessive amount will increase the crystallisation of the TPS molecules leading to fragility as depicted by the XRD results. So also the DSC indicated that higher concentration of glycerol reduces the TPS heat resistance.

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REFERENCES


Preparation and Characterization of Activated Carbon from *Cocos nucifera* L. (coconut) Shell and Sugarcane Bagasse

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**ABSTRACT.** The aim of this study is to synthesis and characterize activated carbon from *Cocos nucifera* L. (coconut) shell and sugarcane bagasse by carbonization and activation process. The samples were carbonized and activated at 300°C in a furnace. As the concentration of activating agent increased, the percentage of weight loss also increased due to more volatiles in samples that were released. Addition of phosphoric acid (H₃PO₄) and potassium hydroxide (KOH) resulting more porous structure in the activated carbon. The result indicated that the activated carbon derived from coconut shell has higher carbon content compared to sugarcane bagasse. Besides, the elements that contained in the samples were analysed using X-ray Diffraction (XRD) and surface chemical was characterized using Fourier Transformation Infrared-Attenuated Total Reflection (FTIR-ATR). It was concluded that production of activated carbon from coconut shell and sugarcane bagasse can be used in a lot of applications like dye absorbent for waste water treatment.

**Keywords:** Activated carbon, Agriculture waste, Activating agent;

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**1. INTRODUCTION**

In recent years, activated carbon is very popular among the researchers because they are focusing on recycling the agricultural waste into beneficial usage [1-2]. This green approach is aimed to reduce the impact of waste to the environment [3-4]. Furthermore, application of waste to wealth concept would allow the agricultural byproducts which do not have any economic value to be commercialized into a new high value product [5-7].

Activated carbon is commonly derived from carbonaceous materials such as egg shells, coffee husks, coconut shells and husksas well as sugarcane bagasse [8]. For the production process, at the beginning, the carbonaceous sources are carbonized and followed by physical or chemical treatment. The surface modification process which occurs at the molecular level allows the carbon to be fully functionalized into...
activated carbon [9]. High degree of porosity that exists in activated carbon is well known to be an excellent candidate for adsorption process such as dye removal in waste water or air filter [10]. In this research, activated carbon was produced from coconut shell and sugarcane bagasse. Both of them are available all year around and have advantage properties like high carbon content, low ash content, high yield, mechanical strength and resistance to attrition [11]. Activating agents namely phosphoric acid (H₃PO₄) and potassium hydroxide (KOH) were used for chemical activation purpose. Weight loss of the synthesized activated carbons was recorded and characterizations of physical properties were conducted by using XRD and FTIR-ATR.

2. MATERIALS AND METHODS

The coconut shells were collected from local market nearby in Jeli, Kelantan, Malaysia. KOH (ACS reagent) with purity ~ 85% and H₃PO₄ (ACS reagent) with purity ~ 85% were purchased from Sigma–Aldrich. Distilled water was also used to remove any impurities.

2.1 Preparation of Activated carbon. The coconut shells were crashed into smaller pieces using hammer. The smaller pieces of coconut shells then washed with distilled water to remove any impurities. Next, they were grinded using grinder before dried in an oven at 105°C for overnight to remove the moisture. Then, the grinded coconut shells were blended to get the sample in powder form. To make sure the powder in similar size, the powder samples were sieved in 250 μm.

For the sugarcane bagasse sample, firstly, it was washed with distilled water to remove any impurities. Then, the sugarcane bagasse was dried in oven at 105°C for overnight. After that, it was cut into smaller size before blending process. The grinded coconut shells and sugarcane bagasse were filled in the crucible before putting in the furnace at temperature of 300°C for pre-carbonization process.

The samples then added with activating agents, H₃PO₄ and KOH. These activating agents solution then mixed with the activated carbon using impregnation ratio which was 1:3. The 5, 10 and 15% different concentrations for H₃PO₄ and KOH were applied for the activation process. For the carbonization process, the samples were placed in furnace at 300°C for another 2 hours. Then, the samples were distilled with deionized water until the pH of water became neutral. Finally, the samples were dried in oven for several hours to remove the moisture.

2.2 Determination of Percentage of Weight Loss. The coconut shell and sugarcane bagasse samples before carbonization and the final product (activated carbon produced after chemical activation) weighed using an electronic weighing balance. The shell samples carbonized in a furnace for durations of 1, 2 and 3 hours to measure the percentage weight decrease or weight loss of the materials during preparation from the original weight of the raw materials. The mathematical expression as shown in Eq. 1.

\[
\text{Percentage of weight loss (\%)} = \frac{W_i - W_f}{W_i} \times 100
\]  

where \(W_i\) is the initial weight of the raw material and \(W_f\) is the final weight of the product.

XRD was conducted for determination of phase identification of activated carbon using Bruker D2 Phaser instrument. DIFFRAC.EVA software was used for qualitative analysis as well as the elemental analysis of the charcoal and activated carbon. In addition, the powder of XRD pattern was analyzed to investigate the crystallographic structures changes during activation process.

FTIR-ATR is a nondestructive analysis that can identify chemicals either organic or inorganic. FTIR-ATR analysis was used to study the surface organic structures and functional group presence at the surface of
activated carbon by Perkin Elmer Spectrum™ 400 FTIR-ATR Spectrometer. The samples were put into the FTIR-ATR spectrometer sample holder and the spectra were recorded between 400 and 4000 cm⁻¹.

3. RESULTS AND DISCUSSION

Weight loss of the prepared activated carbon from coconut shell and sugarcane bagasse for different concentration of H₃PO₄ and KOH (before and after activation processs) as shown in Figs. 1 and 2, respectively. Fig. 1 illustrated the weight loss of activated carbon from both coconut shell and sugarcane bagasse in different concentration of H₃PO₄ and KOH. It can be seen from Fig. 1(a) that approximately 30, 22 and 21% the weight loss occurred for coconut shell activated carbon while for sugarcane bagasse it was about 43, 38 and 32%. The weight loss of coconut shell after impregnation with KOH was about 49, 60 and 26% while for sugarcane bagasse was about 38, 47 and 32% as shown in Fig. 1(b). Weight loss increased in Fig. 1(b) due to the high excess of potassium hydroxide that promote gasification of char which caused the increased total weight loss of carbon.

![Fig.1 Weight loss of activated carbon from both coconut shell and sugarcane bagasse in different concentration(a) H₃PO₄, (b) KOH](image)

XRD analysis of coconut shell and sugarcane bagasse activated carbon as depicted in Fig. 2. The XRD spectra of native carbon and the activated carbon indicated that all those chars are amorphous. This was denoted by the existence of two peaks at the 2θ = 25° and 2θ = 45° for the samples from all figures [12]. The peak at the 2θ = 45° in all figures became stronger after impregnation process with KOH and H₃PO₄ which explained that the carbon have a tendency to crystallize at an elevated temperature [5].

Surface chemistry of the synthesized activated carbon was characterized by using FTIR-ATR. All figure in Fig. 3 showed that the first peak was around 3420-3440 cm⁻¹ which corresponded to as O-H stretching mode of hydroxyl groups and absorbed water [13]. For Fig. 3 (c) that shows sugarcane bagasse activated carbon impregnated with 5, 10 and 15% of KOH, the results showed the aromatic phenone compound. It was due to C=O stretching vibration that the most intense in the spectrum. For Fig. 3 (b), result showed that the 10% H₃PO₄ was resulted as aliphatic isothiocyanates compound and 15% H₃PO₄ showed as primary aliphatic alcohols. Primary aliphatic alcohol had one other carbon atom that attached to the oxygen bound carbon. For the primary alcohols, -C-O stretching and -OH deformation vibrations were at 1050 cm⁻¹ [14].
Fig. 3 (d) showed the C-O stretching at 1200-1180 cm$^{-1}$ and -C-O-C- stretching absorption at 1270-1230 cm$^{-1}$ [15]. According to Yakout & El-Deen [13], the most important changes revealed in this characterization were the development of C-H vibration which might happen due to disappearance of oxygen at the surface of the carbon material [8].

![Fig.2 X-ray diffractogram of (a) Coconut shell samples with different impregnation ratio of KOH, (b) Coconut shell samples with different impregnation ratio $\text{H}_3\text{PO}_4$, (c) Sugarcane bagasse samples with different impregnation ratio of KOH, and (d) Sugarcane bagasse samples with different impregnation ratio of $\text{H}_3\text{PO}_4$](image-url)
Fig. 3: Coconut shell impregnation with (a) KOH and (b) $\text{H}_3\text{PO}_4$, Sugarcane bagasse impregnation with (c) KOH and (d) $\text{H}_3\text{PO}_4$

4. SUMMARY

In this study, activated carbon was prepared from coconut shell and sugarcane bagasse. Addition of $\text{H}_3\text{PO}_4$ and KOH gave rise to more porous structure in the activated carbon. The results indicated that the activated carbon derived from coconut shell has higher carbon content compared to sugarcane bagasse. XRD results depicted that the activated carbon samples are amorphous. Surface chemistry analysis by FTIR-ATR revealed the surface functional groups that related to synthesized activated carbon from coconut shell and sugarcane bagasse.
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Structural and Thermal Properties of Extracted Cellulose Treated with 1-Butyl-3-Methylimidazolium Chloride

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ABSTRACT. In this work, alpha cellulose extracted from Mahang wood were successfully pretreated with BMIMCl. The structural and thermal properties of microcrystalline cellulose (MCC), untreated alpha cellulose and BMIMCl treated alpha cellulose at 2 wt.%, 5 wt.% and 8 wt.% were analyzed by X-ray diffraction (XRD), Fourier transform infrared analysis (FTIR) and thermogravimetric analysis (TGA) analysis. The results showed that the crystal structures of cellulose were transformed from cellulose I to II with different degree of crystallinity after BMIMCl pretreatment. FTIR and X-ray diffraction analyses indicated that the regenerated cellulose was a mixture of amorphous and crystalline cellulose. The thermal stability of cellulose decreased after BMIMCl ionic liquid treatment. The used of high amount of BMIMCl during pretreatment can be potentially produce regenerated cellulose that is very correlate to the real properties and characteristics of nanocellulose (NCCs).

Keywords: Ionic liquid, Pretreatment, Regenerated cellulose, Crystallinity

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1. INTRODUCTION

Cellulose is abundantly found on earth especially in wood and other lignocellulosic biomass. There are many sources of cellulose that can be isolated and extracted from various types of plants [1]. Mahang (Macaranga spp.) is a pioneer and soft-wooded tree species that consider as light density wood types and have abundant quantity in the logged-over forest in Southeast Asia [2]. Apart from fast-growing ability, Mahang also has the great advantages such as exotic colours and texture, cheaper price and also abundance availability. From the other sides, Mahang is still under-utilized plants due to it poor properties and the information regarding the species is also limited, but it can greatly contribute the great potential in composite production by added value into the wood types [3].

Recently, ionic liquid has been used widely as the new type of green solvent pretreatments used in lignocellulosic field. Many researchers proved that ionic liquids can dissolve cellulose and have great versatility in the field of cellulose technology. Pretreatment with ILs more environmentally friendly than other pretreatment methods such as mechanical milling, steam explosion, acid, base, or organic solvent processes. Many researchers proved that ionic liquids can dissolve cellulose and have great versatility in the field of cellulose technology [4]. By the addition of water, ethanol or acetone, cellulose can be easily generated from its ionic liquid solutions [5].

In this study BMIMCl is used to dissolve the alpha cellulose extracted from Mahang wood. The effect of BMIMCl on structural and chemical properties of alpha cellulose extracted from Mahang wood will be investigated.
2. MATERIALS AND METHODS

Cellulose was extracted from Mahang wood according to TAPPI Test Method T204. The alpha cellulose was then dissolved in BMIMCl at 2 wt.%, 5 wt.% and 8 wt.%. The solutions were then heated in an oil bath at 80 ºC under continuous vigorous stirring for 12 hours. The solutions were then cooled at room temperature and regenerated using distilled water. The regenerated cellulose was freeze dry for 24 hours prior the characterization process. The structural and thermal properties of the regenerated cellulose were analyzed using XRD, FTIR and TGA and were then compared to the microcrystalline cellulose (MCC) and untreated alpha cellulose.

2.1 X-ray Diffraction (XRD). The crystalline phase and crystallinity index of the samples were studied using an X-ray diffractometer (D2-Phaser Bruker XRD) equipped with a monochromatic CuKα radiation source (λ = 0.154 nm). The samples were scanned in the step-scan mode with a 2θ angle ranging from 5º to 60º with a step of 0.01º and a rate of 1º min⁻¹ under room temperature. The operating voltage was 40 kV and the current was 40 mA. The crystallinity of the samples, the crystallinity index (CI) was determined based on the reflected intensity data using method of Segal et al. [6]:

\[
CI (\%) = 100 \times \left( \frac{I_{002} - I_{am}}{I_{002}} \right)
\]

Where \(I_{002}\) is the maximum intensity for the crystalline portion in samples (i.e., cellulose) at about \(2θ=22º\) and \(I_{am}\) is the intensity attributed to the amorphous portion of samples (i.e., hemicellulose and lignin) at \(2θ=18º\).

2.2 Fourier transform infrared analysis (FTIR). The FTIR spectra of the samples were recorded on a FTIR instrument (Nicolet iZ10 FT-IR Microscope) in the range of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹.

2.3 Thermogravimetric analysis (TGA). The thermal stability of the samples was determined using a Mettler Toledo thermogravimetric analyser (TGA/DSC) under the following operational conditions: sample weight approximately 7 mg was transferred into the alumina, temperature range 25 to 550 ºC and heating rate 10 K min⁻¹. In order to prevent any premature thermoxidative degradation, all measurements were performed under a nitrogen atmosphere with a gas flow rate of 20 cm³ min⁻¹.

3. RESULTS AND DISCUSSION

The crystallinity of samples was characterized by XRD. Fig. 1 showed all of the XRD patterns with ordered structure of crystalline and amorphous region. Three characteristics peaks of MCC showed at \(2θ = 14.9º, 16.5º,\) and \(22.6º\) which corresponded to crystallographic plane of crystals (110), (111), and (002) respectively. Alpha cellulose showed a slightly different pattern which more amorphous and less sharp at \(2θ = 19.75º\) compared to MCC. The differences are probably due to the disrupted of ordered structure of the crystalline region of the alpha cellulose by the extraction process. It is clearly shown that BMIMCl treated alpha cellulose at 2 wt.% has high crystalline cellulose pattern with the occurrence of a most intense and sharp peak (002) at \(2θ = 26.10º\). On the other hand, 5 wt.% and 8 wt.% of regenerated cellulosic indicate amorphous pattern after IL pretreatment because the peak (101) disappeared and the peak (002) became broader and weaker (Fig.1).

The intense and sharper peak pattern of 2wt.% alpha cellulose (Fig. 2) compared to the others is very correlate to the real properties and characteristics of nanocellulose (NCCs) which is high crystallinity. Besides, 2wt.% alpha cellulose pattern indicates that the regenerated cellulose obtained with high amount of IL have more crystalline region because BMIMCl has selectively removed the amorphous region pattern. The higher crystallinity of 2 wt.% alpha cellulose may due to the highest amount of ionic liquid treated ratio compared to 5 wt.% and 8 wt.%.
Fig. 1 XRD pattern of (a) MCC, (b) alpha cellulose, (c) 2 wt.% alpha cellulose, (d) 5 wt.% alpha cellulose and (e) 8 wt.% alpha cellulose

Fig. 2 XRD pattern of 2 wt.% BMIMCl treated alpha celluloses

The crystallinity index (%) of all samples has been tabulated in Table 1. As shown in Table 1, the crystallinity index (Crl) and crystallite size of MCC are higher than the alpha cellulose. This indicates alpha cellulose has lower amount of crystallinity compared to MCC. Except for 2 wt.% that shows high crystallinity index, both 5 wt.% and 8 wt.%, exhibit lower crystallinity index relative to its origin, alpha cellulose.

The crystallite size of 2 wt.% of regenerated cellulose also is the largest size which is 15.22 nm compared to 5 wt.% and 8 wt.% of regenerated cellulose which are only 0.40 nm and 0.32 nm respectively. The improved crystallinity index for 2 wt.% of regenerated cellulose can attributes to the elimination of the amorphous parts as the amount of BMIMCl increased [7]. Dissolution of the amorphous regions is predominant as it is more prone to IL treatment than the crystalline parts.
Fig. 3 illustrates the FTIR spectra of MCC, alpha cellulose and BMIMCl treated alpha celluloses. It was observed that the bands in the five spectra are somewhat similar, implying the similar structure of the cellulosic samples either with or without ionic liquid treatment. All the cellulosic samples show the almost identical basic structure which suggested no changes in the functional groups. However, a slight difference can be detected in the infrared spectra in terms of different absorbance values and shapes of bands and also their location.

Table 1 The crystallinity index (Crl) of MCC, alpha cellulose and cellulose treated with ionic liquid at 2 wt.%, 5 wt.% and 8 wt.%

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity index (%)</th>
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<tbody>
<tr>
<td>MCC</td>
<td>78.10</td>
</tr>
<tr>
<td>Alpha cellulose</td>
<td>59.74</td>
</tr>
<tr>
<td>2 wt.%</td>
<td>74.76</td>
</tr>
<tr>
<td>5 wt.%</td>
<td>56.33</td>
</tr>
<tr>
<td>8 wt.%</td>
<td>35.90</td>
</tr>
</tbody>
</table>

Spectra of all the cellulosic samples show the strongest absorption band at about 1019 cm⁻¹. This band corresponds to the stretching vibration of the C-O-C pyranose ring (antisymmetric in phase ring) of cellulose molecules [8]. The peak near 3331 cm⁻¹, which was observed in all spectra, is attributed to characteristic hydrogen bond O-H stretching vibrations due to the presence of water. The absorption around ~2982 cm⁻¹ observed in the five spectra which indicates the aliphatic saturated C-H stretching associated with methylene groups in cellulose. Moreover, the O-H bending of absorbed water bound to the cellulose structure gave rise to peak at 1637 cm⁻¹. Besides that, the absorption bands are clearly observed around 895 cm⁻¹ corresponding to β-glycosidic linkages. In addition, the absence of peaks of IL (BMIMCl) in the spectra implied the complete removal of IL during the washing process [9].

Compare between five spectrums, there were small differences of absorbances in spectrum of BMIMCl treated alpha cellulose. The peak around 896 cm⁻¹, assigned to C-O-C stretching at β-1-4-glycosidic linkages, increased in intensity in the amorphous samples, compared to the other samples. The increase in the
intensity of the peak around 896 cm\(^{-1}\) for 2 wt.%, 5 wt.% and 8 wt.% regenerated cellulose compared to untreated cellulose as shown in Fig. 3 indicates the structure of cellulose become more amorphous after BMIMCl pretreatment. The intensity around 896 cm\(^{-1}\) band is very sensitive to the amount of crystalline versus amorphous structure of cellulose. The higher intensity of this band reflects higher amounts of disordered structure [10].

Figs. 4 and 5 show the thermogravimetric (TG) and its derivatives (DTG) of all samples. At the temperature below 100 °C, all of the samples had an initial small amount of weight loss that indicates to the evaporation of water [6]. Decomposition MCC and alpha cellulose took place at the temperature of (310 °C-380°C) and (250 °C-370°C) respectively which both illustrated one step pyrolysis process. Conversely, the decomposition of the regenerated cellulose occurred within a wider range of weight percentage with two distinct pyrolysis process that well separated in close proximity. The first pyrolysis of regenerated cellulose occurred from 220°C to 280 °C with the \( T_{\text{max}} \) peak at 240°C that attributes to the decomposition of amorphous regions, while the second pyrolysis had greater dominance over the first pyrolysis, ranging from 280 °C to 350 °C with \( T_{\text{max}} \) at 325 °C that represented to the breakdown of the crystal interior [6].

![Fig. 4 TG curves](image)

**Fig. 4** TG curves for (a) MCC, (b) alpha cellulose, (c) 2 wt.%alpha cellulose, (d) 5 wt.%alpha cellulose and (e) 8 wt.% of BMIMCl treated alpha cellulose

The value of \( T_{\text{max}} \) derived from TGA data represents the temperature at which the maximum decomposition occurs. Hence, \( T_{\text{max}} \) is used to evaluate the impact of IL pretreatment on the thermal stability of samples. This difference in thermal degradation was probably due to the degree of crystallinity. Besides, the two peaks that observed in two-step pyrolysis process could be due to the presence of both crystalline and amorphous components in the regenerated cellulose. In general, it is easier to breakdown the amorphous region at a lower temperature followed by weight loss due to the crystalline components, which decompose at high temperature.
The decreasing trend of decomposition temperature concludes that the thermal stability of regenerated cellulose was lower than MCC. Besides, this reduction in thermal stability could be due to several factors [6] such as the thermal stability that reduces for regenerated cellulose due to the higher surface area of fiber dimensions than macroscopic cellulose which increases the heat exposure and also the delignification occurring at higher pretreatments temperature may also contribute to lower the thermal stability.

4. SUMMARY

In this work, alpha cellulose extracted from Mahang wood were successfully pretreated with BMIMCl. The crystal structures of cellulose were transformed from cellulose I to II with different degree of crystallinity after BMIMCl pretreatment. FTIR and X-ray diffraction analyses indicated that the regenerated cellulose was a mixture of amorphous and crystalline cellulose. The thermal stability of cellulose decreased after BMIMCl ionic liquid treatment. The used of high amount of BMIMCl during pretreatment can be potentially produce regenerated cellulose that is very correlate to the real properties and characteristics of nanocellulose (NCCs).

REFERENCES


Structural Defect(s) in CaCu$_{3+x}$Ti$_4$O$_{12+δ}$ Solid Solution Estimated via Reitveld Refinement Method

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**ABSTRACT.** The structural defect(s) in CaCu$_{3+x}$Ti$_4$O$_{12+δ}$ (-0.02 ≤ x ≤ 0.02) solid solution prepared by conventional solid-state reaction method was comprehensively investigated. X-ray diffraction (XRD) pattern of the materials exposed that a monophasic CCTO without any traces of secondary phase was presented in all samples. Refinement analysis on the structure of solid solution exposed that the crystallite size and strain as determined by Scherrer's equation and Reitveld method is not matched to each other. However, further refinement analysis exposed that the Reitveld method is more reliable to elucidate the structure of solid solution since it has more broadening parameters (e.g. particle, instrument, etc.) than that of Scherrer's equation. The possible mechanism of the solid solution formation was studied by correlating the lattice parameter and bonds length to the several defects and compensation mechanisms of oxygen/cation vacancy and cation disorder substitution. The change of bond length (Δd) with variation of x was evaluated, and the result showed that the Ti-O (6x) and Cu-O (4x) bond for Cu-deficient sample (x < 0) have the smallest Δd value as compared to other bonds due to Coulombic attraction between affective charge carrier of (TiO$_5$V$^-$ and TiO$_5$V$^{**}$) and (CuO$_4$′ and TiO$_5$). Similarly, the smallest Δd value in the Cu-excess sample (x > 0) has been correlated due to Coulombic attraction of TiO$_5$′ and (Cu$_{Ti}$)O$_5$V$^{**}$.

Keywords: CCTO, Nonstoichiometry, Structural defect, Reitveld refinement;

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1. INTRODUCTION

CaCu$_3$Ti$_4$O$_{12}$ (CCTO) perovskite-like ceramic oxide has received considerable attentions in recent years due to its colossal relative dielectric constant ($\varepsilon_r$) up to $10^5$, which is nearly constant over a wide range of frequencies (static field dc - 1 MHz) and temperatures (100 - 600 K), without undergoing any ferroelectric phase transition [1]. Such properties are essential to allow smaller capacitive components, which offers an opportunity to reduce the dimension of microelectronic devices. Unfortunately, the loss tangent (tanδ) of CCTO was still too large (0.05 – 0.2 at 1 kHz), its breakdown field was just at 2 kV/cm and even shows non-Ohmic properties similarly to the ZnO varistor [2], but still not fit in the standard of a relaxor either, thus has become the roadblock for many technical applications.
Besides the application of views, the colossal dielectric constant of CCTO also have attracted attentions for researchers to clarify the main origin of this phenomenon. So far, the internal barrier layer capacitor (IBLC) model of Schottky-type potential barriers arising from n-type semiconducting grains and insulating interfaces as been widely accepted [3,4]. The real origin mechanism responsible for the electrical heterogeneity between grain and grain boundary has been explained related to the nonstoichiometry oxygen and cations, even though the starting reactant was prepared in a perfect stoichiometry formulation of CCTO. Models based on oxygenloss [5], cation reduction/oxidation [6] and cation deficiency/excess [7] are reported responsible for semiconductivity of grain, while the accumulation of defects such as twin boundaries, dislocation and stacking faultsin the intergranular regions of grain boundary is responsible for insulating property.

The oxygen loss mechanism (e.g. \( \text{O}_5^2- \rightarrow \text{V}_{\text{O}}^{\ast} + 2e^\ast + \frac{5}{4} \text{O}_2 \)) is commonly observed for many perovskite-based titanates when heated at >1000 °C and/or in reducing atmosphere [5] and the formation of oxygen vacancy and free electron. The compensation occurs by partial reduction of Ti^{4+} into Ti^{3+} (or TiO_5^\ast) to preserve the local electro neutrality. On the other hand, Cu vacancy and segregation are commonly observed in the CCTO ceramic prepared by solid-state reaction due to the diffusion distance of atoms is longer than wet-chemistry methods. Based on this fact, three mechanisms were proposed namely (1) Cu deficiency mechanism relates to the formation of Cu vacancy during heating and the compensation occurs via partial reduction of neighbour Cu^{2+} into Cu^{+} (or CuO_{\ast}) and partial occupation of Ti^{4+} into Cu site [8], (2) Cu segregation mechanism only valid for CCTO ceramic heated at >1025 °C lead to Cu moved outward from the perovskite structure and the formation of Cu vacancy. Compensation occurs via partial oxidation of Cu^{2+} to Cu^{3+} [9] and (3) Cu excess mechanism is responsible for the formation of vacancies at Ti and O sites, whose compensated by partial occupation Cu at Ti site (or (Cu_{\ast})O_{\ast}^{\ast}) and the formation of O vacancy [9]. Besides that, the last mechanism is proposed due to limited diffusion of oxygen at grain boundary during the cooling stage, which prevent reoxidation of Cu^{+} into Cu^{2+} [10], while the compensation is possibly by partial reduction of Ti^{4+} into Ti^{3+}. The presence of compensating ions e.g. Cu^{\ast}, Cu^{2+} and Ti^{3+} is recorded by XPS analysis [9,11], Cu loss detected by EDX analysis [9] and cation disorder is proposed by first principle calculation methods [12]. However, the detection of those structural defects via XRD analysis is scarcely reported in literatures, while the estimation study to relate structural defects formation to the certain ion(s) and its bond length still not been attempted.

To best of our reviews and knowledges, it is actually possible to detect some structural defects in CCTO ceramic through the details examination of crystal structure. The presence of extra local-charges due to defects and compensation mechanisms at the certain ions would increase the contraction force of cation-oxygen and cation-cation, hence slightly reducing the bond length or vice versa. Therefore, in this work, Cu nonstoichiometry CCTO ceramic samples were prepared via conventional solid-state reaction method. The possible defects formation in the CCTO perovskite was investigated via Reitveld refinement method.

2. MATERIALS AND METHODS

The CCTO samples were prepared via SSR method from commercial starting raw materials of CaCO_3 (purity >99%, Sigma-Aldrich), CuO (purity >99%, Sigma-Aldrich) and TiO_2 (purity >99.9%, Merck). Appropriate amounts of powder were prepared according to the various stoichiometry ratios of CaCu_3+\textit{x}Ti_4O_{12+\textit{x}} (\textit{x} = -0.02, -0.01, 0, 0.01 and 0.02), which further designed as SCu-2, SCu-1, SCu0, SCu+1 and SCu+2, respectively. All powder ratios were dry-mixed separately using a rotary mill machine with zirconia ball as grinding media and deionized water as solution media at a constant speed of 150 rpm for 24 hours. Afterwards the mixed powders were calcined in air at 900 °C for 12 hours. The degranulation powder was adopted manually by agate mortar and pestle, before being compacted into a green body (rectangular) form (14 x 14 x 4 mm^3) and then sintered in air at 1040 °C for 10 hours with a constant heating and cooling rate of 5°C/min. The phase composition and structure of all samples were recorded using an X-ray diffractometer (D8 Advance, Bruker-AXS) with Ni-filtered CuKα (\( \lambda = 1.54056 \text{ Å} \)) radiation in a wide range 20 of 10 – 90°.
The phase identification and composition of obtained XRD profiles were determined by PANalytical X’Pert High score (Plus) 3.0 software (Reitveld refinement method - automatic mode). Priors to structure calculation, the details of peaks profile e.g. position (Y), intensity (I), d-spacing (d) and full-width at half maximum (FWHM) or peak width (β) was determined by fitting technique (automatic - default), then the lattice parameter (a) was calculated according to Eq. 1.

\[ a = \sqrt[3]{d_{(hkl)}^2 + k^2 + l^2} \]  

(1)

Meanwhile, the crystallite size (Lc) and strain (ε) of CCTO were calculated using Scherrer’s equation (using single-line peak width of (220) plane: designed as Lcs and es, respectively) and Reitveld refinement method (using full-pattern integral breath: designed as Lcr and εr, respectively). The fully crystalline NIST 660a SRM LaB6 standard material with β equal to 0.087° was used as the instrument broadening affects. The bond length (d) of cation-oxygen/cation was computed directly from the software after the refinement process is completed. Noted that the refinement steps of structure determination were followed well-known Ray Young’s refinement strategy.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern for cubic CCTO perovskite (SCu0) and solid solutions and their Reitveld refinement results are further listed in Table 1. Apparently, all diffraction peaks could be fully indexed to all planes of body-centered cubic perovskite-related structure under Im3 (No. 204) space group, agrees well with those reported in Inorganic Crystal Structure Database (ICSD file no. 96-100-8181). No extra peaks associated to the secondary phase or contaminations has been observed, indicated that the variation of x value for both system (deficiency and excess) is under solubility limits of Cu atom in CCTO lattice structure. However, it is worth to mention that the absence of diffraction peaks for the secondary phase does not mean that the excess of CuO is avoided as an amorphous impurity phase in the intergranular regions of grain boundaries. In addition, at low content (below 2-3%), the Cu-related impurity phase may not be able to be detected by XRD machine due to its detection accuracy. The convergence was achieved for most samples, where the agreement indices for three reliabilities of residual (Rp, Rexp and Rwp) and GoF value are less than 10% and in the range of 1-2, respectively.

Fig. 1 XRD pattern of CaCu3+xTi4O12+δ ceramics sintered at 1040 °C for 10 hours in air

Further interpretation of the peak profiles indicated that the CuO composition (x) has strong affects to the crystallite size and strain, lattice parameter and bonds length. Noted that the crystallite size and strain were
determined by Scherrer’s equation and Reitveld method, in order to make clear distinctive of broadening parameters involved: Scherrer’s (refined only instrumental and particle size, while the others e.g. size + microstrain + temperature + solid solution inhomogeneity are not involved) and Reitveld method (all factors above are refined except solid solution inhomogeneity).

Table 1 Reitveld refinement results of cubic CCTO perovskite and CaCu\textsubscript{3-x}Ti\textsubscript{4}O\textsubscript{12+δ} solid solution

<table>
<thead>
<tr>
<th>Properties</th>
<th>Sample</th>
<th>SCu-2</th>
<th>SCu-1</th>
<th>SCu0</th>
<th>SCu+1</th>
<th>SCu+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y\textsubscript{(220)}(°)</td>
<td></td>
<td>34.2971(4)</td>
<td>34.3062(4)</td>
<td>34.3099(9)</td>
<td>34.2942(4)</td>
<td>34.2853(5)</td>
</tr>
<tr>
<td>I\textsubscript{(220)} (Count)</td>
<td></td>
<td>9448(81)</td>
<td>9445(82)</td>
<td>9688(65)</td>
<td>9107(82)</td>
<td>7537(67)</td>
</tr>
<tr>
<td>β\textsubscript{(220)}(°)</td>
<td></td>
<td>0.099(1)</td>
<td>0.100(1)</td>
<td>0.106(3)</td>
<td>0.096(1)</td>
<td>0.122(1)</td>
</tr>
<tr>
<td>d\textsubscript{220}(Å)</td>
<td>Scherrer</td>
<td>2.61251</td>
<td>2.61184</td>
<td>2.61157</td>
<td>2.61272</td>
<td>2.61338</td>
</tr>
<tr>
<td></td>
<td>Reitveld</td>
<td>Maximum</td>
<td>Maximum</td>
<td>Maximum</td>
<td>Maximum</td>
<td>2047</td>
</tr>
<tr>
<td>Scherrer</td>
<td>L\textsubscript{CS}(Å)</td>
<td>7236</td>
<td>6680</td>
<td>4570</td>
<td>Maximum</td>
<td>2481</td>
</tr>
<tr>
<td></td>
<td>ε\textsubscript{S}(%)</td>
<td>0.067</td>
<td>0.070</td>
<td>0.086</td>
<td>0.057</td>
<td>0.121</td>
</tr>
<tr>
<td>Reitveld</td>
<td>L\textsubscript{CR}(Å)</td>
<td>Maximum</td>
<td>Maximum</td>
<td>Maximum</td>
<td>Maximum</td>
<td>2047</td>
</tr>
<tr>
<td></td>
<td>ε\textsubscript{R}(%)</td>
<td>0.029</td>
<td>0.031</td>
<td>0.037</td>
<td>0.036</td>
<td>0.038</td>
</tr>
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</table>

CCTO

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>SCu-2</th>
<th>SCu-1</th>
<th>SCu0</th>
<th>SCu+1</th>
<th>SCu+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-0 (12x)</td>
<td>2.60405(2)</td>
<td>2.60339(2)</td>
<td>2.60311(5)</td>
<td>2.60426(2)</td>
<td>2.60492(1)</td>
</tr>
<tr>
<td>Ca-Ti (8x)</td>
<td>3.19966(2)</td>
<td>3.19884(2)</td>
<td>3.19850(5)</td>
<td>3.19992(2)</td>
<td>3.20072(1)</td>
</tr>
<tr>
<td>Cu-O (4x\textsubscript{1})</td>
<td>1.96049(1)</td>
<td>1.95999(1)</td>
<td>1.95979(3)</td>
<td>1.96065(2)</td>
<td>1.96115(1)</td>
</tr>
<tr>
<td>Cu-O (4x\textsubscript{2})</td>
<td>2.78246(2)</td>
<td>2.78175(2)</td>
<td>2.78146(5)</td>
<td>2.78269(3)</td>
<td>2.78339(2)</td>
</tr>
<tr>
<td>Cu-Ti (8x)</td>
<td>3.19966(2)</td>
<td>3.19884(2)</td>
<td>3.19850(5)</td>
<td>3.19992(2)</td>
<td>3.20072(1)</td>
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<tr>
<td>Ti-O (6x)</td>
<td>1.96189(2)</td>
<td>1.96138(2)</td>
<td>1.96118(4)</td>
<td>1.96205(2)</td>
<td>1.96254(1)</td>
</tr>
<tr>
<td>O-O (1x\textsubscript{1})</td>
<td>2.63945(2)</td>
<td>2.63878(2)</td>
<td>2.63850(6)</td>
<td>2.63967(3)</td>
<td>2.64033(2)</td>
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<tr>
<td>O-O (1x\textsubscript{2})</td>
<td>2.89956(3)</td>
<td>2.89882(3)</td>
<td>2.89851(7)</td>
<td>2.89980(3)</td>
<td>2.90053(2)</td>
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<tr>
<td>O-O (4x\textsubscript{1})</td>
<td>2.76351(2)</td>
<td>2.76280(2)</td>
<td>2.76251(5)</td>
<td>2.76373(2)</td>
<td>2.76443(1)</td>
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<tr>
<td>O-O (4x\textsubscript{2})</td>
<td>2.78550(2)</td>
<td>2.78479(2)</td>
<td>2.78449(5)</td>
<td>2.78573(2)</td>
<td>2.78643(2)</td>
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Agreement Indices

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<th>Residual (%)</th>
<th>R\textsubscript{p}</th>
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<th>2.01541</th>
<th>2.73154</th>
<th>2.82596</th>
<th>1.73432</th>
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<tr>
<td>R\textsubscript{exp}</td>
<td>4.63535</td>
<td>4.54480</td>
<td>4.74822</td>
<td>5.85630</td>
<td>3.78061</td>
<td></td>
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<tr>
<td>R\textsubscript{wp}</td>
<td>7.55384</td>
<td>7.54799</td>
<td>5.87419</td>
<td>8.22005</td>
<td>7.60132</td>
<td></td>
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<tr>
<td>GoF</td>
<td>1.62962</td>
<td>1.66080</td>
<td>1.23714</td>
<td>1.40363</td>
<td>2.01061</td>
<td></td>
</tr>
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</table>

*Noted that the maximum value for L\textsubscript{CS} and L\textsubscript{CR} that could be calculated via Scherrer’s equation and Reitveld method is ≥10000 Å and 27913.4 Å, respectively.

The results showed that the crystallite size and strain obtained from those methods are not matched to each other, except SCu+2 sample shows comparable L\textsubscript{C} value, conveying that the standard broadening parameters using Scherrer’s equation seems not appropriate to elucidate the effects of solid solution. Therefore, further clarification of lattice structure by using Reitveld method only will be taken into accounts. As seen from Table 1, the crystallite size of all samples is comparable to each other (27913.4 Å), except SCu+2 sample shows smaller size (2047 Å). Interestingly, the lattice strain has changed linearly with the variation of
x, where the highest value is recorded for the SCu+2 sample, which is consistent to the previous literature's propositions of (1) partial substitution of bigger Cu²⁺(~0.62 Å) ions into Ti⁴⁺(~0.605 Å) site [8] and (2) partial reduction of Ti⁴⁺ to Ti³⁺ (~0.67 Å) ions [5], hence affects the size broadening related to solid solution. Besides that, the lattice parameter of CCTO is increased proportionally with the increase or decrease of x value. This relationship is actually following the defects and compensation mechanisms as proposed from many literatures [5-12]. The deficiency of CuO could promoted the formation of V_{Cu} and V_{O}. Compensations occur via partial reduction of Cu²⁺ into Cu⁺ (0.77 Å) and partial occupation of Ti⁴⁺ into V_{Cu} site, hence increase the lattice parameter. With continuous increase in lattice parameter with decreasing of x value proof that the compensating Cu⁺ ions is dominated. In contrast, the excess of CuO in CCTO would lead to the formation of (i) V_{Ti} and V_{O} within crystal structure and (ii) Cu segregation produces V_{Cu} at the faced-centered of crystalline. Compensation occurs via (partial occupation of Cu²⁺ into V_{Ti} site and partial reduction of Ti⁴⁺ to Ti³⁺) and partial oxidation of Cu²⁺ to Cu³⁺ (~0.64 Å), respectively. The continuous increasing of a value with the increase of x is only preserve for the domination of compensating Ti³⁺ and Cu³⁺ ions, whilst the CuTi can be ignored because it’s has an opposite effect.

To support numerous defect mechanisms above, the change of bond length (Δd = d_i - d_o; where d_i and d_o are bond length of solid solution and cubic CCTO perovskite, respectively) was used to illustrate the effect of CuO variation (Fig. 2). It is clearly seen that the bond length increases monotonically with the increase/decrease of x value. Among them, only Cu-O (4x1) and Ti-O (6x) bonds displayed a lowest change, while Ca-Ti (8x), Cu-O (4x3) and Cu-Ti (8x) bonds considerably displayed the highest change. Both Cu-O (4x1) and (4x3) bonds are located at face-centred positions of the cubic perovskite (Fig. 2b), but shows not comparable in Δd value, implying that the defect clusters with different of charges would be introduced in the ceramics. In principle, the detection of oxygen vacancy at faced centered (TiO_5V_o• and TiO_5V_o••) and corner (CaO_11V_o• and CaO_11V_o••) of cubic perovskite structure has been proposed by Oliveira et al. [13]. For Cu deficient sample, both TiO_5V_o• and TiO_5V_o•• defects could attracted to CuO_4 and TiO_6 (due to limited oxygen content), thus reducing the Ti-O (6x) and Cu-O (4x1) bond length. However, the lowest change of Ti-O (6x) and Cu-O (4x1) bonds for Cu excess CCTO is associated to the presence of TiO_6 and (CuTi)^O3V_o••.

4. SUMMARY

![Fig2](a) Change of bonds length for CCTO ceramic with variation of Cu content (noted that the dash-line across each line is representing the average value) and (b) Schematic diagram of partial CCTO perovskite representing the location of Cu-O bond.
The structural defect(s) in CaCu$_{3+x}$Ti$_4$O$_{12+\delta}$ (x = -0.02, -0.01, 0, 0.01 and 0.02) solid solution prepared by conventional solid-state method was investigated via Reitveld refinement method. A monophasic CCTO without any traces of secondary phase was observed for all prepared samples. The first distinctive of crystallite size and strain by using Scherrer’s equation and Reitveld method revealed that they are generated the different values, probably due to the different of computing data (peak width and integral breath) applied, but further analysis exposed that the Reitveld method is more suitable to elucidate the effects of Cu nonstoichiometry because its refined more broadening effects than that of Scherrer’s equation. The possible formation of structural defects in CCTO ceramic was studied by correlated the present result (e.g. crystallite size and strain, lattice parameter and bonds length) to the previous defects and compensation mechanisms as proposed in the literatures. The results show that the variation of CuO composition has a great influence to the lattice structure of CCTO by creating a substantial amount of defects with different in charges.

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Structural Evolution of YIG during Microwave and Conventional Sintering at 1000 °C

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ABSTRACT. Microwave heating (MH) has emerged in recent years as a new method for sintering a variety of materials against conventional sintering (CH) procedure. However, the phenomenon of microwave-materials interaction is still under debate. In this work, the effect of microwave heating on YIG phase formation was investigated at 1000 °C under the electromagnetic field (2.4 GHz). The phase stability fired samples were qualitative and quantitative analyzed using X-ray diffraction (XRD) techniques. The obtained data were compared with CH to track the phase evolution. XRD revealed MH has produced YIG with 94% faster than CS. The calculated activation energy at this temperature via diffusion control model shows that MH (39.20 kJ/mol) can effectively promote the phase growth rather than CH (90.96 kJ/mol).

Keywords: Microwave heating, Reaction kinetic, Diffusion controlled, Refinement method;

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1. INTRODUCTION

Garnet ceramics with a chemical formula of \(A_3B_2O_{12}\) have gained much attention because of their wide range of applications. These include YIG, YAG, and LLZ ceramics which have been investigated in a solid-state laser, wireless communication, storage devices and solar cell applications, recently [1-3]. Owing to their remarkable properties, various synthesizing techniques such as sol-gel route, hydrothermal, chemical vapor deposition (CVD), self-combustion, mechanochemical milling and co-precipitation techniques have been improvised to ensure the final product is in high purity and density. Compared to the above-mentioned techniques, the microwave heating (MH) has been found to be able to boost the production rate at a shorter time (10 times faster than conventional heating, CH) with low energy consumption without deteriorating materials’ properties. It is also reported that MH has been effectively densified materials up to 99% [4]. There are many reports on the usage of MH to enhance the garnet properties [3,5-7]. However, due to ponderomotive effect and local thermal effect, most of the final product synthesized via MH was end up with the presence of “unwanted” phases (e.g., secondary phase) [8,9]. These phases in garnet ceramics are
detrimental because they can degrade the device’s performance. Therefore, it is important to understand the reaction mechanism and mass transport of these materials so that the presence of any unwanted phases can be prevented. However, the reaction mechanism and mass transport of these materials under MH has not been well clarified in the literature. The study is of necessity as fine garnet’s structure with high purity and density can be synthesized quickly.

There are several diffusion models that could explain the kinetic behavior or reactivity of the materials at the solid-state regime. Ginstling-Brounshtein, Dunwald-Wagner, Jander, Valensi-Carter models are among them [10,11]. These models with the aid of Arrhenius plot could portray the cation transport through the reacted layer. In MH, the cation transport is assumed increases since the reaction is induced by the electromagnetic field (EMF). The reaction is related to the ease of moving atoms from their normal sites to neighbouring sites in order to reach a state of chemical equilibrium which in return, resulting in the formation of a new compound [12,13]. For that reason, some insight on diffusion mechanism in MH can be derived by correlating garnet phases and reaction kinetic.

The purpose of this work is to investigate the enhancement of the reaction using microwave heating and measure the conversion rates for YIG at various reaction temperatures and times. The first series of investigation is to determine the mass fraction of the reacted layer followed by developing multi-step reaction model based on the kinetics rate of garnet formation and it disassociation reactions under microwave field.

2. MATERIALS AND METHODS

A standard stoichiometry formulation of garnet was applied; 3:5 of A to B ratio based on A3B5O12 garnet chemical formula. A mixture of garnet starting precursors was mixed in ethanol- reagent grade (C2H4O) to enhance the particle surface contact. The process was assisted by the addition of the cylindrical zirconia ball at 1:10 powder to ball weight ratio. The mixing process has taken place for 8 hours at 25 rpm using Heidoph Overhead Mixer (Reax 2) to form a homogeneous slurry before dried in an oven (Memmert Oven-UM 400) at 80 °C for 24 hours to produce a dried cake. The cake was crushed using agate mortar and later, uniaxially pressed into 13 mm cylindrical pellets.

For reaction kinetic and mass transfer investigation, the compacted pellets were heated from 800 °C to 1250 °C using DAWNXY microwave furnace and were held at various heating rates; 15, 30, 45, 60 min, respectively. The samples were placed in Al2O3 crucible while the temperature of the samples was measured using a Pt-Rh thermocouple (B-type thermocouple)-direct touching that is installed and placed in contact with the pellets surface. The characterization of fired samples was carried out using X-ray diffraction analyses (XRD) to study the phase changes. Rietveld refinement method was performed using the Expert Highscore Plus program and the reliability of the refinement result was judged by the goodness of fit (GOF) and the weighted pattern R factor (Rwp).

3. RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 showed the qualitative and quantitative analyses of phases formed at different heating; microwave heating (MH) and conventional heating (CH). All phases presence are matched and corresponded well with ICSD number of 98-000-6274 (Fe3O4, hematite), 98-000-8038 (YFeO3, YIP), 98-005-3764 (Y3Fe5O12, YIG) and 98-002-3761 (Y2O3, Yttria), respectively. It is worth to note the goodness of fit (GOF) for quantitative analyses as per Fig. 1(b) and Fig. 2(b) obtained are approximate ~1.5 (closer to 1 is an ideal fitting).

It can be seen that YIG phase presence after 10 minutes under microwave heating whereas none of YIG phase was found even after 60 minutes of firing under conventional heating. It has been found that phase
transformation of $5\text{Fe}_2\text{O}_3 + 3\text{Y}_2\text{O}_3 \rightarrow 2\text{Y}_3\text{Fe}_5\text{O}_{12}$ is relatively quick in MH compared to CH. This showed that MH can promote phase transformation at a lower temperature. It was worth noting that this phenomenon was quite different from the conventional heating. In microwave heating, the electromagnetic waves propagate within the sample. The heat generation has caused dipole interaction between $\text{Fe}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ to heat and react. This phenomenon is called absorption resonance. This promising result is believed to be the reason behind the accelerated diffusion growth of the phases with the application of the electromagnetic field.

![XRD analysis](image1.png)

**Fig. 1** (a) XRD analysis $\text{Fe}_2\text{O}_3-\text{Y}_2\text{O}_3$ calcined via microwave heating 1000 $^\circ$C and (b) quantitative analysis using Rietveld refinement method.
Fig. 2 shows that, the less energy surmounted for YIG formation is because of dipolar loss from Y2O3. The oscillating electric fields create agitation of molecular dipoles and have caused the changes in orientations of molecules; subsequently, increases molecular kinetic energy and resulted in the bonding reorientation that caused the formation of YIP and YIG. According to Mehra et al. [2], the formation of unwanted phase; YIP may due to coarser particle size (>100 μm) of Fe2O3 that offers non-uniform heating characteristic than fine particles. In this works, the initial starting raw materials for both oxides are less than 50 μm which are contradicted with their finding.

**Fig. 2** (a) XRD analysis Fe2O3-Y2O3 calcined via conventional heating 1000 °C and (b) quantitative analysis using Rietveld refinement method.
It is suggested that the formation of YIG is obeying the core-shrinking rule. The reaction between Fe$_2$O$_3$ and Y$_2$O$_3$ has created an outer layer called YIP. The depth of this layer is assumed to be increased with reaction times and temperature which later inhibit the heat transfer for further reaction with Fe$_2$O$_3$ particle core, thus makes YIG difficult to form under conventional heating. This thermally-unstable condition has resulted in the major formation of YIP. Unlike microwave heating, the electromagnetic waves can penetrate YIP layer to enhance the reaction. At each moment of the heating process, the microwave power is absorbed in the samples and increase its core temperature and compensate the concurrent heat losses. It is believed that this microwave effect may also lead to the formation of single phase YIG only if the microwave irradiation is property controlled and well-tailored. The microwave energy has overcome the energy barrier to promote atoms to diffuse.

4. SUMMARY

In the present works, YIG formation mechanism at 1000 °C has been investigated under both microwave heating (MH) and conventional heating (CH). It is found that electromagnetic field has affected the diffusion rate of YIG formation. The calculated activation energy at this temperature via diffusion control model shows that MH (39.20 kJ/mol) can effectively promote the phase growth rather than CH (90.96 kJ/mol). The observed effect is explained by both preferential microwave absorption and enhanced mass transport between Fe$_2$O$_3$ and Y$_2$O$_3$ particles.

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REFERENCES


Synergism Effects of Coating and Concrete Plaster to Reduce $^{222}$Rn Emanations from Red Brick

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Abstract. The study revealed the synergism effects of concrete plaster and coatings in reducing $^{222}$Rn from a marketable red brick. The methodology applied is the common practice in construction industry for wall finishing. $^{222}$Rn concentrations level from red brick coated with three different type of coatings were measured within 5 consecutive days within 30 min times interval. The nett $^{222}$Rn concentration of raw red brick (uncoated) was -0.22 pCi/L. From the results, $^{222}$Rn concentration has drastically decreased after coated with coating B and C. $^{222}$Rn concentration seems to decreased with the range of -0.9 pCi/L to -0.3 pCi/L after coated with coating B and -0.8 pCi/L to -0.7 pCi/L after coated with coating C. Coating B shown the best performance in reducing $^{222}$Rn emanations with lowest $^{222}$Rn range concentration, high adhesion strength and good dynamic viscosity properties.

Keywords: α particle, Health implications, Coating adhesivity, Radon sentinel;

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1. INTRODUCTION

Radon ($^{222}$Rn) is one of the radiation sources which occurs naturally in the environment. It is a form of radioactive gas and one of the contributors for lung cancer besides smoking due to the emission of alpha particles [1]. $^{222}$Rn concentration released from brick was originated from its aggregates which are sand, cement and clay [2].

The red brick as shown in Fig. 1 (a) is widely used in building construction without knowing the presence of high radioactivity of $^{222}$Rn gas. Theoretically, $^{222}$Rn was emanated from the red brick through the porosity and cracking line along its surface [3-5]. Furthermore, this radioactive gas continuously emanated from the wall and floor of buildings, which significantly increased with poor ventilation system [6-7].
Throughout this research, three types of coating as well as cement plaster were applied on the red brick in preventing the emanation of $^{222}$Rn gas. The coating characteristics will influence the brick porosity level and directly reduce the amount of radon emanations in the building.

2. MATERIALS AND METHODS

To prevent emanation of $\alpha$-particles ($^{222}$Rn progenies) from red bricks, a layer of plaster was applied. This plaster was then coated with selected coating which are coatings A, B, and C as shown in Figs. 1(b,c). Coatings A, B and C were purchased from hardware nearby Jeli district, Kelantan, Malaysia which was the common brand that had been used among Malaysian contractors and community for building wall painting and industrial purposes. In this study, Radon Sentinel 1030 monitor manufactured by Sun Nuclear Corporation, United State of America (USA) was used to measure the concentrations of $^{222}$Rn gas that emanates from the coated and uncoated red brick as shown in Fig. 2.

Prior to start the $^{222}$Rn gas measurements, the adhesive testing has been conducted on each coated brick using Postest Adhesion Tester manufactured by DeFelsko Corporation, USA. This test revealed the coating adhesive force on the brick surface, which is one of the major factors for $^{222}$Rn concentration emanations. The characteristics of these type of coatings was presented in Table 1.

**Table 1** Coating characteristics; Adhesive force, dynamic viscosity and its main components

<table>
<thead>
<tr>
<th>Type of coatings</th>
<th>Adhesive Force (N)</th>
<th>Dynamic Viscosity (Pa.s)</th>
<th>Main Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating A</td>
<td>0.05</td>
<td>149.58</td>
<td>Poly(oxy-1,2-ethanediyl), alpha-nonylphenyl-omega-hydroxy-5-chloro-2methyl-4-isothiazolin-3-1, 2-methyl-2H-isothiazol-3-1</td>
</tr>
<tr>
<td>Coating B</td>
<td>0.06</td>
<td>315.83</td>
<td>Titanium dioxide (TiO$_2$), Iron oxide (Fe$_2$O), Carbon (C), Black and organic pigments and mineral extender</td>
</tr>
<tr>
<td>Coating C</td>
<td>0.04</td>
<td>33.37</td>
<td>Naphta (Petroleum), hydreated heavy, Talc, Magnesium silicate, Ethyl methyl ketoxime</td>
</tr>
</tbody>
</table>

Radon Sentinel 1030 monitor was setup to record the reading within 30 min time interval. Each coated and uncoated bricks were measured in 24 hours for 5 consecutive days. Hence, there were 240 of $^{222}$Rn data have been recorded for each type of coated and uncoated bricks. Through this method, average of $^{222}$Rn concentrations for each coated and uncoated red bricks as well as raw materials were obtained.
3. RESULTS AND DISCUSSION

$^{222}$Rn concentrations for each raw material was obtained within 5 consecutive days; a. empty room prototype, b. cement, c. sand, d. red brick, e. beaker, f. water, g. coating A, h. Coating B and i. Coating C as shown in Fig. 3. From the graph, room prototype with 0.977 pCi/L was fixed as the background reading in this study. Hence, each average of $^{222}$Rn reading for raw materials were deducted to the background reading (0.977 pCi/L) to obtain the nett $^{222}$Rn concentrations by using the formula in Eq. 1 [2,8]. Thus, nett of $^{222}$Rn concentration from raw red brick was revealed at -0.22 pCi/L. All the recorded reading becomes negative values due to the background of close air in the prototype room was measured as the highest $^{222}$Rn concentrations in this experiment. This is due to the random characteristics of radiations [9-10].

Nett $^{222}$Rn = (Avg$^{222}$Rn) – (Bck$^{222}$Rn)  

$^{222}$Rn concentrations from red brick will be decreased after being coated with coating materials. However, the red brick coated with coating A shows the opposite result, where the $^{222}$Rn concentrations was slightly higher than raw red brick. This result might be due to the characteristics of
coating material itself, where the $^{222}\text{Rn}$ concentrations emanated from coating A was significantly higher than other coatings as shown in Fig. 3 (0.215 pCi/L). High $^{222}\text{Rn}$ concentrations possibly contributed from the components into coating A as shown in Table 1.

In this study, nett concentrations of $^{222}\text{Rn}$ was in between -1.0 pCi/L to 0.8 pCi/L for layered with plaster and coated with coating A, -0.9 pCi/L to -0.3 pCi/L for layered with plaster and coated with coating B whereas -0.8 pCi/L to -0.7 pCi/L for layered with plaster and coated with coating C as shown in Figs. 4-6, respectively.

![Fig. 4 Nett, minimum and maximum of $^{222}\text{Rn}$ concentrations in red brick layered with plaster and coated with coating A](image)

![Fig. 5 Nett, minimum and maximum of $^{222}\text{Rn}$ concentrations in red brick layered with plaster and coated with coating B](image)

Meanwhile, $^{222}\text{Rn}$ emanations from coated bricks were increased from time to time within 5 consecutive days’ measurement as shown in Figs 4-6. This phenomenon is closely related with natural characteristics of $^{222}\text{Rn}$ gas, which has half-life of 3.8 days and decayed to its progenies of α particles, polonium, bismuth, and lead [8]. Hence, the reading obtained was continuously increased in close air, depending on the natural half-life and random emanations of $^{222}\text{Rn}$ progenies originated from internal aggregates material of the respected brick.
In additions, the coating materials with high viscosity and adhesivity is believed to be more effective in reducing the emanation of $^{222}\text{Rn}$ concentration towards the surrounding. Viscosity of coating materials was measured by using Stoke’s Law as shown in Equation 2 and represented in Table 1.

$$\eta = \frac{2}{9} \left( \rho_2 - \rho_1 \right) \left( g \frac{r^2}{v^2} \right)$$  \hspace{1cm} (2)

* $\eta$ = viscosity
** $\rho_2$ = Density of coating materials
*** $\rho_1$ = Density of ball bearing
**** $g$ = Standard gravity
***** $r$ = Radius of ball bearing
****** $v$ = Particle velocity.

It can be observed that the highest viscosity recorded from coating B, followed by coating A and C, respectively. The higher viscosity of coating can be considered as the most effective coating type in reducing the emanation of $^{222}\text{Rn}$. This is because the good viscosity coating has good tendency in filling the brick porosity, which directly blocking $\alpha$ particles emanations. Moreover, high adhesivity of coating will tightly close any micro porous along the brick surface, and resulted to reduce the emanations of energetic $\alpha$ particles. This was proved by the lowest of nett $^{222}\text{Rn}$ emanations ranges in Fig. 5 with -0.9 pCi/L to -0.3 pCi/L, where coating B shows the best viscosity and adhesive characteristics than to other comparative coatings. Nevertheless, the paint somehow will lose their viscosity as the thickening agents was used in degree of polymerization [11,12].

4. SUMMARY

From conducted research, reduction of $^{222}\text{Rn}$ emanation from the red brick was achieved by using coating B and C. The concentration of $^{222}\text{Rn}$ seems to decreased with the lowest ranges of -0.9 pCi/L to -0.3 pCi/L after coated with coating B and medium ranges of -0.8 pCi/L to -0.7 pCi/L after coated with coating C. $^{222}\text{Rn}$ concentration was increased for red brick coated with coating A, which was contributed from coating material itself. Overall, each type of coating materials used have different strength and compatibility in reducing $^{222}\text{Rn}$ emanation from marketable red brick, depending on their physical and chemical
characteristics. Coating B was observed as the best material in reducing $^{222}$Rn emanations from red brick with lowest $^{222}$Rn concentration range, high adhesion strength and good dynamic viscosity properties.

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Thermal Stability of Plasticized Durian Skin Fibre Biocomposite

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ABSTRACT. Packaging is an essential component in food industries. Packaging protects food from spoilage between processing and usage by the consumer. In this study, biocomposites of poly(lactic acid) (PLA) reinforced with durian skin fibre (DSF) were prepared by extrusion and compression moulding. Epoxidized palm oil (EPO) was added into PLA/DSF biocomposite as a plasticizer. The results showed that the thermal stability of PLA/DSF biocomposite with EPO has not much difference compared to without EPO. The degradation time of PLA/DSF biocomposite also faster after it was disposed to the landfill as it took around 65 days to degrade. Fourier transform infrared (FTIR) confirmed the stability of EPO where the oxirane group of EPO existed in the PLA/DSF biocomposite. Therefore, PLA/DSF biocomposite with addition of EPO can be effectively used for food packaging application.

Keywords: Biodegradable polymer, Durian skin fibre, Epoxidized palm oil, Thermal properties;

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1. INTRODUCTION

In recent years, most of the food packaging are made from the plastics in various sizes and shapes. Generally, these plastics are made from synthetic polyolefin such as polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP) and polystyrene (PS) [1,2]. This is due to their good properties as they are light, soft and transparent. However, these plastics are petroleum-based polymers, which are from non-renewable resources. The utilization of these plastics may give an impact to the environment as they are neither fully biodegradable nor environmentally friendly.

The agricultural and agrofood industries is the major cause that lead to large amount of wastes generated. To overcome this problem, the most effective way is to recycle and reuse waste into a new product. Durian produce a lot of waste as it contains only 50-65% of flesh while the rest such as skin and seed are considered as waste [3]. These residues are discarded in the landfills and it may affects the surrounding environment. Thus, durian skin fibre (DSF) that extracted from durian can be used as reinforcement in polymer to produce composite products.
Biodegradable polymer is gaining much attention recently as an alternative material to conventional petrochemical polymers. This is due to its biodegradability, environmentally friendly characteristics and biocompatibility. Polylactic acid (PLA) is a biopolymer synthesized from biomass. It is a natural resources thermoplastic polymer and it can be produced over 140,000 tonnes per year [4]. Generally, PLA is used as a replacement to petroleum-based polymer especially in food packaging containers [5]. The first commercialization of PLA was in 1990 and its production was highly demanded from year to years. Karamanlioglu et al. [5] stated that Japan and USA are the major producers of PLA and by 2020, the worldwide production of PLA is estimated of at least 800,000 tons. However, the drawbacks of PLA such as high brittleness and low tensile elongation limit its application. Therefore, it is essential to add plasticizer into PLA to enhance its properties.

Plasticizer from natural resources such as rubber seed oil, olive oil, corn oil, soybean oil, palm oil and neem oil are widely used due to their lower toxicity, low cost, renewable resources, biodegradability, good lubricity and lower volatility [6]. Ali et al. [7], Chieng et al. [8] and Al-Mulla et al. [9] studied the effect of epoxidized palm oil (EPO) incorporated into PLA on mechanical properties. They found that the flexibility was increased about 16% and elongation at break of PLA also was improved from 60 to 100% when 5 wt.% of EPO was added.

This paper reported thermal stability, functional groups and degradation time of PLA/DSF biocomposite. Epoxidized palm oil (EPO) was added as plasticizer to obtain PLA/DSF biocomposite with enhanced properties in order to produce food packaging.

2. MATERIALS AND METHODS

The inner skins of durian were removed and cut into smaller pieces. After that, durian skins were washed with tap water to remove any dirt and dust. The skins were dried in an oven for 24 h at 70 ºC. The dried skins were crushed and then sieved for 100 µm size to get durian skins fibre (DSF). The DSF was soaked in 4 wt.% of sodium hydroxide (NaOH) solution for 2 hours at room temperature. Next, treated DSF was washed with distilled water to remove any excess NaOH and then was dried at 60 ºC for 48 hours. PLA/DSF biocomposite was extruded using twin screw extruder (Brabender, Germany) at 170 ºC. Epoxidized palm oil (EPO) with amount of 5 wt.% was added into PLA/DSF biocomposite.

After extrusion process, PLA/DSF biocomposite was compression moulded for degradable testing specimen. Thermogravimetry analysis (TGA) was carried out in the temperature range between room temperature and 300 ºC at a heating rate of 10 ºC/min in nitrogen gas condition. The degradation time of PLA/DSF biocomposite was investigated by exposing the specimen to the landfill. The functional groups of PLA/DSF biocomposite was obtained through the Fourier transform infrared (FTIR) analysis. FTIR spectra of biocomposite was recorded by FTIR spectrometer between 3500 cm⁻¹ and 500 cm⁻¹ frequency ranges.

3. RESULTS AND DISCUSSION

Fig. 1 illustrated the thermal degradation curves due to weight loss of neat PLA, PLA/DSF and PLA/DSF/EPO. The onset temperature (Tₒ), maximum degradation temperature (T_max) and final degradation temperature (T_f) were tabulated in Table 1. Tₒ of neat PLA was 306 ºC and it decreased to 257 ºC after DSF was added. When EPO was incorporated into PLA/DSF, Tₒ was further decreased to 251 ºC due to the decreasing of relative molecular weight of PLA. The thermal stability of PLA was reduced with the presence of DSF as it is hydrophilic and it contains hydroxyl group. PLA/DSF degraded at 315 ºC while PLA/DSF/EPO had slightly lower degradation peak at 12 ºC. The char residue of neat PLA was low because of the hydrogen and carbon atoms in PLA formed volatile compound as it decomposed at higher temperature.
**Fig. 1** TGA curves for PLA, PLA/DSF and PLA/DSF/EPO biocomposites

**Table 1** Thermal properties of PLA, PLA/DSF and PLA/DSF/EPO biocomposites obtained from TGA

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_o$</th>
<th>$T_{max}$</th>
<th>$T_r$</th>
<th>Char residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>306</td>
<td>360</td>
<td>421</td>
<td>1.1</td>
</tr>
<tr>
<td>PLA/DSF</td>
<td>257</td>
<td>316</td>
<td>378</td>
<td>10.8</td>
</tr>
<tr>
<td>PLA/DSF/EPO</td>
<td>251</td>
<td>313</td>
<td>376</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Fig. 2 showed the pictures of PLA/DSF/EPO specimens after 65 days left in a landfill. Discoloration of the specimens probably occurs because of the microbial growth after 30 days. PLA/DSF biocomposite decomposed into water and carbon dioxide in less than 90 days. The degradation time was faster compared to the petrochemical polymer which not degraded by microorganisms in the environment and remain until million years. As stated by Shah et al. [10], they revealed that the degradation of PLA initially was through hydrolysis to water soluble compounds and lactic acid. Then, it decomposed into water, CO$_2$ and biomass by biological activities [5,10].
The FTIR spectra of PLA/DSF biocomposite were shown in Fig. 3 to know its functional groups presence. The peaks located around 1180-1181 cm$^{-1}$ exhibited as O-C=O stretching. The stretching vibrations of CH$_2$ and C=O in PLA/DSF were 2996 and 1748 cm$^{-1}$ and it shifted to 2916 and 1746 cm$^{-1}$ upon EPO was added. It may exhibited some intramolecular interactions and compatibility between EPO and PLA/DSF. Furthermore, the peak at 868 cm$^{-1}$ and around 1258 cm$^{-1}$ suggest the presence of EPO where C-O-C stretching from oxirane vibrations. The peak at 1258 cm$^{-1}$ usually overlays with others such as C-O ester which presents in oil [11,12]. C-O stretching at peak 1082 cm$^{-1}$ shifted to 1084 cm$^{-1}$ after blend with EPO which showed miscibility and interaction of PLA/DSF and EPO. Tee et al. [6] stated that the interaction between PLA/DSF and EPO occurred from the hydrogen bonding between terminal hydroxyl groups of PLA and the oxirane groups of the EPO.

![Fig. 2 Degradation time of PLA/DSF/EPO](image1)

![Fig. 3 FTIR spectrum of PLA/DSF/EPO](image2)
4. SUMMARY

Polylactic acid reinforced durian skin fibre is a potential material to produce biodegradable food packaging. PLA/DSF biocomposite has good thermal stability and it degraded in soil faster than petroleum-based polymer, thus the volume of waste dumps can be reduced. PLA/DSF biocomposite decomposed naturally and returned to soil, indirectly reduce the disposal of conventional plastics and reducing the volume of waste. PLA/DSF biocomposite is potential to be used as a biodegradable food packaging as an alternative to the conventional plastics.

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The Relationship of Cutting Chip Type, Length and Thickness to Wear of Zirconia Toughened Alumina Added with Magnesium Oxide (ZTA-MgO) Cutting Tool

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ABSTRACT. The effect of cutting chips on the performances of ZTA-MgO ceramic cutting tool investigated. The aim of this project is to discover the effect of cutting chip type, length and thickness on the wear of the ZTA-MgO cutting tool. CNC turning machining performed by using Rom-Bridgeport CNC turning machine at cutting speed range from 2250 to 3000 rpm, the feed rate 0.1, 0.3 and 0.5 mm/rev while the depth of cut is kept constant at 0.2 mm. The flank wear and crater wear were measured accordingly using optical microscope, Matlab programming and SEM. The chip type, length and thickness were classified and measured. The variation of cutting parameters influenced the chip geometry and it relation to tool wear were analysed. The chips were collected. The chip type, length and thickness analysed using optical microscope and SEM. Result shows chip started with tubular and ribbon form of chip. Increment of feed rate, make the chip break to smaller part. The chip length increase when cutting speed was increased. The chip is 2.49 cm length at cutting speed 2250 rpm increased up to 4.61 cm at 3000 rpm. The chip thickness was increased with increasing of feed rate where the average thickness is at lowest when the feedrate is at 0.1mm/rev and highest at 0.5 mm/rev all cutting speed. The increment of chip length caused the crater wear increased on cutting tool from 5.66 mm² at chip length of 2.49 cm and increased to 7.40 mm² when the length increased to 4.61 cm. The high chip thickness caused higher flank wear on the cutting tool. Based on the analysis, the chip type, length and thickness have influence on flank and crater wear of the ZTA-MgO cutting tool which may lead to failure of the cutting tool.

Keywords: Chip formation, Chip morphology, Wear, ZTA, Turning;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

ZTA-MgO cutting tool can be described as additive yttria stabilized zirconia (YSZ) and magnesium oxide (MgO) introduced into alumina (Al₂O₃). The purpose of the additive addition is to toughen the brittle properties of the ceramic [1]. Addition of MgO into the ZTA composition improve the microstructure, hardness and fracture toughness of the cutting tool [2,3]. ZTA is an excellent cutting tool for machining due to their high melting temperature, excellent erosive wear, resistance toward corrosion and toughness. There are
many studies relation to wear by using ZTA cutting tool, but no study involved on chip morphology by using various parameter. Generation of various types and forms of chip influences the contact zone between the tool and chip, i.e. the friction at tool-chip interface. Such changes generate various forms of tool vibrations, influence work surface quality, and intensify tool wear [7].

In high speed machining of steel by using the ceramic cutting tool, Dutta et al. [4] stated that continuous chips produced during the machining caused slow progressing of crater wear on the tools and continuous machining affect the flank wear progress greatly causing tool failure due to the tool-chip contact. Gatto and Iuliano [5] in their research observed the chips upon machining to analyse the wear mechanisms along the tool-chip contact length. They found that the chip segments size increase by increment of feedrate. Research results by Salem and Bayraktar [6] also agreed that feedrate significantly influence the chip morphology. While machining the hardened steel (62 HRC) at constant cutting speed, they found that continuous chip at low feedrate and the chip start to scallop approaching the saw-tooth chip shape when the feedrate is further increased. Other than that, chip formation also leave impact on the tool rake face surface which change the geometry of the tool [7]. Progressive crater wear will weaken the tool edge causing nose wear. Consequently, surface roughness of the workpiece will be affected. The effects of chips length and form leads to the study on the simulation of cutting chips and their effects on the work as presented by Childs et al. [8]. Their research shows that length of the cutting chip significantly affect the contact time on the cutting zone. Long continuous chip causing wider and deeper crater wear. As the crater wear become wider and deeper, the tool nose became vulnerable and tool breakage might take place.

In this research, the relationship of cutting chip to wear of ZTA-MgO cutting tool will be investigated. The type, length and thickness of the cutting chips were analysed thoroughly in order to investigate their influence to the performance of the ZTA-MgO ceramic cutting tool.

2. MATERIALS AND METHODS

Alumina (Al₂O₃) and yttria stabilised zirconia (YSZ) were wet mixed with distilled water at the ratio of 80:20 with addition 1.1wt.% of 20 nm particle size magnesium oxide (MgO). The composition were dried before powdered and compacted into rhombus shape cutting insert. The X-Ray Diffraction analysis (XRD) performed on the ZTA-MgO cutting tool. Machining is then conducted by using ROMI Bridgeport CNC turning. Cutting speed are varied in range of 2250-3000 rpm, feedrate 0.1-0.5mm/rev and constant depth of cut of 0.2 mm as shown in Table 1. Workpiece stainless steel 316L with diameter 50mm used for the machining process. The cutting chip produced during machining were collected and analysed. Optical microscope (Olympus BX41M) was used to observed the chip type while chip length measured by using thread and ruler. Chip thickness were analysed by using the SEM. The photo of wear on the cutting tool were captured using the optical microscope and the wear area was measured using the Matlab software.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition / Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cutting Speed</td>
<td>2250, 2500, 2750, 3000 rpm</td>
</tr>
<tr>
<td>Feed rate</td>
<td>0.1, 0.3, 0.5mm/rev</td>
</tr>
<tr>
<td>Depth of cut</td>
<td>0.2 mm</td>
</tr>
<tr>
<td>Cutting length</td>
<td>20 mm</td>
</tr>
<tr>
<td>Cutting Condition</td>
<td>Dry</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1 Materials Characterization. Characterization on ZTA-MgO after sintering performed and presented in Fig. 1. In this XRD graph, it can be seen that presence of both tetragonal and monoclinic phase of ZrO₂ can be
detected where tetragonal phase matches the (ICDD 81-1544) and monoclinic (ICDD 65-1023). The corundum presented as (ICDD 10-1073). Apart from that, presence of MgO identified in MgAl₂O₄ phase (ICDD 73-1959).

![XRD graph of ZTA-MgO cutting tool](image)

**Fig. 1** XRD graph of ZTA-MgO cutting tool

### 3.2 Type, Length and Thickness of Cutting Chip

Observation on the chip form, length and thickness at different machining parameters for ZTA-MgO ceramic cutting inserts presented. The chip forms are compared to the standard chip form (ISO 3685:1993). The result presented in Table 2. From this table, it can be observed that at 0.1 mm/rev, the chip start with short tubular and turns to long tubular with increasing of cutting speed. Changing of feed rate to 0.3 mm/rev, make the chip turns snarled ribbon with increasing of cutting speed. At 0.5 mm/rev, the chip form a short tubular due to high feed rate and cutting speed which is 3000 rpm. The short tubular chip also can be related to the chipping at the cutting tool at high feedrate that act as chip breaker causing long tubular chip to be cut into short tubular chip.

**Table 2** Chip type with changes of parameters

<table>
<thead>
<tr>
<th>Feed Rate (mm/rev)</th>
<th>2250</th>
<th>2500</th>
<th>2750</th>
<th>3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Short Tubular</td>
<td>Long Tubular</td>
<td>Long Tubular</td>
<td>Long Tubular</td>
</tr>
<tr>
<td>0.3</td>
<td>Snarled Ribbon</td>
<td>Snarled Ribbon</td>
<td>Snarled Ribbon</td>
<td>Short Tubular</td>
</tr>
<tr>
<td>0.5</td>
<td>Snarled Ribbon</td>
<td>Snarled Ribbon</td>
<td>Snarled Ribbon</td>
<td>Short Tubular</td>
</tr>
</tbody>
</table>
The chip length in the other hand change due to the changes of cutting speed. It is found that the chip length increased with increment of the cutting speed as presented in Fig. 2. There is no significant change of chip length when the feedrate is increased.

![Effect of cutting speed to chip length](image1)

**Fig. 2** Effect of cutting speed to chip length

Feedrate affect the thickness of the chip where the chip thickness increase with increment of feedrate from 0.1 to 0.5 mm/rev for all cutting speed. It can be seen also higher thickness of chip when the cutting speed is increased. This result is parallel to the explanation of George et al. [9] where the feedrate is the determining factor to chip thickness.

![Effect of feedrate to chip thickness](image2)

**Fig. 3** Effect of feedrate to chip thickness

### 3.3 Effect of Chip Type, Length and Thickness to Wear

Chip type also have contribution to the performance of the cutting tool. In this research, it is found that long tubular chip have a great impact on the crater wear as crater wear area is bigger when long tubular chip present compared to other type of chip. The crater wear
area also increased when the length of the long tubular chip increased as presented in Fig. 4. This condition is related to the tool-chip interface where long tubular chip has greater contact area to the tool rake face compared to the ribbon type (straight type) chip. The curl of the tubular chip also able to plough the rake face causing bigger area to abrade compared to other type of chip.

The effects of chip length can be seen on the crater wear. Based on the analysis as presented in Fig. 5. As the chip become longer, the crater wear area also become bigger. Long cutting chips will interact with the tool surface longer and abrade the cutting tool surface while shorter chip indicates shorter time contact between chip and rake angle because the chip leave the cutting tip faster thus reduce the crater wear. In order to reduce the crater wear at high cutting speed, it is suggested for chip breaker to be used during the machining process. The crater wear is not affected at high feedrate as the chip break to shorter length when the feedrate is increased [9].

The effect of chip thickness observed to be affecting the flank wear compared to the crater wear. As the chip thickness increased due to increment of feedrate and cutting speed, the flank wear also start to increased. Fig. 6 illustrate the effect of the chip thickness to the flank wear.
Fig. 6 The effect of chip thickness to the flank wear

4. SUMMARY

The conclusion that can be made from the results are cutting speed increase the length of the cutting chip while feedrate increment increase the thickness of chip. As the length of the chip increase, the crater wear increased. Frank wear increased with increment of chip thickness. Chip type also influence the wear as long tubular cutting chip CAUSED INCREMENT OF CRATER WEAR.

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Enhancement of Singgora Roof Tile Using Chemical Modification Method

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\textbf{ABSTRACT.} Singgora roof is a Malay traditional design of roof construction. Singgora was very popular among Malay traditional houses and buildings long time ago but now suffering declining of customer demand. Several problems were known such as low fracture toughness, growth of fungus and the irregular surface finishing. Extensive work should be conducted to sustain the historical heritage and the mentioned problem must be overcome. Throughout this research, the properties of commercial Singgora roof was identified and characterized. To enhance the properties, Feldspar was added to the raw clays as flux materials at different concentration (0, 10, 15, 20 wt.\%) during mixing process. Samples were shaped by using POP and fired at 800 °C for 16 hours. The final products were characterized for mechanical and physical properties such as density, impact and three-point bending test. From the result, enhanced product showed higher density and toughness based from Charpy impact test.

\textbf{Keywords:} Singgora, Roof, Clay, Chemical modification;

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1. INTRODUCTION

Singgora roof is a Malay traditional architecture design for roof construction. Most of the traditional Malay houses at Eastern Malaysia were using this type of roof for more than 200 years ago. The roof is in pyramid-like shape and known as the roof of Perak (Fig. 1). It is also called as Senghora brick or simply as roof brick among Kelantanese when referring to the roof tile. However, the name of Singgora itself is came from Thai words which means Lion City and speculated due to lion shape of a hill in Songkhla, Thailand. At the end of 20\textsuperscript{th} century, when Malaysia joined other developing countries, major development model overhauled classic housing structures and the architectures as well that caused the popularity of Singgora roof is reducing and recently was abandoned at all. Currently, only one place that manufacturing Singgora roof tiles in Kelantan which is Kampung Beris, Bachok [1].

Limited manufacture of Singgora roof is due to lack of demand and less popular among current society. The remaining usage of this roof tile is coming from conservation of old heritage building by the government agency or private sector. The weaknesses of Singgora roof become public well known as it mechanically weak and short life span. In this study, the properties of commercial Singgora roof tile will be defined and improved by adding feldspar. Clay based product including Singgora roof is a porous body and adding flux materials like feldspar will improve the properties.
2. MATERIALS AND METHODS

Commercial Singgora roof tiles and raw clay material were bought from a Singgora manufacturer in Bachok, Kelantan. They were crushed and ground to fine powder for phase and elemental analysis using XRD and EDXRF. To fabricate the Singgora product, similar procedures that were done in factory were followed in this study. Clays were mixed with feldspar at 0, 10, 15, and 20 wt.% and shaped into samples. They were dried for 1 days and fired at 800 °C for 16 hours. Samples were tested for physical and mechanical properties and for commercial product, the sampling was carried on cut body. The studied mechanical properties are tensile test, three points bending and impact test.

3. RESULTS AND DISCUSSION

Analysis of EDXRF on Singgora raw clays and ground fired commercial Singgora roof are showed in Table 1. Based on the result, there are a few oxides presented, which were SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, K$_2$O, TiO$_2$, SO$_3$, P$_2$O$_5$, Cl, CaO and ZrO$_2$. The raw materials are having high concentration of SiO$_2$ (52.5 wt.%), followed by Al$_2$O$_3$ (16.5 wt.%), Fe$_2$O$_3$ (15.7 wt.%), K$_2$O (5.94 wt.%) and TiO$_2$ (2.59 wt.%). Others are existed at small part lower than 2 wt%. EDXRF analyzed the concentration of samples based on the characteristic x-ray energy come from the elements. The compound chemical compositions are calculated as assumption of all the elements existed in from of oxide in the soil. Three compounds are very high in the samples, which are silica, alumina, and iron oxide. Based from the literatures [1–7], silica and alumina are common compounds in clays. Iron rich clay in this study are common in Kelantan state, which gave reddish color of the clay products including Singgora roof [4,6]. The high amount of SiO$_2$ in clay will increase the amorphous phase in the microstructure [8]. The small amount of Cl is expected from NaCl salt in the clay and the missing of Na in the result is because of out of detection limit by EDXRF. Hassan et al. [3] reported that, the clay raw materials are taken from the clash of saltwater and freshwater at Kemasin River. The high content of the salt in clay is considered suitable and gives strength to the tile compared to other clay source without the salt. This can be assumed that, the salt reacted as flux naturally as we did in this study by adding feldspar as flux materials.
Table 1 Chemical composition of grinded commercial Singgora roof tile and clay raw materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Clay raw materials (wt.%)</th>
<th>Ground and fired Singgora roof</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>52.5</td>
<td>58.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>16.5</td>
<td>17.4</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>15.7</td>
<td>12</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>5.94</td>
<td>5.3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>2.59</td>
<td>2.05</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>1.78</td>
<td>1.42</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>1.69</td>
<td>1.34</td>
</tr>
<tr>
<td>Cl</td>
<td>1.26</td>
<td>0.756</td>
</tr>
<tr>
<td>CaO</td>
<td>1.25</td>
<td>0.848</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.194</td>
<td>0.131</td>
</tr>
</tbody>
</table>

XRD patterns of the raw clay, crushed commercial Singgora roof, and feldspar added samples are showed in Fig. 2. From the pattern, three major mineral compounds were found in the raw clay and commercial Singgora which are quartz (COD 9012600), muscovite (COD 9015623) and kaolinite (COD 9014999). Samples produced for 0 and 20 wt.% added feldspar doesn’t appear the muscovite/mica and kaolinite peak. It is suggested, firing for 800 °C for 16 hours in furnace decomposed mica and kaolinite compounds. According to Gabor et al. [10] kaolinite decompose at 315 °C and 700 °C for mica. The existence of mica compound from commercial Singgora proved that temperature to produce Singgora in factory is less than 700 °C. The sharp peak and higher intensity of quartz are due to long firing time (3 days) of the commercial Singgora and caused high crystallinity of product atomic structure. Missing of feldspar phase in the sample of feldspar added Singgora is expected due to liquid phase formation during firing and form amorphous structure at the clay porous microstructure. The increasing of amorphous phase can be noticed from the pattern in Fig. 2 when comparing to 0 wt.% samples.

Fig. 2 XRD pattern of raw clay, crushed commercial Singgora and feldspar added samples

Modulus of rupture (MOR) or flexural strength was measured for commercial, and felspar added samples (Fig. 3). The results showed that the highest MOR was obtained from 20 wt.% feldspar which is 173.643
The lowest MOR was 0 wt.% feldspar added product which the value is 44.593 N/mm². Increasing the feldspar up to 20 wt.% was proven to increase the MOR to three times. However, the MOR for 15 wt.% and 20 wt.% are not much differ and this can be assumed by the effect of flux to reduce the porosity is already enough and their effect to mechanical properties is insignificance. The enhanced MOR for the sample proved that adding feldspar mineral is capable to improve their strength and lowered the firing time for sintering process. The 0 wt.% feldspar has low MOR and this is suggested by insufficient firing time which is only 16 hours compared to industry 3 days and very low flux content (only NaCl).

Fig. 3 Modulus of rupture of commercial and feldspar added product of Singgora

Fig. 4 Toughness of commercial and feldspar added sample of Singgora clay
Fig. 4 displayed results of energy used to break the different samples of Singgora (commercial and feldspar added clays) using Charpy impact test. Adding feldspar to the clay proved the increasing of energy to break the sample from 53.557 N/mm$^2$ of the commercial Singgora, 53.836 N/mm$^2$ for 0 wt.% added feldspar and 53.957 N/mm$^2$ for 20 wt.% added feldspar. Feldspar content in the sample caused the increasing of density or reducing of porosity which will strengthen the clay body. This can be seen on the Fig. 5, the density of clays body increases with the feldspar content. There had other factors that affects the energy to break the sample which are presence of impurities, pores, small stones, dry dusts from grass or leaves.

![Fig. 5 Bulk density of commercial and feldspar added product of Singgora](image)

**4. SUMMARY**

Mixed commercial clay with feldspar for 20 wt.% caused improvement of modulus of rupture up to 173.643 N/mm$^2$ from 79.475 N/mm$^2$ for commercial Singgora roof samples. The firing time also can be decreased from 3 days for commercially firing method to 16 hours at 800 °C. The improvement of the mechanical properties are caused by the pore elimination by the feldspar that melt and hold the clays particles. At the 15 wt.% concentration of feldspar, the mechanical properties start to stagnant and density also decreased a bit. Based on this study, 15 wt.% of feldspar is enough to improve the mechanical properties and suitable to be applied in the industries.

**ACKNOWLEDGEMENT**

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**REFERENCES**


Comparison Studies on Phase Formation and Transformation Behavior between Ni-Ti and Ni-TiH₂ Synthesized via Solid State Sintering

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ABSTRACT. Solid state synthesis is an alternative processing technique that has been attempted for producing novel-structured NiTi such as porous NiTi and other novel forms. Whilst shape memory effect is a unique advantage of NiTi shape memory alloy like, no successful attempt so far to produce single phase NiTi with good martensitic transformation behavior. As oxidation of Ti is the main problem that may retard the formation of single phase NiTi, the preliminary study of the effect of powder precursor was done. In this research, a systematic comparative investigation was performed on phase formation and transformation behavior of Ni-Ti and Ni-TiH₂ sintered specimen. It revealed that no martensitic transformation was observed for Ni-Ti specimen, attributed to minor NiTi phase formation. In addition, the XRD result of powder analysis indicates that part of Ti powder was oxidized during specimen preparation which creates imbalance composition for Ni-Ti reaction. In contrast, Ni-TiH₂ specimen displayed martensitic transformation behaviour attributed to high amount of NiTi phase formation. This reflects that the use of TiH₂ to replace Ti as powder precursor has a significant effect towards NiTi phase formation and its transformation behaviour.

Keywords: Shape memory alloy, Transformation behavior, Solid state synthesis;

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1. INTRODUCTION

Near-equatomic NiTi alloys have gained much interest particularly in its porous form for its intended application in medical implant due to its good shape memory effect of monolithic NiTi. This porous form of NiTi requires solid state sintering technique, other than the conventional melt-casting method. Several research groups have published studies on solid state synthesis of NiTi from elemental powder of Ni and Ti by using different techniques such as conventional pressureless powder sintering [1], hot isostatic pressing [2], self-propagating high temperature synthesis [3], spark plasma sintering [4,5], and microwave sintering [6], though little success has been achieved in terms of satisfactory shape memory behaviour, as evidenced by the absence of visible applications of these materials.

The desired phase for shape memory effect is the equatomic NiTi. Almost all NiTi produced via solid state sintering from elemental powder of Ni and Ti, have complex microstructures involving multiple phases including Ti₂Ni and TiNi₃ [1]. These phases do not exhibit martensitic transformation and destroy the shape
memory behaviour of the alloys. It is believed that the main obstacle to producing single phase NiTi is the oxidation. During sintering, Ti is easily oxidized to form TiO₂. The formation of this oxide may depletes Ti content for Ni-Ti reaction, leaving abundance of Ni that may reacts with remaining Ti to form TiNi₃. As a result, multiple phases may form.

Therefore, this research investigates the preliminary effect of Ti and TiH₂ powder precursor mixed with Ni on phase formation and transformation behaviour of NiTi. The use of TiH₂ to replace Ti as powder precursor may protect the specimen from oxidation as high decomposition temperature of TiH₂ at above 400 °C may prevent the formation of TiO₂ not only during specimen preparation but also during sintering.

2. MATERIALS AND METHODS

In this work, high purity Ni (particle size < 30 µm) and TiH₂ (particle size ≤ 44 µm) have been mixed at equiatomic composition by means of low energy ball milling for 24 hours. After mixing, the powder mixture was cold compacted into cylindrical shape of φ12 x 4 mm to 3 tonnes of force. Then, the specimens were sintered at different temperatures and time in flowing argon. Phase formation analysis was carried out using scanning electron microscope (SEM) of Hitachi S-3400N equipped with energy dispersive spectroscopy (EDS) and X-ray diffractometer (XRD). Quantitative analysis of the area fractions of phases formed was performed by means of image analysis of SEM backscattered micrographs using ImageJ software, free software provided by the National Institute of Health (NIH), USA. This phase fraction analysis was done by differentiating contrast levels among the different phases present which had been previously identified through EDS. Differential scanning calorimetry (DSC) was conducted using a TA Q20 instrument to analyse martensitic phase transformation behaviour of the sintered specimens. The occurrence and the magnitude of this martensitic transformation are good indicators of the formation of the B₂-NiTi phase in the specimens, an essential requirement for shape memory effect.

3. RESULTS AND DISCUSSION

3.1 Phase Characterization. Fig. 1 shows the SEM micrographs with EDS analysis of Ni-Ti specimen sintered at different temperatures for 6 hours. For the specimen sintered at 750 °C, the Ni(Ti) solid solution containing >5 at%Ti phase appears as isolated islands whereas Ti with <1 at %Ni presents in a matrix structure. The formation of Ti₂Ni indicates that the diffusion process has already commenced at 750 °C. The specimen sintered at 850 °C and 900 °C showed an increased degree of diffusion. The dominant structure is the products formed in between the original Ni(Ti) and Ti(Ni), which have obviously been reduced in volume. The enlarged view reveals that the products contained several phases, including TiNi₃, NiTi and Ti₂Ni. Referring to high magnification of Fig. 1I, it is observed that NiTi formed in an extensive cob-web structure inside the Ti₂Ni phase, appearing to propagate from the Ni side towards the Ti side. In most parts, the NiTi network has consolidated into continuous matrix, with small Ti₂Ni entrapped inside NiTi. In the specimen sintered at 1080°C, only three phases were found, i.e., NiTi, Ti₂Ni and TiNi₃, where NiTi forms the continuous matrix with TiNi₃ network emerged within the NiTi matrix.

Fig. 2 shows the SEM images of the microstructures of the Ni-TiH₂ specimen sintered at different temperatures from 750 °C to 1080 °C for 6 hours. Specimen sintered at 750 °C shows the formation of multiple phases such as NiTi, Ti₂Ni, TiNi₃, and Ni(Ti). When sintering temperature increases to 850 °C, NiTi increased aggressively, forming the matrix with small patches of Ti₂Ni scattered everywhere. The NiTi matrix is heavily embedded with "needles-like structure" as indicated in high magnification figure as indicated in Fig. 2(b). This needles-like structure is believed to be Ni-rich precipitates, Ni₄Ti₃ as reported by [7]. Increasing sintering temperature to 930 °C and 1080 °C, the amount of Ti₂Ni phase reduced, while more Ni₄Ti₃ precipitates were observed in the NiTi matrix.
Fig. 1 SEM micrographs of Ni-Ti sintered at different temperatures (a) 750 °C, (b) 850 °C, (c) 900 °C and (d) 1080 °C for 6 hours. The micrographs shown on top are of lower magnifications and the micrographs shown on bottom are of high magnifications.

Fig. 2 SEM micrographs of Ni-TiH$_2$ sintered at different temperatures (a) 750 °C, (b) 850 °C, (c) 930 °C and (d) 1080 °C for 6 hours. The micrographs shown on top are of lower magnifications and the micrographs shown on bottom are of high magnifications.

Fig. 3 shows the XRD spectra for Ni-Ti and Ni-TiH$_2$ specimen sintered at different temperature for 6 hours. For Ni-Ti specimen, at 750 °C, almost no new phase formation took place except Ti$_2$Ni phase. However, the EDS analysis confirmed that NiTi, Ti$_3$Ni, and TiNi$_3$ were all present as shown in Fig. 1(a). This is due to the limitation of XRD in detecting phases of low volume fractions less than 5%. NiTi in the form of austenite was observed to form in the specimen sintered at 850 °C, however the original precursor of Ni is still the dominant phase even after 900 °C, implying early stages of diffusion sintering. Increasing the sintering temperature to 1080 °C led to the disappearance of both Ni and Ti where only three phases were observed, i.e., NiTi, Ti$_3$Ni and TiNi$_3$ with NiTi being the dominant phase and consistent with the SEM observation (refer...
Fig. 1(d)). In contrast, for Ni-TiH$_2$ specimen, the peaks of B2-NiTi increased as the temperature increased. At higher temperature, the diffusion rate is greater, thus leading to more phase formation at the expense of Ni and Ti.

![XRD spectra of (a) Ni-Ti (b) Ni-TiH$_2$ specimen sintered at different temperatures for 6 hours](image)

**Fig. 3** XRD spectra of (a) Ni-Ti (b) Ni-TiH$_2$ specimen sintered at different temperatures for 6 hours

### 3.2 Phase Fraction Analysis

Fig. 4 shows NiTi area fractions of both Ni-Ti and Ni-TiH$_2$ specimen sintered at different temperature to see the effect of replacing the powder precursor of Ti to TiH$_2$ on NiTi phase fraction. Surprisingly, the area fraction of NiTi increased aggressively to double (in average) for each temperature. This reflects that the use of TiH$_2$ as powder precursor to replace Ti can effectively increase the total area fraction of NiTi by reducing the oxygen contamination that cause oxidation during specimen preparation and sintering.

![Comparison of NiTi phase fraction between specimen Ni-TiH$_2$ and Ni-Ti sintered at various temperatures for 6 hours duration as determined by ImageJ software](image)

**Fig. 4** Comparison of NiTi phase fraction between specimen Ni-TiH$_2$ and Ni-Ti sintered at various temperatures for 6 hours duration as determined by ImageJ software
3.3 Oxide Analysis. Ni+Ti powder mixture was further analysed using XRD to detect the oxide formation at this stage. The result of Ni+Ti powder mixture was then compared to the as-received Ti powder. According to XRD result as shown in Fig. 5, only Ti peaks were observed for as-received Ti powder, implying no oxidation was detected at this stage. However, the TiO$_2$ peaks were detected for Ni+Ti powder mixture. This indicates that part of Ti powder was oxidized during specimen preparation i.e. ball milling. As a conclusion, the loss of Ti due to oxidation during specimen preparation (mixing) creates imbalance composition for Ni-Ti reaction, thus formation of single phase NiTi can't be achieved using Ti as powder precursor. This implies that oxidation impedes the formation of single phase NiTi.

![XRD spectra of Ti powder and powder mixture of Ni+Ti after ball milling](image)

**Fig. 5** XRD spectra of Ti powder and powder mixture of Ni+Ti after ball milling.

3.4 Transformation behaviour. Fig. 6 shows the plot of DSC curves of Ni-Ti and Ni-TiH$_2$ specimen sintered at different temperatures. For Ni-Ti specimen, none of the specimens show transformation either on cooling or heating, even though they have significant amount of B2-NiTi phase present in the matrix. One possible explanation for the absence of transformation in these specimens is the high Ni content in the B2-NiTi phase as measured by EDS. According to SEM Fig. 1, it is evident that B2-NiTi phase generally contained >52 at%Ni. It is known that B2→B19' martensitic transformation temperatures are highly dependent on the Ni content in NiTi. The transformation temperatures decrease rapidly with increasing Ni content in the B2-NiTi and no transformation can be observed for the specimen with Ni content >51.7 at% [8]. However, transformation peaks were detected for Ni-TiH$_2$ specimens. For specimen sintered at 750 °C, transformation occurs both on cooling and heating with $\Delta H_{A\rightarrow M} = 3.04$ J/g and $\Delta H_{M\rightarrow A} = 1.6$ J/g, respectively. The enthalpy change increased with increasing sintering temperature both upon cooling and heating, implying more B2-NiTi participate in the transformation. However, the overall total value of enthalpy change (≤9 J/g) is still lower compared to the bulk NiTi alloy (~24-28 J/g) [9].
Table 1 Transformation temperature and enthalpy change for Ni-TiH₂ specimen sintered at different temperatures for 6 hours

<table>
<thead>
<tr>
<th>Specimen</th>
<th>A→M</th>
<th>M→A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ms</td>
<td>Mr</td>
</tr>
<tr>
<td>750 °C</td>
<td>67.2</td>
<td>47.5</td>
</tr>
<tr>
<td>850 °C</td>
<td>15.5</td>
<td>-50</td>
</tr>
<tr>
<td>930 °C</td>
<td>30</td>
<td>-43</td>
</tr>
</tbody>
</table>

4. SUMMARY

For Ni-Ti specimen, no martensitic transformation was observed attributed to minor NiTi phase formation. In contrast, Ni-TiH₂ specimen has high amount of B2-NiT and displayed martensitic transformation behavior. This reflects that the use of TiH₂ to replace Ti as powder precursor has a significant effect towards NiTi phase formation and its transformation behaviour.

REFERENCES


Effect of Alloying Element on Microstructure and Mechanical Properties of Sn-0.7Cu Solder

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ABSTRACT. Due to environment concern of lead Sn-0.7Cu eutectic solder has been successfully applied to practical production of consumer products. However, Sn-Cu has been reported to exhibit somewhat inferior mechanical properties compared to Ag containing lead free solder alloys. In this work, 1.0wt.% In and 0.1wt.% Fe had been added into Sn-0.7Cu eutectic solder. Three different solders have been fabricated by adding In and Fe into the solder, i.e., Sn.0.7Cu, Sn.0.7Cu.1.0In and Sn.0.7Cu.1.0In.0.1Fe. DSC result showed that adding indium decreases the melting point of Sn-Cu solder. The addition of In and Fe is expected to refine the $\beta$-Sn grains with fine Cu$_6$Sn$_5$ distributed within the eutectic colony of the bulk solder and contribute to higher solder strength. Characterization of the solder alloys focused on the bulk solder microstructure, IMC evaluation and wettability of solder alloys in reflowed and aged conditions. Reflow temperature was 270°C. Aging was done for 100, 250 and 500 hours at 150 °C and 180°C. The IMC observed for reflowed samples seem to decrease in thickness with addition of In and Fe. Isothermally aged samples on the other hand, did grow at higher rate when In and Fe was added. The IMC formed at the interface between solder and the copper substrate was identified as Cu$_6$Sn$_5$ in reflowed samples, and both Cu$_6$Sn$_5$ and Cu$_3$Sn when aged. The shear strength of samples improved as In and Fe were added.

Keywords: Lead-free solder, Sn-Cu alloy, Isothermal aging, Microstructure, Intermetallic compound;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

The soldering process has been a fundamental aspect in the realisation of all electronic products since the commencement of the electronic age and has been used extensively in the electronic industry. Due to environmental issue over the toxicity of lead (Pb) in eutectic Sn-Pb solders, has induce the development of lead free solder alloys for electronic packaging [1]. Sn-Pb solder have been long considered as the most common material for electronic packaging, since they have low melting point, low cost and good wettability [2]. There are several lead-free solders develop for better mechanical and electrical properties including Sn-Ag, Sn-Cu, Sn-Zn and Sn-Ag-Cu. Among these alloys Sn-Cu binary alloy, shows most suitable as a low-cost substitute lead-free solder alloy to replace Sn-Pb solder alloy, especially for iron, dip and wave soldering operation [3]. As the addition other alloying element such Zn, In, Fe, Bi can give good properties for solder that will give lower wetting angle, good spreading, lower melting point, smaller grain and others. In this work, 1.0wt.% In and 0.1wt.% Fe had been added into Sn-0.7Cu solder. Addition of In and Fe haves how improved in joint embrittlement, wet ability, lower the melting range and improved shear strength and increasing the fracture toughness this due to better adhesion of solder with substrate and improved interface bonding [4].
The properties of solders include structure of the intermetallic compounds (IMCs), the morphology and thickness, adhesion between the IMC layer and solder, microstructure evaluation after reflow and diffusion properties [5]. The thicker of IMC layer is a sign of good wetting but its excessive growth has a detrimental effect to the reliability of the solder joint since IMC is very brittle in nature. Additions of small amount alloying elements have been reported to help reducing the thickness of the interfacial IMC layer [6,7]. It also been reported that the thickness of Cu$_5$Sn$_5$ and Cu$_3$Sn IMC layers increased linearly with the cube root of reflow time [8].

2. MATERIALS AND METHODS

The alloys investigated had a composition of Sn-0.7wt.%Cu, Sn-0.7Cu-1.0wt.%In and Sn-0.7wt.%Cu-1.0wt.%In-0.1wt.%Fe. They were prepared from high purity (99.998%) Sn ingot, Cu shots, In shots and Fe beads as raw material via casting. For bulk solder sample preparation, the solder alloys were ground with SiC abrasive paper grit 100 until 2000 before polished using 1 µm alumina powder. Once mirror-like surface was obtained, the samples were chemically etched with 5% HNO$_3$-2% HCl-93% CH$_3$O etching solution to reveal the microstructure before observed using field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray (EDX). The wettability of the solder was determined using a solder checker model SAT-5100 from Rhesca Co. Ltd. The temperature was set to be 270 °C with 2 mm immersing depth and 10 s immersing time. Maximum wetting force and wetting time were obtained from the wetting balance curve that was plotted automatically by the embedded software.

To make solder joint, small piece of the solder alloys was cold roll to form solder sheet with a thickness of 0.5 mm. The solder sheet was punched to form a solder disk with a diameter of 6 mm. Dimensions of 0.5 × 10 × 10 mm Cu substrate was applied with activated rosin (RA) flux to remove contaminants prior to reflow. Reflow process was done inside a reflow oven with the reflow temperature set at 270 °C. Reflowed solders were then isothermally aged at 100 °C and 150 °C for 100 hours, 200 hours and 500 hours, respectively. Subsequently, reflowed and isothermally aged solders were cut to reveal the cross section of the joint before mounted into epoxy resin. Wetting angle was measured after grinding and polishing process while IMC analysis via FESEM was done after the joint was chemically etched with the same solution as mentioned above. The grain size and the IMC thickness were measured using i-Solution DT image analyzer software.

3. RESULTS AND DISCUSSION

3.1 Differential Scanning Calorimetry (DSC). The result of DSC measurement is summarized in Table 1. The melting temperature of Sn-0.7Cu-1.0In-0.1Fe solder was found 235.25°C which is significantly higher compared to other solder alloys. This due to melting point of pure Fe is much higher than Sn [5]. The decrease in the melting point of Sn-0.7Cu-1.0In solder alloy may due to the addition of low melting temperature element, such as In (T$_m$=157°C) [9].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melting temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-0.7Cu</td>
<td>233.73</td>
</tr>
<tr>
<td>Sn-0.7Cu-1.0In</td>
<td>231.78</td>
</tr>
<tr>
<td>Sn-0.7Cu-1.0In-0.1Fe</td>
<td>235.25</td>
</tr>
</tbody>
</table>

3.2 Microstructure of bulk solder. The microstructure of a) Sn-0.7Cu, b) Sn-0.7Cu-1.0In and c) Sn-0.7Cu-1.0In-0.1Fe bulk solder alloys are present in Fig 1. From Fig. 1, the addition of In and Fe in solder alloys can markedly refinement β-Sn and intermetallic compounds are more uniformly distributed. Based on EDX analysis as shown in Table 2. From the analysis, there is no formation of InSn$_4$ IMCs, although 1.0wt.% of In was added. In is only spotted near the β-Sn phase where it adhered next to the Sn of the solder alloy. According to previous work being done by other researchers, InSn$_4$ IMCs only form when 2wt.% and
4wt.% of In was added into solder sample [10,11]. In also has maximum solubility inside Sn, it would suggest that In is distributed within β-Sn phase and not formed into In₄Sn IMC [12]. Therefore, in this work, the In added could be too low for InSn₄ to form.

![Image](https://example.com/image1)

**Fig. 1** FESEM micrographs of (a) Sn-0.7Cu, (b) Sn-0.7Cu-1.0In and (c) Sn-0.7Cu-1.0In-0.1Fe bulk solder alloys

<table>
<thead>
<tr>
<th>Composition</th>
<th>IMC</th>
<th>Cu</th>
<th>Sn</th>
<th>In</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-0.7Cu</td>
<td>Cu₆Sn₅</td>
<td>55.80</td>
<td>40.20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sn-0.7Cu-1.0In</td>
<td>Cu₆Sn₅</td>
<td>58.33</td>
<td>41.67</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>InSn₄</td>
<td>4.29</td>
<td>94.16</td>
<td>1.55</td>
<td>-</td>
</tr>
<tr>
<td>Sn-0.7Cu-1.0In-0.1Fe</td>
<td>Cu₆Sn₅</td>
<td>58.33</td>
<td>41.67</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>FeSn₂</td>
<td>-</td>
<td>69.14</td>
<td>1.55</td>
<td>30.86</td>
</tr>
</tbody>
</table>

**Table 2** Chemical composition of IMCs (At.%)  

**3.3 Microstructure of IMCs layer.** The average thickness of IMC formed on each sample before and after aging are listed in Table 3. From the overall view on the IMC thickness, Sn-0.7Cu-1.0In solder samples have lowest IMC thickness compared to other two samples due to In hindered the dissolution of Cu to liquid solder [5,13], followed by Sn-0.7Cu and Sn-0.7Cu-1.0In-0.1Fe solder samples, this may be due to the formation of elongated scallops of Cu₆Sn₅ IMC [5].

![Image](https://example.com/image2)

**Fig. 2** Microstructure of IMC layer at solder-substrate interface for as reflowed condition (a)Sn-0.7Cu, (b) Sn-0.7Cu-1.0In and (c) Sn-0.7Cu-1.0In-0.1Fe solder alloys

![Image](https://example.com/image3)

**Fig. 3** Microstructure of IMC layer at solder-substrate interface after isothermally aged for 250 hours at 150 °C (a)Sn-0.7Cu, (b) Sn-0.7Cu-1.0In and (c) Sn-0.7Cu-1.0In-0.1Fe solder alloys.
The average thickness of IMC formed on each sample before and after aging are listed in Table 3 and Table 4. From the overall view on the IMC thickness, Sn-0.7Cu-1.0In solder samples have lowest IMC thickness compared to other two samples, followed by Sn-0.7Cu and Sn-0.7Cu-1.0In-0.1Fe solder samples. The low overall thickness of Sn-0.7Cu-1.0In samples may due to addition of 1.0wt.% of In hindered the dissolution of Cu to liquid solder and thus reduced the thickness of the Cu₆Sn₅IMC layer compared to Sn-0.7Cu sample [5,13]. The high overall IMC thickness in Sn-0.7Cu-1.0In-0.1Fe sample may be due to the formation of elongated scallops of Cu₆Sn₅IMC [5].

The aging temperature and duration significantly increased the IMC thickness in solder samples because during aging, excess Cu will diffuse and reacts with existing intermetallic compounds and increases the size of nuclei. As results, the thickness of IMC layer increased [5,14].

**Table 3** Average thickness and growth rate constant of IMC 150°C at different aging condition

<table>
<thead>
<tr>
<th>Condition</th>
<th>Sn-0.7Cu</th>
<th>Growth rate (cm²/s)</th>
<th>Sn-0.7Cu-1.0In</th>
<th>Growth rate (cm²/s)</th>
<th>Sn-0.7Cu-1.0In-0.1Fe</th>
<th>Growth rate (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As reflowed</td>
<td>3.61</td>
<td>0</td>
<td>3.53</td>
<td>0</td>
<td>3.77</td>
<td>0</td>
</tr>
<tr>
<td>100 h 150 °C</td>
<td>4.76</td>
<td>3.67x10⁻¹⁴</td>
<td>4.18</td>
<td>1.17x10⁻¹⁴</td>
<td>5.85</td>
<td>1.2x10⁻¹³</td>
</tr>
<tr>
<td>250 h 150 °C</td>
<td>6.75</td>
<td>1.96x10⁻¹³</td>
<td>6.04</td>
<td>7.00x10⁻¹⁴</td>
<td>6.09</td>
<td>5.98x10⁻¹⁴</td>
</tr>
<tr>
<td>500 h 150 °C</td>
<td>7.04</td>
<td>6.53x10⁻¹⁴</td>
<td>6.38</td>
<td>4.51x10⁻¹⁴</td>
<td>7.56</td>
<td>7.98x10⁻¹⁴</td>
</tr>
</tbody>
</table>

**Table 6** Average thickness and growth rate constant of IMC 180°C at different aging condition

<table>
<thead>
<tr>
<th>Condition</th>
<th>Sn-0.7Cu</th>
<th>Growth rate (cm²/s)</th>
<th>Sn-0.7Cu-1.0In</th>
<th>Growth rate (cm²/s)</th>
<th>Sn-0.7Cu-1.0In-0.1Fe</th>
<th>Growth rate (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As reflowed</td>
<td>3.61</td>
<td>0</td>
<td>3.53</td>
<td>0</td>
<td>3.77</td>
<td>0</td>
</tr>
<tr>
<td>100 h 180 °C</td>
<td>8.07</td>
<td>5.53x10⁻¹³</td>
<td>6.21</td>
<td>1.99x10⁻¹³</td>
<td>8.33</td>
<td>5.7x10⁻¹³</td>
</tr>
<tr>
<td>250 h 180 °C</td>
<td>11.25</td>
<td>6.49x10⁻¹³</td>
<td>9.34</td>
<td>3.75x10⁻¹³</td>
<td>12.16</td>
<td>7.82x10⁻¹³</td>
</tr>
<tr>
<td>500 h 180 °C</td>
<td>13.63</td>
<td>5.58x10⁻¹³</td>
<td>12.42</td>
<td>4.39x10⁻¹³</td>
<td>12.67</td>
<td>4.40x10⁻¹³</td>
</tr>
</tbody>
</table>

**3.4 Single Lap Joint.** In this testing, Sn-0.7Cu-1.0In-0.1Fe gave the highest shear strength, but from the stress strain curve shown Fig.5 and summarize in Table 7, this samples exhibited lesser plastic deformation if compared to Sn-0.7Cu-1.0In solder alloy. The lesser plastic deformation is due to the addition of 0.1wt.% of Fe that caused the abnormal growth of IMCs at the interface of Cu substrate. The abnormal growth may due to the increase in the chemical activity of Cu element with the solder. This elongated IMC led to the lower fracture...
strain in Sn-0.7Cu-1.0In-0.1Fe solder alloy due to the IMC embrittlement [13].

### Table 7 Average shear strength of solder samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load, N</th>
<th>Area, $\mu m^2$</th>
<th>Shear Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-0.7Cu</td>
<td>2385.04</td>
<td>9.88</td>
<td>24.15</td>
</tr>
<tr>
<td>Sn-0.7Cu-1.0In</td>
<td>2479.07</td>
<td>9.61</td>
<td>25.80</td>
</tr>
<tr>
<td>Sn-0.7Cu-1.0In-0.1Fe</td>
<td>2541.20</td>
<td>9.80</td>
<td>25.93</td>
</tr>
</tbody>
</table>

4. SUMMARY

This study found that addition of In had lowered the melting temperature of Sn-0.7Cu. In contrast, addition of Fe led to an increased in melting temperature. From the FESEM and EDX analysis, it shows that the grain size decreases as addition of In and Fe on microstructure of solder. The shear strength of samples improved as In and Fe added. From FESEM and EDX analysis, aging had led to the formation and growth of Cu$_6$Sn$_5$ and Cu$_3$Sn IMC, and this had increase the thickness of IMC layer.

REFERENCES


Effect of pH in Production of Cu-Sn-Zn via Electroplating Using Less Hazardous Electrolyte

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ABSTRACT. Cu-Sn-Zn ternary alloy have been prepared by an electroplating process on carbon substrate from a less hazardous electrolyte containing chloride solution, complexing agent and reducing agent at room temperature. In this study, the effect of pH on deposit composition was investigated in details. pH 9 was found to be the best condition as it was non-acidic and less alkaline solution with composition of Cu₅₄.₅ Sn₃₂.₅ Zn₁₃.

Keywords: Less hazardous, Electrolyte, Ternary alloy, Electroplating;

Received: 15.10.2017, Revised: 15.12.2017, Accepted: 30.02.2018, and Online: 20.03.2018;


Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Electroplating is both art and sciences. It is an electrodeposition process for producing a dense, uniform and adherent coating, usually of metal or alloys, upon a surface by the act of electric current. This process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. Electroplating is used extensively in a variety of industrial applications as for appearance, protection, special surface properties and engineering or mechanical properties. Process of electroplating is also used for electrical oxidation of anions onto solid substrate, to change the surface properties of an object. Electroplating products are widely used for many industries, such as automobile, ship, air space, machinery, electronics, jewelry, defense, and toy industries.

Alloy can be deposited from two types of plating solutions: the alkaline cyanide copper and formaldehyde [1]. These electrolyte is primarily used for decorative and in electronic applications. Unfortunately, cyanide is one of the most toxic chemicals available and therefore its use carries an extremely high risk to human health and to environment. The use of cyanide salts in plating electrolytes has becomes environmentally disfavored because of ecological considerations including the catastrophic accidental acidification of cyanide, disposal of the exhausted plating bath and waste water treatment are becoming increasingly difficult and expensive, rendering this approach highly unattractive from an industrial perspective [2]. This project have been proposed for use as replacements for the well-known and conventional commercially employed cyanide
counterparts and it will reduce the waste treatment costs for destroying cyanide along with fire and liability insurance premiums.

2. MATERIALS AND METHODS

Cu-Sn-Zn alloy were plated by electroplating from a less hazardous electrolyte containing copper (II) chloride, tin chloride and zinc chloride with the help of reducing agent and complexing agent. The details composition and operating condition are given in Table 1. A graphite was used as anode. For coating and morphology studies, carbon was used as cathode. Carbon substrate with dimension 45 mm length, 0.9 mm thickness and 1.8 mm width was heated at 500 °C for 45 min to remove any impurities. The substrate was then degreased in acetone solution. Prior to electroplating, the substrate was activated in 10% sulfuric acid (H₂SO₄) solution to produce a highly clean active surface [3]. After each of these pretreatment process, the substrate were cleaned in distilled water. Plating processes via electroplating was performed for 30 minutes at room temperature in less hazardous electrolyte and was agitated mechanically at room temperature with current density range to 15mA/mm².

Table 1 The composition of electrolyte

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl₂</td>
<td>0.30 M</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>0.15 M</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>0.45 M</td>
</tr>
<tr>
<td>Reducing agent</td>
<td>0.45 M</td>
</tr>
<tr>
<td>Complexing agent</td>
<td>0.10 M</td>
</tr>
</tbody>
</table>

2.1 Surface morphology and composition analysis. Surface morphology and compositions of the electroplated layers deposited from less hazardous electrolyte bath was investigated under scanning electron microscope equipped with energy dispersive X-ray spectroscopy (JEOL, JSM-6380LA). The thickness was measured by the following formula (Eq. 1):

\[ t = \frac{(m_2 - m_1)}{A \times \rho} \]  

Where \( m_2 \) and \( m_1 \) are respectively the mass of alloy plating and substrates; \( A \) is the area of the coated specimen; \( \rho = \Sigma w \) (\( w \) is the mass fraction of Cu, Sn and Zn in alloy).

3. RESULTS AND DISCUSSION

3.1 Effect of pH on composition and morphology. An analytical parameter that can influence the composition of plating layers is pH of the solution bath used. It is proven that the formation constant of a stable metallic complex species is highly pH dependent on which basically determines the availability of effective reducible metallic species in the solutions [4]. In demand to stabilize the solution from precipitation in the alkaline pH range, sodium citrate as complexing agent was added in the chloride solution.

The effect of pH was studied by keeping current density (15 mA/mm²) and metals concentration constant respectively as shown in Table 1. A 10% of sodium hydroxide was added slowly to achieve desired pH. At lower pH, a coarse layer coating was obtained which turn into smooth layer at higher values of pH. Fig. 1 shows the variation of compositions of deposited alloy in pH range from 1.0 to 14.0. It is clear that, composition of Cu was decrease slowly from 96.7% to 54.5% by increasing pH from 1.0 to 9.0. However, with increasing the values of pH, both Sn and Zn content of the alloy increase from 3.3% to 81.8% and from 2.7% to 13.0%, respectively. The local pH of the substrate was increased with the increasing the value of pH.
solution. The higher pH values of the substrate perhaps are due to the faster recovery of H\textsuperscript{+} ion on the surface of substrate [5]. This process causes the development of hydrogen bubbles and rapid depletion of H\textsuperscript{+} ions around the substrate and causes Cu penetrates in the form of CuOH, so that easily to precipitates. It was observed that at pH9, composition of Cu, Sn and Zn was 54.5, 32.5 and 13%, respectively. This value was almost similar with Miralloy composition (Cu\textsubscript{51} Sn\textsubscript{33} Zn\textsubscript{17}) which has earned widespread acceptance as an excellent alternative to nickel for a broad range of applications.

![Production of Cu-Sn-Zn in the effect of different pH](image)

**Fig. 1** Production of Cu, Sn and Zn in the effect of different pH

The effect of pH on the surface morphology of Cu-Sn-Zn ternary alloy layers was studied using scanning electron microscope. The layers that electroplated from less hazardous electrolyte at several pH and at constant current density are presented in Fig 2. The morphology for pH 1 exhibit a spongy and cauliflower surface in appearance and continuous deposits with the presence of both large and small grains simultaneously. This phenomenon indicate an abnormal growing during deposition process. However, by increasing the value of pH, the morphology change to coarse and porous in appearance. The change of the surface appearance was justified by the hydrogen evolution and stimulus the electrochemical conditions. Fig 3 shows the energy dispersive X-ray spectroscopy spectra of Cu-Sn-Zn plating layer for the study on the effect of different pH deposited at 15 mA/mm\textsuperscript{2}. 
Fig. 2 Effect of pH on the surface morphology of Cu-Sn-Zn alloy coating at pH (a) 1.0, (b) 3.0, (c) 5.0, (d) 7.0, (e) 9.0, (f) 11.0 and (g) 14.0 deposited at 15 mA/mm$^2$.

Fig. 3 EDS spectrum of Cu-Sn-Zn alloy coating at pH (a) 1.0, (b) 3.0, (c) 5.0, (d) 7.0, (e) 9.0, (f) 11.0 and (g) 14.0 deposited at 15 mA/mm$^2$. 
4. SUMMARY

Cu-Sn-Zn ternary alloy was successfully plated on carbon substrate. It was recognized that the pH of electrolyte has significant influence in composition of alloy and on the overall plating process. As in this studies, the optimum pH was found at pH 9 which gave the similar composition of Miralloy at non-acidic and less alkaline solution.

ACKNOWLEDGEMENT

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Volumetric Study of Zinc in Various Concentration of Potassium Hydroxide

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ABSTRACT. Zinc (Zn) was immersed in different concentration of potassium hydroxide (KOH) aiming at the preparation of volumetric measurement of Zn in KOH, which led by producing the hydrogen evolution gas. Zn that been used in this study was 99.9% pure Zn. In this study, the characterization of Zn was studied, this is including hydrogen evolution gas and structural analysis. In this experiment, instruments that used is X-ray diffraction (XRD). The analysis from XRD for the metal of Zn showed that the immersion of KOH electrolyte into Zn gives some effect where the surface of Zn showed white patch. This is due to oxide presence at Zn surface.

Keywords: ZnO, KOH, Volumetric, Hydrogen gas;

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1. INTRODUCTION

Zn is one of the most metals in electroplating and it is favourable anode in primary batteries due to its properties high discharge efficiency and high safety features associated with its manufacturing process and use [1]. While, regarding another researcher Zn metal is a favourable anode in primary batteries because of its high capacity (0.82 Ah/g) [2]. Furthermore, Zn is a material that can be an electrode that has a large surface area, fairly dense, volume consumption is about three times lower than for magnesium and dimension of the Zn anode are correspondingly smaller [3]. This criteria of Zn makes it more preferable as anode in primary batteries due to its properties high discharge efficiency and high safety features associated with its manufacturing process and use [1]. While, regarding another researcher Zn metal is a favourable anode in primary batteries because of its high capacity (0.82 Ah/g) and has a superior performance at the higher current drains and low temperatures and its better shelf life [2]. Besides that, Zn is chosen because properties of the Zn that make it valuable corrosion resistance is its ability to form a protective layer that consist of zinc oxide (ZnO) and hydroxide (OH⁻) or various basic salts, depending on the nature of the environment. The function of the protective layers is to cover the surface of the metal, the corrosion proceeds at a greatly reduced rate [4].

However, in the alkaline battery electrolyte is important as it is functioning as a catalyst that conducts or promote the movement of ions from cathode to anode during charge or in reverse on discharge. There are several types of electrolyte that can be used such as sodium hydroxide (NaOH), sodium chloride (NaCl) and potassium hydroxide (KOH). Moreover, for the electrolyte that currently used in battery needed a strong base. Strong base is a substance that increasing the concentration of OH⁻ where hydrolyses completely can accept proton and donate a pair of electrons. Strong base usually used as electrolyte. Electrolyte is a substance that containing a free ion which are carrying electric current in the electrolyte [5]. Potassium
Hydroxide (KOH) is chosen as an electrolyte because of its character as a strong base that allows the current to flow, do not gas off, and remain in the cell. Besides, it contains loosely bound semi-solid jelly granules and limited amounts of free KOH electrolyte available to the Zn electrode due to the high water retentively of the gel.

The usage of KOH in different concentrations in different applications will determine the limitations of the free charge carrier when the concentration increased. The free ions would tend to come closer to each other's. On the other hand, KOH solution with a concentration of 30 wt.% shows the highest ionic conductivity, a good solubility of ZnO and relatively low viscosity, which is beneficial for high power density flow battery applications [6,7]. In addition, the battery can give some effect where it can undergo the leakage. The battery leaks because of the discharge of batteries (chemistry of the battery changes and some hydrogen gas is generated) [8]. This out-gassing process increases pressure in the battery. Eventually, the excess pressure either ruptures the insulating seals at the end of the battery, or the outer metal canister [8]. The disadvantages of corrosion to the materials will make the materials facing serious problems which tend to damage internal and external of the material such as cracking [9]. In the alkaline battery, the problem with Zn frequently facing corrosion because of the electrolyte. For this reason, the behavior of the Zn is depending on the concentration of KOH being used. Where, basically in corrosion understanding towards metal behavior, corrosion is happen when the metal reacts to the environment such as the presence of $O_2$, reaction toward acidity and alkaline level of environment and the moisture content of surrounding [10,11].

Inherently, at low concentration of KOH, few charge carriers existed so that ionic conductivity correspondingly kept low in value so that the corrosion towards the Zn is least [12]. The addition of higher concentrations of KOH increased the ionic conductivity due to an increase in the number of OH⁻ ions available in the electrolyte [13]. The volume of hydrogen evolution gas expected to increase as a function of KOH concentrations. It is because 6 M of KOH give maximum impact on corrosion behaviour as stated in the previous study [14]. In the previous study, there are many researchers that study on the concentration of 2, 4 and 6 M of KOH with Zn to reveal their characterization and conductivity [15-17]. But, no researcher that doing towards concentration of KOH in 2, 4, 6 and 8 M with Zn by revealing the volume hydrogen evaluation gas of Zn plate.

2. MATERIALS AND METHODS

In this research, the materials will be used are Zn plate with dimension 2 cm x 1 cm (99.9% purity, Merck), KOH (Merck), commercial Zn plate and diesel oil. Measurement of production hydrogen gas was carried out by immersion of Zn in the different concentration of KOH (2, 4, 6 and 8 M) and connected a tube to the burette inside of the beaker that contain tap water as showed in Fig. 1.

The container is contained of Zn plate that immersed in the KOH concentration. Top of the KOH solution is oil. The function of the oil is to collect or prevent the bubbles produce from moving randomly. The bubbles were directly flow to the rubber tube. This procedure was taken for calculate and compare between the volume of hydrogen gas that released by the Zn to concentration of KOH.

XRD (Bruker) was used to observe the composition of the Zn plate. The crystalline phase was identified using the International Centre of Diffraction Data (ICDD) powder diffraction database. The angle of 2θ at the range of 10° to 90°.
3. RESULTS AND DISCUSSION

Fig. 2 shows the hydrogen consumption of Zn commercial that immersed in KOH. In 2 M of KOH showed that gradually decline for 170 hours. 0.1 mL of water was decreased every eight hours due to the low of KOH concentration. This will slow the movement of ion to attack the surface of Zn and unproductive air bubble is produced.

The pattern lines for 4 M KOH showed that lines are drawn through most of the data points. However, surprisingly at 110 hours there is small difference that there is indicates a lower volume of water at the increasing of time. Every four hours the volume of water decreasing by 0.1 mL.

Compared to 6 M that slightly decrease in pattern until at the 17 hours, but, then steeply dropped up to 45 hours and steadily until 170 hours. The water constantly decreases by 1.0 ml every hour. While at 8 M of KOH, showed data that decrease steadily for 82 hours and volume of water remain constant from 82 hours until 170 hours. The water keep diminished by 0.6 ml for every hour.

Fig. 2 Rate of hydrogen gas for Zn immersed in different concentration of KOH
**Fig. 3** Comparison peak analysis for XRD of (a) Zn commercial and Zn after reaction with (b) 2, (c) 4, (d) 6 and (e) 8 M of KOH

Fig. 4 shows the illustration of reactions happen in the media. The existing of hydrogen evolution is causing by the corrosion on the reactions of KOH and Zn by reactions of $\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}_2$. Zn is reacted to the KOH and caused the white patch (OH$^-$) on the surface after the observation at the end of experiment. The higher concentration of KOH, the reactions and corrosion to Zn will be faster.

**Fig. 4** Illustration of Zn reaction in KOH solution
4. **SUMMARY**

The volume of hydrogen evolution gas was increasing until it attains the maximum level concentration of KOH, 6 M and the higher concentration of KOH will produce more oxygen that can lead the Zn deposited to ZnO. This reaction will have led Zn to corrode due to the appearance of oxygen increasingly.

**ACKNOWLEDGEMENTS**

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Experimental Method on Solder Joint of Ball Grid Array Using Reflow Oven

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ABSTRACT. Modern applications need electronic systems to operate at high temperature. Mainly in automotive applications which leads to large temperature differences between ambient and operating temperatures. One of the most critical consequences occurs in dealing with thermo-mechanical stress which are created on solder joints due to mismatch of Coefficients of Thermal Expansion of electronic package and printed circuit board. The thermo-mechanical stress due to temperature cycles plays a fundamental role to increase the life of electronic components. This study to investigate the solder joint strength by using Pb free SAC 305 solder paste on solder joint. Experiment has been carried out by IR reflow oven with different types of solder paste and thermal profile. Importantly, SAC 305 was used during the experimental process with different types of thermal profile setting in order to generate optimum results.

Keywords: Solder paste, Printed circuit board (PCB), Ball grid array (BGA), Solder joint;

Received: 15.10.2017, Revised: 15.12.2017, Accepted: 30.02.2018, and Online: 20.03.2018;

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1. INTRODUCTION

Leading and popular electronics component are very sensitive to the high temperature [1]. Electronic component like solder joint are tend to fail when expose to the high temperature or thermal stress. Such situation happens due to lead-free processes using mixing of tin-lead and lead-free metallurgies [2,3]. Lead-free legislation permits certain products, especially those intended for high-reliability applications. One major concern with these exempt products is that, during assembly or rework, lead-free components will have to be used due to the unavailability of tin-lead components. This will result in the mixing of tin-lead and lead-free metallurgies. The mixing of metallurgies can induce new reliability concerns [4,5]. Present study is focused on enhancing solder joints by using composition of solder paste and nanoparticle. In modern times, CFD is a new area in studying solder joint during reflow oven process to verify the experimental results. Reflow oven
process in solder joint can cause damage to the solder joint due to the excessive temperature [6,7]. Reflow oven process which is an alternate heating and cooling of a material of solder joint until they experience molecular reorganization, which tightens or optimizes the particulate structure of the material throughout, relieving stresses and making it denser and uniform thereby minimizing flaws or imperfections. Main issue with Solder joint happens in its microstructure due to thermal loading conditions [8,9,10]. Microstructure do plays an important role in influencing time to failure for solder joints. Several studies have been conducted to investigate strength and reliability of solder joints subjected to several loading conditions and material combinations [11]. Besides that, reflow oven process at solder joint is of the main factor that made solder joint to broke due the excessive temperature and heat [12]. In the actual process, the reflow oven were used to study thermal stress or thermal resistance of solder joint on printed circuit board (PCB) [13]. The parameters considered in this study can be categorized into two main streams: material properties, mainly Pb-contained or Pb-free, and the geometric parameters, typically height of solder joints. A total of three groups (four same samples in each group) of BGA packages subjected to thermal cycling were analyzed [14].

Existing fatigue damage models for the electronic package are mainly based on the thermal-fatigue test and most of them require stress-strain relations in low-cyclic fatigue (LCF, N < 10^3) to predict life cycle of the electronic board with solder interconnection. Generally, the shapes of the solder joint are random and their sizes range from ten to hundreds of micrometers. Thus, it is impossible to perform direct and accurate measurement of strain on the solder joint surface using the existing methods. Meanwhile, finite element (FE) analysis is used to obtain the stress-strain responses for solder joints with different components [15,16].

2. MATERIAL AND METHODS

The novel approach was presented in solving the solder joint reliability problems during reflow soldering process. Before dealing with numerical techniques, the experimental details for thermal profiling were presented for better understanding in structure and concept of reflow ovens. Furthermore, the procedures of determining the most critical solder joint under ATC were discussed in same section. A batch-type convection-IR reflow oven was designed for reflow the small quantity assembly or for scientific research purpose. The convenience in controlling heating and cooling elements of a convection-IR reflow oven was given the excellent performance in forming a good joint between the PCB and its components. Figs. 1-3 shows an example of experiment setup of the convection-IR lead-free reflow oven. This type of oven was used to validate simulation results for optimization studies of lead-free reflow soldering process.

![Reflow oven](image)

**Fig. 1** Experiment setup for thermal profiling
The fundamental three modes of heat transfer which are radiation, convection and conduction occurs in a convection-IR reflow oven. Radioactive heat transfer occurs from the quartz heating tube over the BGA assembly. Hot air circulated by a fan inside the oven contacts with BGA assembly and heat transfer through convection mode. Finally, the heat transfers by conduction within the multi-material BGA assembly. The slope, temperature and dwell times of lead-free reflow profile were technically programmed via computer into the following stages: preheating, soaking, reflow, and cooling stage. Since the batch-type reflow oven was designed in a single zone, the temperature setting was set according to temperature curve that reached the desired temperature in certain time. The example of oven setting temperature in the present study was set according to Table 1.

<table>
<thead>
<tr>
<th>Reflow Oven Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling Time</td>
<td>40 s</td>
</tr>
<tr>
<td>Preheating Slope (298 K to Soak Temp)</td>
<td>2.5 K/s</td>
</tr>
<tr>
<td>Soaking Slope (Soak Temp to 463 K)</td>
<td>0.3 K/s</td>
</tr>
<tr>
<td>Ramp Slope (463 K to Peak Temp)</td>
<td>1.5 K/s</td>
</tr>
<tr>
<td>Cooling Slope (Peak Temp to 453 K)</td>
<td>-3 K/s</td>
</tr>
<tr>
<td>Soaking Temp</td>
<td>433 K</td>
</tr>
<tr>
<td>Peak Temp</td>
<td>518 K</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

The temperature setting of the reflow oven was compared with three types of setting as shown in Fig. 4(a-c). Significant variations among the temperature setting of ovens were clearly observed, indicating that
the structure and mechanism of batch-type were different, which depends on the temperature setting on thermal profile.

**Fig. 4** Experiment setup for thermal profiling on Pb free SAC 305 at maximum temperature (a) 275 °C, (b) 265 °C and (c) 235 °C
The temperature setting of the reflow oven was compared with three types of setting as shown in Fig. 4(a-c). Substantial change in temperature setting of ovens were clearly observed, implying the structure and mechanism of batch-type were similar, which depends on the temperature setting on thermal profile. Fig. 4(a-c) indicate thermal profile of PCB at high temperature setting such as 265 ºC and 275 ºC causing the solder paste to melting and overheat. The melting temperature for Pb free SAC 305 is 218.8 ºC. When the temperature is over 218.8 ºC, it will cause SAC 305 to melt and overheat. A suitable temperature setting during reflow oven process was very important to provide good solder joint and to avoid overheat and melting.

4. SUMMARY

Snipped results indicate Pb free SAC 305 solder paste has been carried out by IR reflow oven with different types of solder paste and thermal profile. It was evident that SAC 305 was using high temperature profile and tend to melt and overheat. The temperature different between first two settings was 17.02% and 12.77%. The reflow oven process performed by using different types of thermal profile setting in order to generate optimum results.

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Physiochemical Characterization of Sn-Zn Coatings Electrodeposited from an Acidic Chloride Bath in the Absence of Complexing Agent

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ABSTRACT. The purpose of this study is to identify the Zn2+ ions concentration at Sn-Zn coating which could be produced in the absence of a complexing agent. The electrolytic bath comprised of SnCl2 and ZnCl2. The ionic mole ratio Zn2+/Sn2+ of the electrolytic bath studied were 1:2, 1:1, 2:1, 4:1 and 10:1. Pure Zn and Sn electrodeposits were also prepared. The deposition process was performed at constant current of 5 mA and deposition time of 120 min. The electrodeposits were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that in the absence of complexing agent, even an electrolytic bath with Zn2+/Sn2+ ionic ratio of ten folds could not produce Zn-rich of Sn-Zn electrodeposits. Further, a unique method has been introduced to characterize the electrodeposits i.e. using the metal-air electrochemical cell. In this method, the electrodeposits were coupled with an air electrode in an alkaline electrolyte (6 M KOH) and discharged at 1 mA. Specific metallic element content will produce a distinct discharge profile thus enables it to be used in characterizing alloys or composites.

Keywords: Tin-zinc electrodeposits, Electroplating bath, Electrodeposition, Metal-air characterization;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Sn-Zn alloy coatings offer high corrosion protection for steel, good frictional properties and ductility, and good solder ability [1,2,7,8]. They also have low electrical contact resistance and are not subjected to bimetallic corrosion [3,5]. Sn-Zn alloy coatings also serve as substitutes for toxic cadmium and allergenic nickel coating at the end of the last century [3,4,6].

Tin and zinc can in principle be co-deposited from a simple salt solution containing both ions. However, since their standard electrode potentials are substantially wide apart (-0.76 V for Zn and -0.14 V for Sn), the electrodeposited layer is Sn-rich by default. Optimum zinc content required for effective corrosion protective layer is 20-30 wt.% [3]. Numerous electrolytic baths have been investigated to deposit Zn-rich Sn-Zn coatings [4,9-16].

In this study, we report the galvanostatic electrodeposition of Sn-Zn coating using simple acidic electrolytic bath comprising a mixture of tin chloride (SnCl2) and zinc chloride (ZnCl2) without the inclusion of complexing agent such as the gluconate, tartrate, citrate or cyanide baths. The purpose is identify the zinc ions concentration (Zn2+) at which a rich-Zn Sn-Zn coating could be produced in the absence of a complexing agent. Further, we are using a unique method to distinguish whether a Sn-Zn coating is either a Sn-rich or a
Zn-rich i.e. by employing the coating as an anode in a metal-air electrochemical cell. Metal-air cell is popularly dubbed as a breathing battery as it requires oxygen from the ambient air to operate. As the system is supplied with unlimited supply of oxygen from the ambient air, any variation in its discharge profile is attributed to the anode i.e. the electrodeposited Sn-Zn coating in this case.

2. **EXPERIMENTAL METHOD**

The standard bath composition for Sn, Zn and Sn-Zn alloy deposits are given in Table 1. A copper clad laminate printed circuit board (PCB), patterned by the photolithography process employing a negative photoresist, was used as the substrate. The electrochemical cell consisted of tin plate (99.99% purity) as the working electrode (except for pure zinc deposits where a zinc plate (99.99%) was used) and copper substrate as the counter electrode. The copper substrate was clamped by an acrylic board holder with a fixed displacement (d) of 20 mm between the two electrodes. The holder possessed a circular window (11.5 mm in diameter) for deposition to take place on the copper substrate. The deposition current was fixed at 5 mA for a duration of 120 minutes. The surface morphology and chemical composition of the deposit was evaluated by a scanning electron microscope (SEM) and Energy-dispersive X-ray Spectroscopy (EDX); JSM-5600,JEOL(Japan). X-ray diffractometry (XRD) Empyrean PAN alytical was used to identify the phases of Sn-Zn alloy deposited. Metal-air cell was fabricated by pairing the electrodeposits with a commercial air electrode sheet in 60 ml of 6 M potassium hydroxide electrolyte. The cell was discharged at constant current of 1 mA using the AUTOLAB PSTAT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SnCl₂ Molarity/Volume</th>
<th>ZnCl₂ Molarity/Volume</th>
<th>Mole ratio Zn²⁺/Sn²⁺</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 M/60 ml</td>
<td>-</td>
<td>-</td>
<td>Sn electrodeposits</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>1 M/60 ml</td>
<td>-</td>
<td>Zn electrodeposits</td>
</tr>
<tr>
<td>C</td>
<td>1 M/30 ml</td>
<td>1 M/30 ml</td>
<td>1:1</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.5 M/30 ml</td>
<td>1 M/30 ml</td>
<td>2:1</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1 M/30 ml</td>
<td>0.5 M/30 ml</td>
<td>1:2</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0.5 M/30 ml</td>
<td>2 M/30 ml</td>
<td>4:1</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>0.5 M/30 ml</td>
<td>5 M/30 ml</td>
<td>10:1</td>
<td></td>
</tr>
</tbody>
</table>

3. **Results and Discussion**

3.1 **X-ray diffraction patterns**

Fig. 1 shows that the changes in the XRD patterns of Sn as zinc ions were introduced into the electrolytic bath. It is evident that the electrodeposits were Sn-rich by merely referencing with the XRD patterns obtained from the Sn and Zn coatings. Even at zinc ions mole ratio of 10, the electrodeposits was still a Sn-rich coating. An EDX measurement on this sample (10:1), revealed zinc content of only 2.6%. However, note that at 10:1 electrolytic bath composition, the entire XRD patterns shifted towards low 2θ angle. This could probably due to the incorporation of zinc alloying element into the space lattice of tin and thus changes the unit cell parameters (Vegard’s law). The radius of zinc atom (142 pm) is slightly less than that of tin (145 pm). Therefore, this could suggest that in order to obtain a Zn-rich Sn-Zn electrodeposits in the absence of complexing agent, the zinc to tin ionic mole ratio of the electrolytic bath should be in excess of ten folds.
3.2 Surface morphology

The surface morphology observations were conducted to support the XRD results. One distinct feature of tin electrodeposits are their porous nature, unlike zinc electrodeposits which is dense. Thus, all samples of Sn-Zn coatings appear to be Sn-rich as they possess similar morphology to that of pure tin electrodeposits.

3.3 Metal-air cell characterization

This is a unique method proposed to distinguish or to verify a metal element content. Electronegative metals such as aluminum, zinc, iron and tin have been utilized as anode for metal-air cell. Despite the general features of a metal-air system, each element possesses distinctive properties such as the open circuit potential, operating potential and multiple plateaus in the discharge curve. As such, any variation in the metallic composition could be identified and reflected on its discharge curve. Fig. 3 shows the discharge profiles of Sn, Zn, and Sn-Zn coatings. The best profile is shown by zinc electrodeposits (curve B) since zinc is much more electronegative than tin (curve A). There is no particular trend as the zinc ions content was increased from 0.5 M to 2 M. However, when the zinc ions content was increased by ten folds (5 M, curve G), the discharge duration was extended markedly and becomes compatible to the pure zinc deposits. On the other hand, its discharge plateau (the flat region prior to the abrupt voltage drop) remained unchanged. These observations support our conjecture that the metal-air electrochemical system could be used to characterize metallic composition of alloys or composites. Therefore there seems a substantial incorporation of zinc elements into the Sn-Zn deposits from the 5 M bath (10:1) but not reflected distinctively in the X-ray diffractograms.
Fig. 2 SEM images of Sn and Zn by fixed deposition at 120 min and 5 mA, (a) 1 M SnCl₂ (b) 1 M ZnCl₂ (c) 0.5M ZnCl₂: 1M SnCl₂ (d) 1M ZnCl₂: 1M SnCl₂ (e) 1M ZnCl₂: 0.5M SnCl₂ (f) 2M ZnCl₂: 0.5M SnCl₂ and (g) 5M ZnCl₂: 0.5M SnCl₂.
Fig. 3 Discharge profiles of metal-air cells employing the Sn, Zn and Sn-Zn electrodeposits rated at 1 mA, (a) 1 M SnCl₂ (b) 1 M ZnCl₂ (c) 1 M ZnCl₂ : 1 M SnCl₂ (d) 1 M ZnCl₂ : 0.5 M SnCl₂ and (e) 0.5 M ZnCl₂ : 1 M SnCl₂. (f) 2 M ZnCl₂ : 0.5 M SnCl₂ and (g) 5 M ZnCl₂ : 0.5 M SnCl₂

4. SUMMARY

As anticipated, the electrodeposition of Sn-Zn coatings employing simple acidic electrolytic bath (SnCl₂/ZnCl₂) in the absence of complexing agent resulted in Sn-rich electrodeposits. Even an electrolytic bath with zinc to tin ionic mole ratio of ten folds could only produce electrodeposits with zinc content of 2.6 wt.%. We introduced a metal-air electrochemical system in characterizing the metallic element content of alloys or composites.

REFERENCES


Potentiostatic Polarization of Immersed Austenitic Stainless Steel in 3.5 wt.% NaCl at Potential Zero Charge (EPZC)

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ABSTRACT. The consumption of potentiostatic polarization current on austenitic type 304 stainless steel in 3.5 wt.% NaCl solution was studied at pH 4 to 7. The H2SO4 droplet was used to control the solution pH. To obtain the EPZC effect, the sample potential was scanned repeatedly just below Ecorr with magnitude between -3 to -0.3 mV vs Ecorr. The potential scanning was done at the lowest rate 0.01 mV/ min. Potentiostatic polarization shows a lower and steadily stable current consumption on lower potential scanning magnitudes as well as at solution pH that nearly to neutral (pH 7). As predicted, the higher current consumption was found at pH 4 and the highest scanning magnitude (-3 mV to Ecorr) was -9.30 × 10^-7 A/cm², whereas the lowest current consumption occurs at pH 7 at the lowest scanning magnitude (-0.3 mV to Ecorr) was just -0.03 × 10^-7 A/cm². The pH level displays a predictable finding at all potential scanning magnitude. The averages of current consumption were found to reduce with the increasing of studied pH as a manifestation of the passive film on stainless steel surface in the presence of Cl⁻ ions. The current spikes were clearly observed at lower pH (pH 4) resulted by the passivation and the breakdown of the passive film repeatedly. The current spikes gradually disappear as the increasing of the studied pH.

Keywords: Corrosion, Stainless steel, Potentiostatic, Polarization, Potential of zero charge;

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1. INTRODUCTION

Corrosion is one of the destructive attacks of the metals by electrochemical or chemical reaction with its environment. Cathodic protection is the most popular techniques of corrosion prevention. The selection of stainless steel materials is also one of the methods of corrosion prevention. The high corrosion resistance of stainless steel arises from the formation of complex chromium oxide (CrₓOᵧ) which is characterized as a passive and protective [1]. The existence of a CrₓOᵧ layer on the surface acts as a barrier of underneath metal interacting to the solution, hence blocking the ionic charge transfer in the electrode-electrolyte interface. Therefore, the corrosion or oxidation reaction of metal-solutions (M → M²⁺ + 2e⁻) does not occur. It is known that, the CrₓOᵧ layer has an ability to heal itself in a wide variety of environments. Nevertheless, under chloride (Cl⁻) containing environment, the passive behavior may be lost. For that reason, the root cause of failure for most of stainless steel based structure generally resulted by pitting corrosion due to interaction with the Cl⁻ ions [2].

Pitting corrosion is the most dangerous form of localized corrosion in aqueous environment. According to Qiao et al. [3], the presence of complex CrₓOᵧ layers on the stainless steel surface in chloride-containing
solutions results in an increase in charge carrier density when the applied potential was amplified. At large applied potential, the Cl\(^-\) has sufficient energy to penetrate the particular passive films. On the other hand, in the case of sulfuric acid (H\(_2\)SO\(_4\)) solution, sulfate (SO\(_4^{2-}\)) ion is extremely corrosive to stainless steel. The dissolution rate of stainless steel was high resulted in the increase of relative solubility of metal cations in pit solution as the increasing of Cl\(^-\) and SO\(_4^{2-}\) ratio occurred [4]. Wang et al. [5] was reported that the ratio of Cl\(^-\)/SO\(_4^{2-}\) = 0.75 produce highest propagation rate of pits in depth and width.

Potential of zero charge (E\(_{pzc}\)) is the potential of the electrodes for any metal surface which has no electrical charge when in contact with electrolyte. It was initially emphasized by Frumkin and Gorodetzkaya in 1928. Trasatti and Lust [6] stated that the E\(_{pzc}\) is the potential (against a reference electrode) which removes all electronic charges from metal surfaces. The absence of charges on electrode surface lead the loss attraction force of water bipolar and the charge orientation in Helmholtz plane does not occur. At E\(_{pzc}\) the negative (OH\(^-\)) as well as positive charge (H\(^+\)) not be able not to touch the metal surfaces resulted by the sort of electric resistance layer as depicted in Fig. 1.

![Fig. 1 Metal-solution interface (a) before E\(_{pzc}\) and (b) at E\(_{pzc}\) state [7]](image)

Although the corrosion behavior of austenitic stainless steel has been well documented, the systematic studies into the kinetics of the various complex process involved in the studied solutions is rarely reported. Therefore, it is worth to study from the fundamental and practical standpoint of acidity, chloride and sulfate ions. The aim of this paper is to probe the current density consumption on immersed austenitic stainless steel in 3.5 wt.% of sodium chloride (NaCl) in the presence of SO\(_4^{2-}\) at various potential scanning magnitudes.

2. MATERIALS AND METHODS

The raw material used in this study is 304 types austenitic stainless steel (304SS) which was supplied by STG Stainless Steel Sdn. Bhd. The specimens were cut from a rod to desired size. The working surface of specimens exposed to the test solution was 1.23 cm\(^2\) and all other unexposed areas were coated with epoxy-resin mixture. Both chemicals used in this investigation, namely NaCl and sulfuric acid (H\(_2\)SO\(_4\)) were reagent grade supplied by HmbG Chemicals. The test electrolyte was 3.5 wt.% NaCl with different pH (4, 5, 6 and 7) which controlled by addition of diluted H\(_2\)SO\(_4\). Electrochemical studies were carried out in a three-electrode single container cell (K0047, PAR). The potential of the working electrode was measured against saturated calomel electrode (SCE). In order to minimize the solution resistance between the steel and the reference electrode, the tip of SCE was placed as close as possible to the surface of the working electrode. The counter electrode was a 1 cm\(^2\) platinum sheet.

The electrochemical measurement was carried out by a potentiostatic polarization method using a computerized potentiostat (ACM, Gill AC). Potentiostatic polarization was performed at 4 different potential
scanning magnitudes ranging from -3 to -0.3 mV with respect to the corrosion potential (E_{corr}) at very slow scanning potential (0.01 mV/min). All experimental works were conducted at room temperature (25 °C).

3. RESULTS AND DISCUSSION

The curves of potentiostatic polarization for 10 hours of immersed 304SS in 3.5 wt.% NaCl solution at different pH (4, 5, 6 and 7) were shown in Fig. 2. Overall, the curves for all pH variations show a quite similar trend as predicted. It can be observed that the current density curves at all pH starts from higher and rapidly decreases just in a few minutes at all potential scanning magnitudes. This phenomenon describes the rapid nucleation and growth of the passive film compared to the material dissolution rate [8]. At all pH levels, within the applied potential ranging -0.3 to -3 mV against E_{corr}, there were relatively steady state current consumption as a function of time. This occurrence shows the longer the immersed period in the studied solution, the formation of the passive layer on the 304SS surface became steadily stable without film breakdown.

The curve at pH 4 exhibits the noise or instability of the current density against time (Fig. 2a). It exists, particularly at high potential scanning magnitudes. The current instability is associated with the current spikes. Some opinion of the previous researchers stated that these current spikes were either nucleation or metastable pitting events [9]. The formation of metastable pitting, in fact, does not significantly appeared because it occurs in an extremely small scale and in a short period it back to form a passive film [10]. The metastable pits only growth in the early stage of all stable pits before stabilizing. It microscopically difficult to access on the stainless steel surfaces and only can be detected by the high-resolution current sensor of the potentiostat at the slowest scanning rate.

Stainless steel has a large repassivation tendency for metastable pits and transformation to stable pits which can be achieved at higher potential [11]. Additionally, the activation and passivation alternation during pit metastable growth produces a current fluctuation or overlapped peaks as reported by Tian et al. [10]. However, in the case of potential of zero charge, the presence of the pitting can be ruled out. This is because, the potential scanning was carried out slightly below E_{corr}. Therefore, it is quite impossible that pitting can be formed at extremely low applied potential at potential just below E_{corr}. Here, the Cl\(^-\) and SO\(_4\)\(^{2-}\) ions ingress to the passive film by occupying anion vacancies. When the cation vacancies start accumulating at the metal interfaces, a breakdown of the films will start to take place as reported by Szklarska-Smialowska [12]. Theoretically, as the potential scanning magnitude increased, the Cl\(^-\) and SO\(_4\)\(^{2-}\) ions were forced to penetrate the film and causes the formation of complex metal chloride, MCl\(_x\) and metal sulfate, MSO\(_x\) at the metal-solution interface particularly intermingled in between the oxide atoms of metal surface as described by Galvele et al. [13].

The formation of MCl\(_x\) and MSO\(_x\) at a larger molar volume compared to the expansion of metal oxide will cause the abrupt mechanical breakdown of the 304SS passive film. It was easier to understand that the current spikes in the current studies were a fluctuation that generally denotes to the formation and breakdown of passive layers alternately on the 304SS surface. The formation of passive layers causes the consumption of negative currents to be lower while the breakdown of passive layer results in the excessive negative current consumed in order to eliminate the positive charges resulting from the reactions of exposed metal with the solutions. The instability or the current spikes were decreased when the experiments were performed on the solution having pH 5 (Fig. 2b) and the current begin to show the stability at pH 6 (Fig. 2c) and finally displays the steady state at pH 7 (Fig. 2d).
Fig. 2 Current-time transient for immersed 304SS in (a) pH 4, (b) pH 5, (c) pH 6 and (d) pH 7 in 3.5 wt.% NaCl solution (Note: 0 mV referred to $E_{corr}$)

Fig. 3 shows the effects of current consumption against potential scanning magnitudes. The overall current consumption is depicted occur in the steadily stable at pH 5, 6 and 7. However, at pH 4, it was observed the current consumption was increased (-9.30 x 10^{-7} A/cm²) especially on high potential scanning magnitude (-3 mV to $E_{corr}$). Nevertheless, the current consumption was found to decrease (-5.50 x 10^{-7} A/cm²) at the lower magnitude of the potential scanning (-0.3 mV to $E_{corr}$). NaCl solution at lower pH, contains high hydrogen ions ($H^+$). At high magnitude potential scanning, $H^+$ ions were aggressively to cause a breakdown of the passive film on the 304SS surface. The aggressiveness of $H^+$ ion was gradually decreased as lowering the magnitude of potential scanning until it was no longer active when the potential approaching $E_{corr}$. The high scanning potential magnitude, particularly -3 to $E_{corr}$ causes the movement of the anions and/or cations through the passive film become aggressive, which results in the high current consumption in order to repel the positive charges of metal due to the metal-solution reaction. The repellant of positive charges was done by the electrons or negative current supplied by the potentiostat. The damaged passive film causes the adsorption of aggressive anions (such as $Cl^-$ and $SO_4^{2-}$) of the passive film on 304SS surfaces. The presence of $Cl^-$ and $SO_4^{2-}$ anions together at lower pH of NaCl solution results the increase of the current density during
the potential scanning due to the high conductivity of these anions towards the double layer to destroy the passive layer as reported by Roy et al. [14] and Gadala et al. [15] were agreed.

Fig. 3 Average current density for immersed 304SS in (a) pH 4, (b) pH 5, (c) pH 6 and (d) pH 7 of 3.5 wt. % NaCl solution (0 mV referred to E_{corr})

4. SUMMARY

From the experimental studies, it can be concluded that the pH variations with the presence of Cl\textsuperscript{-} ions affect the current consumption in order to maintain the effect of zero charge potential on the metal-solution interface. If a passive layer exists, the current consumption to maintain the E_{pzc} was significantly small and steadily stable. On the contrary, the negative current consumption becomes larger and unstable at low pH. These phenomena occur due to the large metal exposed to the solution that requires a high electron to repel or eliminate the positive charges present on the metal surface as a result of the metal-solution reactions. With E_{pzc}, the current density consumption can be reduced and more economical.

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Cryorolling of Al 5083 Alloy: Microstructure and Mechanical Properties at Various Post Annealing Temperatures

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Abstract: The present work discusses the effect of post annealing at different temperatures on cryorolled Al 5083 alloy. A new method called cryorolling has been widely studied among the researchers due to its potential of obtaining ultrafine grained which contributed to the enhancement of mechanical properties of metal alloys. The samples were immersed in liquid nitrogen followed by cryorolling and then the samples were annealed at various temperatures (150 °C, 200 °C, 250 °C, 300 °C). The hardness and tensile values decreased with increasing post annealing temperatures. The microstructure also showed some coarsening of subgrains after post annealing.

Keywords: Cryorolling, Post annealing, Ultrafine grain, Microstructure, Dislocation;

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1. INTRODUCTION

Cryorolling has been considered as one of the potential route in producing ultrafine grained structure in metal working. It is basically a rolling process carried out in a cryogenic condition (liquid nitrogen temperature), hence giving the name cryorolling [1]. It has been receiving many attentions among researchers due to its likely formation of ultrafine grained structure and also improvement in mechanical properties. In cryorolling, the strain hardened metals is preserved as a result of the suppression of the dynamic recovery [2]. Rolling under cryogenic temperature has been widely used to improve the materials properties especially the strength and hardness. The grain refinement from cryorolling is what makes the method so famous for achieving ultrafine grained structure (UFG) structure in bulk metals. A comparatively lower plastic deformation is sufficient to produce strain for UFG formation in cryorolling than the existing SPD techniques.

The major problem with high strength UFG materials is the low ductility which might limit their usage in practical application. Annealing treatment after cryorolling process had been claimed to be an effective method to improve the ductility. The combination of strength and ductility would give a better range of the application for this alloy. Among Al alloy, the post annealing effect of Al-Cu based alloy has been studied in details and less work is focused on Al-Mg alloy [3]. Thus, Al-Mg based Al 5083 alloy was chosen for the investigation due to its special characteristics such as moderate strength, good corrosion resistance and high formability with reasonable price [4]. Moreover, the alloy also contains a small percentage of magnesium (Mg) which helps to influence the dislocation mechanism in the alloy. This work was carried out to focus on the effect of post annealing behavior on microstructure and mechanical properties of cryorolled Al 5083 alloy.
2. MATERIALS AND METHODS

The commercial Al 5083 alloy sheets of 15 mm × 50 mm size were used for the present investigation. The starting material was first characterized using X-ray fluorescence (XRF) to identify the elemental composition. In order to do so, the samples were grinded and polished for a mirror-like condition. The sample then underwent pre-heat treatment at annealing temperature of 300 °C. The 5 mm thick alloy then was dipped in liquid nitrogen for 1 hour to keep it at cryogenic condition and immediately rolled using a two high rolling mill with 50% reduction. The dipping interval for each rolling passes was set to be 5 min. The final sheet produced having 2.5 mm thickness. After rolling, the samples were post-annealed for 2 hours at four different temperatures; 150 °C, 200 °C, 250 °C, 300 °C. The sample then was characterized for microstructure, hardness value and tensile strength using optical microscope equipped with image analyser, Leco Microhardness Tester Machine LM248AT and Universal Instron 5567.

3. RESULTS AND DISCUSSION

3.1 Material selection. The XRF results showed the elemental composition of as-received Al alloy which consisted of 97.68% Al, 1.47% Mg and a few traces of Fe and Si of 0.37% and 0.17% respectively. The amount of aluminium and magnesium in the sample was comparable with the theoretical composition as shown in Table 1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Wt.%</th>
</tr>
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<tbody>
<tr>
<td>Al</td>
<td>97.68</td>
</tr>
<tr>
<td>Mg</td>
<td>1.47</td>
</tr>
<tr>
<td>Fe</td>
<td>0.37</td>
</tr>
<tr>
<td>Si</td>
<td>0.16</td>
</tr>
<tr>
<td>Cr</td>
<td>0.17</td>
</tr>
<tr>
<td>Mn</td>
<td>0.09</td>
</tr>
<tr>
<td>Cu</td>
<td>0.02</td>
</tr>
</tbody>
</table>

3.2 Hardness Test. The average hardness value of cryorolled sample with different annealing temperatures is shown in Fig. 1. The hardness value of cryorolled sample without post annealled was 128.6 HV. The hardness values continuously decreased with increasing annealing temperature as a result of stress relieved. This might be due to the rearrangement of dislocations including some loss of dislocations, as the recovery proceeded [5].

The hardness decreased slightly up to 200 °C and dropped rapidly to 87 HV at 250 °C. The rapid decrease showed that at 250 °C the sample underwent recrystallization process. Since the rate of recrystallization is mainly influenced by the amount of deformation, it shows that the samples received larger deformation which indicates that the softening rate during annealing would be closely related to the volume fraction of recrystallized grains [6,7].

In addition, the lower hardness value of the samples annealed at 200-250 °C indicates the presence of larger fraction recrystallized grains with minimum residual dislocations. These phenomena showed that the hardness in annealed sample was influenced by the fraction of recrystallized grains.
3.3 Tensile test. The average tensile strength of cryorolled samples with different post annealing temperatures is shown in Fig. 2. Tensile test was performed under controlled condition at the crosshead speed of 2.5 mm/ min. The tensile strength showed similar trend to that of hardness in Fig. 1, where it dropped uniformly as annealing temperature increases. At annealing 150 °C, the tensile strength decreased about 4% from 435 MPa to 417 MPa due to small change in the dislocation densities during post annealing. Large decrease of strength follows afterward at 200-250 °C could be attributed to the changes of dislocation substructures dimension during post annealing [6]. The significant change occurs at annealing temperatures of 200-250 °C where the uniform elongation shows a rapid increase from 19% to 33%. This indicates the rearrangement of the dislocations during recovery. The yield strength of the annealed samples also showed the same decreasing pattern with 4-6% reduction. Annealing above 250 °C has kept the tensile and yield strength value on the same level while the uniform elongation has no significant change. Cryorolled sample with subsequent annealing showed about 5-7% of improvement as compared to un-annealed sample. These results are quite consistent with Lin et al. [8] who have reported the similar trend in the tensile properties due to changes of dislocation densities during recovery process.
3.4 Microstructure. Fig. 3 shows the microstructural observation of cryorolled samples at different post annealing temperatures. The cryorolled sample showed severely elongated grain along the rolling direction. There were no observable changes in the microstructure below 200 °C (Fig. 5b and 5c) which would be expected to have little effect as boundary mobilities are very low [8]. As the annealing temperatures increases, the subgrain formation and rearrangement of dislocation takes place. Elongated grains recovered into subgrain boundaries as recovery proceed. The subgrain width simultaneously increases which resulted in the reduction of the subgrain aspect ratio [6].

Fig. 3 Elongation of cryorolled sample at different post annealing temperatures

Fig. 4 Microstructure of (a) cryorolled sample without annealing, (b-d) cryorolled samples at post annealing temperatures of 150 °C, 200 °C, 250 °C and 300 °C
4. SUMMARY

The effect of post annealing temperatures on cryorolling samples is indeed important as it gives changes to the mechanical properties and microstructure. The mechanical properties of the cryorolled Al 5083 alloy and subsequently annealed at temperatures 200-250 °C were mainly influenced by the volume fraction of recrystallized grains. It can be concluded that at this particular temperature the grains recrystallized best compared with the other temperatures. Post annealing also effected the microstructure by recovered the elongated grains into subgrain boundaries. Although the results of hardness and tensile strength after post annealing is slightly decreasing, it is important to choose the best alloy that can meet the standard of any applications of good strength and adequate toughness.

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The Effect of Milling Time on Properties of Magnesium-Based Composite Fabricated via Powder Metallurgy

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ABSTRACT. The aim of this study was to investigate the effect of milling time on the phase formation, microstructure, densification, microhardness and compressive strength of Mg-Zn/HA composite that possess the ability to be used as biodegradable bone fixation device. The mixture of Mg-6 wt.% Zn/8 wt.% HA composite was mechanically alloyed (MA) in a planetary ball mill. Milling time of the composite powders were varied from 2-8 hours. The effect of milling time on the phase formation and morphology of the composite was investigated by X-ray diffraction (XRD) measurement and optical microscope (OM). The density, microhardness and compressive behavior of the sintered composites were also determined by the principle of Archimedes, Vickers microhardness test and compression test, respectively. The results suggested that a homogenous supersaturated solid solution of Mg-Zn/HA was obtained after 2 hours of milling time and the structures undergo structural refinement after being milled for 8 hours. Significant enhancement of hardness and compressive strength were observed in the composite as the milling time was prolonged to 8 hours. The hardness and compressive strength of Mg-Zn/HA being milled for 2 hours were as low as 47.18 HV and 122.49 MPa, respectively, while the composite achieved the maximum hardness and compressive strength as high as 70.47 HV and 209.39 MPa after mposite achieved the best mechanical properties. being milled for 8 hours. The optimum milling time to fabricate the composite was 8 hours, since the co

Keywords: Mechanical alloying, Milling time, Mg-based composite, Biodegradable metals;

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1. INTRODUCTION

Magnesium and its alloys have recently attracted much attention as the new generation of biodegradable metallic bone fixation devices, owing to its mechanical compatibility which mimic the mechanical properties of the natural bone and its capability to be degraded and subsequently disappeared after the healing process is completed [1]. In term of mechanical compatibility, the Young’s modulus of Mg (about 45 GPa) is much closer to that of natural bones (5-23 GPa for compact bone) which is the most desirable to avoid the stress shielding problem resultant of the mismatch in elastic moduli. In addition, Mg possess good biocompatibility to be used as bone implant materials because it is an essential element to the human body and largely stored in bone tissues [2]. However, a critical problem faced by Mg and it alloys that restricting the commercialization is the rapid degradation rate in physiological environment. In this work, the magnesium-based composite was fabricated through the route of powder metallurgy, which employed the mechanical alloying as the powder processing technique of the powders composite. Mechanical alloying (MA) is a powder metallurgy processing technique for producing composite metal powders which it involves the repeated cold
welding, fracturing and re-welding of the powders particles, in a high energy ball mill [3]. Processing the powders composite using mechanical alloying technique gives the advantages of producing powders with controlled fine microstructure due to the repeated numerous impact between the ball and the powders, in addition with reduction of defects that normally generated from casting process such as porosity and inclusions [4]. Mechanical alloying parameters such as milling time, milling speed, and ball-to-powder ratio (BPR) are among the most dominant process variables that significantly alter the properties of resultant composite. The present study is focused on the effect of milling time to the phase analysis, microstructure, physical and mechanical properties of resultant composite.

2. MATERIALS AND METHODS

A mixture of elemental Mg, Zn and HA was weighed accordingly to weight fraction. The Mg-Zn/HA composite was composed of Mg-Zn/8 wt.% HA (weight of Mg:Zn is 94:6). The powders were then subjected to milling process with the speed of 220 rpm and milling time was varied to 2, 4, 6 and 8 hours using high energy planetary mill (Fritsch Pulverisette P-5). Argon gas was purged into the stainless steel jar to prevent oxidation or any possible contamination of the powders. The ball-to-powder ratio of 8.75:1 was kept constant for all milling process using stainless steel balls. The composite powders were then consolidated into 10 mm pellets using stainless steel mold under the compaction pressure of 400 MPa for 2 min. The pellets were sintered at 300 °C (soaking time: 1 hour) under controlled argon flow. The sintered pellets were then subjected into phase analysis using X-ray diffraction (XRD) and morphological study. Density of the sintered pellets was measured according to Archimedes principle, and the result was correlated with the theoretical density and was calculated as Eqs. 1-3.

Microhardness of the sample was evaluated using Vickers microhardness with indentation load of 300 gf and 10 s of dwell time, while compression test was carried out using universal testing machine (UTM) Instron 5982.

Theoretical Density = \( \rho \text{Mg} V_{\text{Mg}} + \rho \text{Zn} V_{\text{Zn}} + \rho \text{HA} V_{\text{HA}} \)  \\

\( V_{\text{Mg}} + V_{\text{Zn}} + V_{\text{HA}} = 1 \)  \\

Relative density (%TD) = \( \frac{\text{Sintered Density}}{\text{Theoretical Density}} \times 100\% \)

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the Mg-Zn/HA composite being milled for various milling times (2, 4, 6 and 8 hours) after being sintered for 1 hour under argon flow. As the milling was prolonged to 6 and 8 hours, the peaks were slightly shifted to the left and broadened, contributed by grain refinement as the milling induced more energy to reduce the size of the particles. 2 hours milling time was observed to sufficiently form the homogeneous Mg-Zn solid solution, by the elimination of any Zn peaks in the pattern. By prolonging the milling up to 8 hours, there was no observable phase changes in the composite, indicating only \( \alpha \)-Mg solid solution was detected in the patterns. The peaks indicating the presence of HA were not so obvious in the patterns, since the HA was having low intensity in XRD, due to the amorphous behavior of the ceramic particles.
Fig. 1 XRD patterns of Mg-Zn/HA being milled for (a) 2 hours, (b) 4 hours, (c) 6 hours and (d) 8 hours

Micrographs of the Mg-Zn/HA composite that was milled under various milling time from 2 to 8 hours was depicted in Fig. 2. Mg-Zn/HA composite that was milled for various milling time showed significant changes in the grain size formation and lamellae-like formation, as the composite milled for 8 hours experienced the most grain refinement and some numerous pores in the micrograph, as compared to 2 hours milled composite. Formation of the lamellae of Mg-Zn solid solution was more pronounced in the composite that was milled for 8 hours, due to much repeated fracturing and cold welding processes during the milling, which tend to form more homogeneous solid solution between Mg, Zn and HA particles. Extending the milling time up to 8 hours induced more impact between the milled particles, thus assist the refinement of microstructure along with the size of the pores.

The reduction in powder size at longer milling time increased the contact area between grains, leading to enhance the densification, sinter ability and its properties afterward. However, the microstructure of the composite was observed to have lots of small-sized pores after been milled for 8 hours, possibly due to elongated size of the ductile powders after being milled for such long milling time and experienced lots of impact. Elongated size of the composite powders caused the powders to be hard to compact, thus resulted in small and even distribution of pores.

Fig. 3 shows the plot of microhardness and relative density (%TD) of Mg-Zn/HA composite being milled for various milling time. As the milling time prolonged, the microhardness as well as the densification was dramatically increased, except for the composite milled for 8 hours, which less densified than that of 6 hours composite. Details on the values of sintered density, theoretical density and microhardness values were tabulated in Table 1. Decrement in densification of the particular composite is mainly contributed by the presence of small pores inside the microstructure, as portrayed in Fig. 2 (d). At 8 hours milling time, the powders were subjected to excessive impact which caused the powders to be extremely refined in microstructure, but also caused the elongated highly deformed powders to experience low compressibility in compaction. Even though the densification was slightly reduced, the microhardness exhibited higher value.
than those composites fabricated at shorter milling time (2, 4 and 6 hours). Higher microhardness value achieved by this particular composite was contributed by the strain hardening of powder, which longer milling time was accompanied by higher quantity of impact to the powder, and subsequently assist in higher solubility of Zn in the Mg lattice.

Fig. 2 Micrographs of Mg-Zn/HA composite fabricated by planetary mill for (a) 2 hours, (b) 4 hours, (c) 6 hours and (d) 8 hours

![Lamellae of Mg-Zn solid solution](image)

![Lamellae of Mg-Zn solid solution](image)

![Lamellae of Mg-Zn solid solution](image)

![Lamellae of Mg-Zn solid solution](image)

Fig. 3 Plot of microhardness and densification of Mg-Zn/HA composite being milled under various milling time

Table 1 Data tabulation on density and microhardness of the composite
<table>
<thead>
<tr>
<th>Milling time (hours)</th>
<th>Sintered density (g/cm$^3$)</th>
<th>Theoretical density (g/cm$^3$)</th>
<th>Relative density (%TD)</th>
<th>Microhardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.7987</td>
<td>1.8863</td>
<td>95.59</td>
<td>47.18</td>
</tr>
<tr>
<td>4</td>
<td>1.8106</td>
<td>1.8863</td>
<td>96.22</td>
<td>56.83</td>
</tr>
<tr>
<td>6</td>
<td>1.8136</td>
<td>1.8863</td>
<td>96.38</td>
<td>64.07</td>
</tr>
<tr>
<td>8</td>
<td>1.8040</td>
<td>1.8863</td>
<td>95.87</td>
<td>70.47</td>
</tr>
</tbody>
</table>

Fig. 4 shows the ultimate compressive strength of Mg-Zn/HA composite that was milled under various milling time. The compressive strength was noticeably increased as the milling time was prolonged to 8 hours. This increment was mainly contributed by the refinement of the particle size. Generally, the strength of composite is highly dependent on the effectiveness of stress transfer between the matrix and the reinforcement [5]. Finer particle size attributed by longer milling time increased the surface contact area between the particles, thus increased the efficiency of stress transfer between the matrix of Mg-Zn alloy and the reinforcement of HA particles.

**SUMMARY**

In this work, Mg-Zn/HA composite was prepared through powder metallurgy route, with the mechanical alloying (MA) as the powder processing technique. With variation in milling time, XRD diffraction pattern shows only α-Mg solid solution was formed in the composite that was mechanically milled at 2 hours and prolonged milling time. Composite prepared at 8 hours milling time shows the best microhardness (70.47 HV) and compressive strength (209.39 MPa), due to refinement of the powders at the particular milling time, but exhibited a considerable slightly lower value in densification (95.87%). Extending the milling time of the composite might result in further enhancement in the microhardness and compressive strength as the microstructure experienced the extent in grain refinement. However, reaching to some extent, the mechanical properties might stay constant as the milling time is prolonged, indicating the maximum refinement can be achieved for the particular composite.

**ACKNOWLEDGEMENT**

The authors would like to thank to Universiti Sains Malaysia for FRGS Grant No. 203/PBAHAN/6071304 and financial scholarship from Ministry of Higher Education.
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The Effect of Reinforcement Amount and Sintering Temperature on Mg Matrix Composite Fabricated by Powder Metallurgy

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ABSTRACT. A metal matrix composite (MMC) is known as high tech composites and useful and magnesium (Mg) is among the suitable metal for producing composites. Combining Mg, Zinc (Zn) and Alumina (Al₂O₃) powders will yield a composite with improved corrosive resistance, mechanical properties and abrasive wear behavior. So, the aim of this research is to study the effect of reinforcement (Al₂O₃) and sintering temperature (300 °C and 550 °C) on Mg-Zn alloy matrix composite fabricated by powder metallurgy. The powder mixture of pure Mg, Mg-Zn alloy and Mg-Zn/15% Al₂O₃ composite was milled separately in a planetary mill under gas argon atmosphere using a stainless steel container and balls. Milling process was carried out at 220 rpm for 2 hours and 3% of n-heptane solution was added prior to milling process to avoid the excessive cold welding of the powder. The powder was compacted under 400MPa and sintered with different sintering temperature with 300 °C and 550 °C in a tube furnace for 1 hour under the flow of argon. The density of the sintered pellets was then determined by Archimedes principle. Mechanical properties of the sintered pellets were characterized by microhardness and compressive test. The results shows that the density, hardness and compressive strength of Mg-Zn/15% Al₂O₃ composite was higher compared to pure Mg and Mg-Zn alloy at temperature 300 °C compared to 550 °C.

Keywords: Metal matrix composites, Zinc, Alumina, Powder metallurgy;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

In order to limit the fuel consumption and carbon dioxide emission, the structural weight of the vehicles need to be reduced [1]. Mg as the lightest metallic structural material, low density, excellent damping capacity and good machinability [2,3] becomes potential candidates for a variety in engineering application. However, the limitations of Mg which include poor elastic modulus and high temperature strength properties [4] restrict its utilization in critical engineering application [3-6]. In order to minimize these limitations, Mg metal matrix being developed with reinforced Mg with Zn and Al₂O₃. In the past, to manufacture MMC, ceramic reinforcing phases such as oxides (Al₂O₃, SiO₂), carbides (SiC, B₄C) and nitrides (Si₃N₄) were used in order to optimize their structure and properties [6].

Powder metallurgy (PM) is one of the best methods in preparation of MMC [7]. The main advantages of PM are relatively low processing temperature, provide great freedom degree in tailoring the microstructure such as volume fraction and morphology, where better distribution of the reinforcement is possible in PM compacts [8]. It also approved by experiment and theoretical studies. For composite fabricated by the powder metallurgy method, it is possible when the matrix to reinforcement particle size ratio is close to unity [9]. With increasing metal working characteristics, particulate reinforced MMCs improved both mechanical and physical properties. Besides that, powder metallurgy processing is one of the methods for fabricating these
materials [10]. MMCs are important because of their high Young modulus, high abrasive properties and high ratio of strength and weight [11]. The present study aims to investigate the effect of Zn and Al₂O₃ content on Mg and to study the effect of sintering temperature on the density, relative density, hardness and compressive strength of Mg.

2. MATERIALS AND METHODS

A mixture of elemental Mg powder (99.0% pure), Zn powder (99.0% pure) and Al₂O₃ (99.0% pure) corresponding to Mg-Zn was mechanically milled. Proper proportional of the powders were placed in a planetary ball mill for 2 hours and 220 rpm using high-energy Fritsch Pulversiste P-5 planetary mill under argon atmosphere. 3% of n-heptane solution was used as a process control agent to prevent excessive cold welding of the elemental alloy powders. A number of 20 mm diameter stainless steel balls were loaded together with all the powders in a 250 ml stainless steel vial and the vial was sealed with rubber O-ring. Ball to powder ratio was 1:8.75 was kept constant during the milling process. Conventional powder metallurgy (uniaxial pressing) was employed to produce the samples. Green compacts were cold pressed under 400 MPa and were sintered in argon at 300 °C and 550 °C for 1 hour. Density measurements were done using pycnometer density equipment according to Archimedes's principles. Vickers microhardness test was carried out by applying an indentation load of 300 gf for 10 s. Compression test were done using machine instron 5982 with diameter 10 mm and length of 10 mm.

3. RESULTS AND DISCUSSION

Fig. 1 portrayed the sintered density of the pure Mg, Mg-Zn alloy and Mg-Zn/15% Al₂O₃ composite that was sintered with different sintering temperature of 300 °C and 550 °C. The sintered density was found to increase as two particles Zn and Al₂O₃ were added into Mg. The sintered density for Mg-Zn/15% Al₂O₃ composites increased as compared to pure Mg and Mg-Zn alloy. The sintering temperature at 300 °C shows higher sintered density as compared to 550 °C in pure Mg, Mg-Zn alloy and Mg-Zn/15% Al₂O₃ composites. The addition of 15% Al₂O₃ increased the sintered density as compared to pure Mg and Mg-Zn alloy. This is due to the fact that the density of alumina is higher than that of magnesium. However this phenomenon is not comparative to the amount of alumina since alumina additions leads to the formation of pores. The density of Al₂O₃ is 3.97 g/cm³ while the density of pure Mg is 1.736 g/cm³. So, the sintered density with addition of alumina gave affect to the result of sintered density compared to pure Mg and Mg-Zn alloy.

Fig. 2 displayed the relative density of pure Mg, Mg-Zn alloy and Mg-Zn/15% Al₂O₃ composite. Relative density of Mg-Zn/15% Al₂O₃ composite showed lowered compared to pure Mg and Mg-Zn alloy. Five readings were taken for each run and the average density was reported. The relative density (pr) was calculated by;

\[\rho_r = \frac{\rho_{ac}}{\rho_{th}} \times 100\%\]  \hspace{1cm} (1)

\[\rho_{th} = \rho_{Mg} V_{Mg} + \rho_{Zn} V_{Zn} + \rho_{HA} V_{HA} + \rho_{Al2O3} V_{Al2O3}\]  \hspace{1cm} (2)

\[V_{Mg} + V_{Zn} + V_{HA} + V_{Al2O3} = 1\]  \hspace{1cm} (3)

Where \(\rho_r\), \(\rho_{ac}\) and \(\rho_{th}\) represent the relative density, actual density and theoretical density of the samples, respectively; \(\rho_{Mg} = 1.74\) g/cm³, \(\rho_{Zn} = 7.14\) g/cm³, \(\rho_{HA} = 3.16\) g/cm³ and \(\rho_{Al2O3} = 3.97\) g/cm³. The addition of alumina reduced the relative density in 300 °C compare to 550 °C. This may be due to the reduction in compressibility of the powder during sintering process. Besides that, this may be due to inhibiting effect of alumina in the rearrangement of the particles during sintering process. Furthermore, the melting points of the matrix and the reinforcement also give effects to the relative density. The melting point of alumina is 2072 °C and at higher sintering temperature 550 °C, the activation energy required for sintering mechanism to proceed neck growth and gave result to the surface and volume diffusion.
Fig. 1 Sintered density of pure Mg, Mg-Zn alloy and Mg-Zn/15% Al$_2$O$_3$ composite

![Density Chart](image)

Fig. 2 Relative density of pure Mg, Mg-Zn alloy and Mg-Zn/15% Al$_2$O$_3$ composite.

The microhardness results of pure Mg, Mg-Zn alloy and Mg-Zn/15% Al$_2$O$_3$ composites are shown in Fig. 3. It can be noticed that adding of 15% Al$_2$O$_3$ particles into alloy matrix increased the hardness value. This can be attributed to the presence of harder reinforcements which offer high constraints during indentation. The microhardness of Mg-Zn/15% Al$_2$O$_3$ composites revealed higher hardness values as compared to pure Mg and
Mg-Zn alloys at different sintering temperature of 300 °C and 550 °C. An Al₂O₃ particle acts as a barrier to the rearrangement, deformation and diffusion of the particles [12].

The harder Al₂O₃ particles provide sufficient strength to the soft matrices and hence the microhardness values increases due to the dispersion strengthening effect. With gradual increases on Al₂O₃ content the microhardness values increases as a result of uniform dispersion of the reinforcement within the matrices. The peak value of hardness was achieved with 15 wt.% Al₂O₃ compare to pure Mg and Mg-Zn alloy. This mainly due to uniform dispersion of Al₂O₃ and acts as hard particles that hinders the mobility of the defects (dislocations) in the matrix.

<table>
<thead>
<tr>
<th>Powder Content (wt.%)</th>
<th>Pure Mg</th>
<th>Mg-Zn</th>
<th>Mg-Zn/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>300°C</td>
<td>50</td>
<td>60</td>
<td>70</td>
</tr>
<tr>
<td>550°C</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
</tbody>
</table>

**Fig.3** Microhardness of pure Mg, Mg-Zn alloy and Mg-Zn/Al₂O₃ composite

The results of compressive strength have been presented in Fig. 4. Ultimate compressive strength of the Mg-Zn/15% Al₂O₃ composite appeared to have an increment in the compressive strength at sintering temperature 300 °C compare to 550 °C. It shows that sintering temperature gave effect to the result of compressive strength. The addition of Al₂O₃ to Mg-Zn alloy increased the strength by a dispersion hardening mechanism. Al₂O₃ particles being hard and brittle lead to dispersion hardening of matrix. These particles act as second phase in the matrix and resist the movement of dislocations and hence harden the composites [13].
4. SUMMARY

In this study, pure Mg, Mg-Zn alloy and Mg-Zn/15% Al₂O₃ composites were synthesized through powder metallurgy method. Superior density, relative density, hardness and compressive strength were achieved in the case of Mg-Zn/15% Al₂O₃ at sintering temperature of 300 °C as compared to pure Mg and Mg-Zn alloys in 550 °C.

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UV Performances and Corrosion Behavior of Nanocoating on Carbon Steel

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**ABSTRACT.** Corrosion is gradual degradation process of metal through chemical reaction. Mostly happen by electrochemical and reaction with the surrounding environment. It affects material properties. Coating industry continuously working on the growing demand on modern coating and strives to improve their products especially to meet requirement in petrochemical industries. This paper reviews ZnO\(-\)SiO\(_2\) as formulation as the agent for new and improved corrosion and UV resistant coating industry.

**Keywords:** Nanocoating, ZnO\(-\)SiO\(_2\), UV, Epoxy, Corrosion, Carbon steel;

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1. **INTRODUCTION**

Corrosion is always the major reason of energy and material loss. It was reported that 1/5 of energy globally and average 4.2% of gross national product (GNP) is lost every year due to corrosion behavior and the economic impact of corrosion is estimated to be greater than $1 billion/year in the United States alone [1-6]. According to Cabrera-Sierra et al. [2] plants have suffered from continuous economic loss and human casualties because of metallic materials corrosion. Over the past years nanotechnology has become more and more important in the development of coatings. Nanocoatings offer great potential for various applications due to their superior characteristics that are not typically found in conventional coatings. Applying coating nanomaterial on the steel surfaces can prevent corrosion. According to the research study by Thomas [1], the nanocoatings market is envisaged to grow over the next 5 to 10 years across all market segments. This is attributed to growing need for better facilities and advances in nanocoating technology. This industry is segmented by type of future markets that includes anti-bacterial, anti-fouling, anti-fingerprint, easy to maintain and self-cleaning nano-coatings. In addition, the anti-corrosive nanocoatings market is expected to grow on the strength of demand from oil and gas industries for protection of pipeline surfaces [10-12]. Behavior of the coating was studied by exposing the coated test panels to UV Test according to ASTM D 4587. The purpose of testing was to observe how a material would react to long-term sunlight exposure. Salt spray test based on ASTM B117 was used to evaluate the performance of the nanocoating samples.
2. MATERIALS AND METHODS

In UV testing, the apparatus located in an area maintained between 18-27°C. The ambient temperature was measured at a maximum distance of 150 mm from the plane door of the apparatus. The apparatus was 300 mm from walls or other apparatus. The purpose of testing was to observe how a material would react to long-term sunlight exposure. At the every 24 hours exposure the samples was observed. The salt spray test was an accelerated corrosion test by samples exposed to salt condition. The salt solution employed was prepared with NaCl analytical grade reagent and distilled water. All the samples were placed in the salt spray chamber for 24 hours until 2000 hours. Then all the samples were cleaned in running water not warmer than 38°C to remove salt deposits from the surface and then immediately dried with compressed air at 60°C. Photographs were taken before and subsequent to exposure to document the surface conditions.

The samples were exposed to a salt fog generated from a 3.5% sodium chloride solution with a pH between 6.5 and 7.2 in salt spray testing. The test condition as showed in Table 1. Table 2 shows MSDS of UV epoxy resin.

<table>
<thead>
<tr>
<th>Test</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durometer Hardness 2hr@60°C</td>
<td>82±3</td>
</tr>
<tr>
<td>Tensile Strength, psi</td>
<td>7700</td>
</tr>
<tr>
<td>Flexural Strength, psi</td>
<td>12200</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>400848</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

Fig. 1 shows the surface micrographs of UV exposed samples after 24 hours, where the source of irradiation used was UV lamp that emits wavelength of 368 nm as stated in Table 1. At the very early stage of exposure (24-1560 hours), the neat sample and in corporation nanoparticles into coating was good. Instead no appearance of surface defects was observed. After 2000 hours of exposure, all samples still in good condition since no any pinholes were observed on sample. Table 2 showed MSDS of UV epoxy resin used. Table 3 showed that, the thickness before and after exposure to UV was not fully changed especially for 3ZnO+2SiO₂ of hybrid sample. The reason because, the type of epoxy resin used was purposely for preventing UV exposure. The type of epoxy resin used was epoxy UV clear coat. It has been formulated to improve UV resistance in order to reduce yellowing and surface degradation from UV exposure. The degradation of coating due to photochemical interaction was preventing. There was also no presence of surface heterogeneity seen clearly indicates that the degradation of coating due to long term exposure to UV radiation was prevent (Fig. 2a-i).

The improvement of UV resistance of the modified coating can be attributed to the fact that, nano-ZnO
has a wide band gap (3.37 eV) and large excitation binding energy of 60 meV, therefore it can absorb light that matches or exceeds their band gap energy and which lies in the UV range of the solar spectrum [1-2]. Thus, a well-dispersed nano-ZnO particle attenuates UV radiations and protects the polymer matrix from degradation. It appears that the addition of the nanoparticles lowers the degradation rate of the coating. The degradation time of neat resin and coating with the addition of nanoparticles remains unaffected until 2000 hours. This may be attributed to the fact that, at nanoscale the particles themselves effectively absorb rather than scatter the UV radiation providing UV protection to the polymer [3-4]. It also proved that small surface area per unit mass and a volume of nanoparticles increases the effectiveness of blocking UV radiation and prevents photo degradation of polymer matrix. Good UV blocking property to the coating system achieved since photochemical activity was low. Thus, prevent interacting with UV radiation as shown in Fig. 2

Fig. 1 UV images of nanocoatings in 24 hours. (a) 2wt.% ZnO coating, (b) 3wt.% ZnO coating, (c) 2wt.% SiO\textsubscript{2} coating, (d) 3wt.% SiO\textsubscript{2} coating, (e) 1wt.% ZnO+4wt.% SiO\textsubscript{2}, (f) 2wt.% ZnO+3wt.% SiO\textsubscript{2}, (g) 3wt.% ZnO+2wt.% SiO\textsubscript{2}, (h) 4wt.% ZnO+1wt.% SiO\textsubscript{2}, and (i) Plain epoxy
To improve the corrosion performance of the coating, nanoparticles were added to the epoxy. Nanoparticles having ability to penetrate and adhere in coating on the metal surface and work under the gaps and micro cavities providing a molecular layer of corrosion protection. Based on Fig. 5, sample containing nanoparticles was greatly improved the properties of metal. The effectiveness of nanoparticles in preventing corrosion was clearly demonstrated. The amount of addition nanoparticles in epoxy coating was important. It was approved that the thickness of nanocoating samples still remains almost same for all samples as shown in Fig. 4.

The addition of nanoparticles increased the corrosion resistance of the coating. The level of corrosion area was reduced when compared with samples without any nanoparticles. It was because by the ability of nanoparticles to migrate underneath the micro gaps and voids that exist between the nanoparticles and metal substrate as explained in proposed mechanism before. Nanoparticles works as protective network layer in epoxy coating as clearly shown in Fig. 5. Fig. 6 shows XRD of nanocoating.
Table 3 Thickness of nanocoating on mild steel with different wt.%

<table>
<thead>
<tr>
<th>Different loading (wt.%)</th>
<th>Thickness (milimeter)</th>
<th>0 hour</th>
<th>1560 hours</th>
<th>1680 hours</th>
<th>1848 hours</th>
<th>2000 hours</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td></td>
<td>5.01</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>0.01</td>
</tr>
<tr>
<td>2ZnO(single)</td>
<td></td>
<td>5.02</td>
<td>5.02</td>
<td>5.01</td>
<td>5.01</td>
<td>5.01</td>
<td>0.01</td>
</tr>
<tr>
<td>3ZnO(single)</td>
<td></td>
<td>5.03</td>
<td>5.03</td>
<td>5.02</td>
<td>5.01</td>
<td>5.01</td>
<td>0.02</td>
</tr>
<tr>
<td>2SiO₂(single)</td>
<td></td>
<td>5.03</td>
<td>5.03</td>
<td>5.02</td>
<td>5.01</td>
<td>5.01</td>
<td>0.02</td>
</tr>
<tr>
<td>3SiO₂(single)</td>
<td></td>
<td>5.03</td>
<td>5.03</td>
<td>5.02</td>
<td>5.01</td>
<td>5.01</td>
<td>0.02</td>
</tr>
<tr>
<td>1ZnO+4SiO₂(hybrid)</td>
<td></td>
<td>5.02</td>
<td>5.02</td>
<td>5.02</td>
<td>5.01</td>
<td>5.01</td>
<td>0.01</td>
</tr>
<tr>
<td>2ZnO+3SiO₂(hybrid)</td>
<td></td>
<td>5.02</td>
<td>5.02</td>
<td>5.02</td>
<td>5.01</td>
<td>5.01</td>
<td>0.01</td>
</tr>
<tr>
<td>3ZnO+2SiO₂(hybrid)</td>
<td></td>
<td>5.02</td>
<td>5.02</td>
<td>5.02</td>
<td>5.02</td>
<td>5.02</td>
<td>0.00</td>
</tr>
<tr>
<td>4ZnO+1SiO₂(hybrid)</td>
<td></td>
<td>5.02</td>
<td>5.02</td>
<td>5.02</td>
<td>5.01</td>
<td>5.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Additionally, when sample failed to overcome UV radiation, it is because crosslinking and simultaneous chain reduction caused embrittlement and a weakening of internal resistance. Degradation of ether groups in epoxy resins takes place via the intermediate stage of peroxides, which then suffer cleavage in the molecular chains on account of ultraviolet light. Consequently, by increasing temperature it is possible to detect not only the expected accelerations of esterification and oxidation reactions but also direct cleavage due to depolymerization and statistically distributed opening of the base chain. Side chains are cleaved homolytically by the ultraviolet light of the sun. Various radicals occur on account of the opening of C-C and C-O bonds, which stabilize owing to hydrogen abstraction or combination with other radicals. The connecting of new bonds involves crosslinking. As a result, embrittlement of the coating happened as showed in Fig. 3 below.

![Fig.3 Crosslinking of epoxy resin in UV radiation](image-url)
Fig. 4 Thickness of nanocoating after UV test

Fig. 5 Images of nanocoatings in salt spray after 1080 hours exposure. (a) 1wt.% ZnO+4wt.% SiO₂, (f) 2wt.% ZnO+3wt.% SiO₂, (g) 3wt.% ZnO+2wt.% SiO₂, (h) 4wt.% ZnO+1wt.% SiO₂
4. SUMMARY

As conclusion, nanoparticles significantly improve the long-term corrosion protection of epoxy coating that was applied directly to the metal. The additional network layer of nanoparticles provides multi-layer defense of corrosion resistance. Salt spray test revealed that nanoparticles giving higher level of service life of metal coating.

REFERENCES

Growth Behavior of TiO$_2$ Nanotube Arrays in Different Electrolyte pH

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**ABSTRACT.** TiO$_2$ nanotube arrays grow on Ti metal would be the best candidate as an implant material. The excellent biocompatibility appears to depend on the presence of a passive oxide layer (TiO$_2$ layer) formed on the surface. In this study, the effect of electrolyte pH (pH 1 up to pH 9) on length of the TiO$_2$ nanotubes arrays was investigated. The nanotubes length increased significantly with the increase of the electrolyte pH value and the longest TiO$_2$ nanotubes obtain at pH 8. Lower pH value at the pore tip and higher pH value at pore mouth are necessary to obtain desired TiO$_2$ nanotubes length. Therefore, it is significantly controlled the electrolyte pH to gain desired TiO$_2$ nanotubes.

**Keywords:** Anodization, Biomaterials, Electrolyte, Nanotopography, pH, TiO$_2$ nanotubes arrays;

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1. INTRODUCTION

Ti implants are commonly used in orthopedics and dentistry for their favorable biocompatibility and corrosion resistance [1]. Upon exposed to the atmosphere, the Ti metal spontaneously forms a thin, dense and protective oxide layer (approximately 10 nm thick) on its surface, which act like a ceramic with superior biocompatibility. When Ti implant is inserted into human body, the surrounding tissue directly contact the TiO$_2$ layer on the implant surface [2]. In the field of biomaterials and implant technology, nanometric scale of surface topography, roughness and chemical surface modification becoming critical factor for cell survival. The excellent biocompatibility appears to depend on the presence of a passive oxide layer (TiO$_2$ layer) formed on the surface [3]. In an effort to enhance the cell implant material interaction and increase lifetime, bioactive ceramic based coatings have been applied to Ti implants [4].

Geometry and surface topography are very important parameter for the short and long term success of implant materials [5]. Various nanotopography modifications have been proposed to enhance the cell responses to the Ti-based implant. For example, Ti with micron size rough surface features and higher degree of nanometer surface features were develop by Raimondo et al. [6]. Surface topography such as TiO$_2$ nanotubes have been shown to alter cell behaviors such as adhesion, orientation, differentiation and migration significantly. It is due to nanotubes topography that can provide more abundant topographical cues
similar to dimensional scale of bone collagen fibrils and elasticity resembling bones [7]. However, the dimensionality (diameter and length) of TiO\textsubscript{2} nanotubes on cell interaction is not well understood.

Raja et al. [8] reported that pH of an electrolyte can affect the formation of nano-porous structure significantly. At lower pH, the length of the TiO\textsubscript{2} nanotubes was limited by higher dissolution rate. On the other hand, increasing the pH value will decrease the chemical dissolution rate and electrochemical oxide formation rate. This will affect the TiO\textsubscript{2} nanotubes length to a certain extent. In order to elucidate the influence of electrolyte pH on the pore morphology, a set of experiments was conducted with different electrolyte pH and discussed in this paper.

2. MATERIALS AND METHODS

High purity titanium foils (99.6% purity) with thickness of 0.1 mm from STREM Chemicals was used in this study. Anodization was done in a standard two-electrode bath with titanium as the working electrode and platinum as the counter electrode. Prior to anodization, Ti foils were degreased by sonicating in acetone for 15 min followed by rinsing in deionised water. After drying, the foil was exposed in glycerol with 0.5 wt.% NH\textsubscript{4}F. Different pH of the bath was used in each experiment (pH 1-9) by adding H\textsubscript{2}SO\textsubscript{4} (acidic) and NaOH (alkaline). The anodic potential was carried at 20 V with sweep rate of 1 V/sec in room temperature for an hour. The bath was kept at room temperature. After the anodization was completed, the titanium foil was annealed at 400 °C in an air atmosphere furnace for 2 hours. It is anticipated that the formation of anatase phase will lead to enhanced cell growth. The morphologies of the anodized titanium were characterized using a field emission scanning electron microscope (FESEM Supra 35VP ZEISS) operating at working distances down to 1 mm.

3. RESULTS AND DISCUSSIONS

The different pH levels of the electrolyte lead to different current density profile and TiO\textsubscript{2} surface structure. Fig. 1 shows the current density as a function of the anodization time at pH 1, 6 and 8. The patterns of the curves (Fig. 1) indicating mechanism of TiO\textsubscript{2} nanotubes formation. At pH 1, within 9 min of voltage supply, the current density dropped to 42.7 mA/cm\textsuperscript{2}. Fig. 1(i) shows the FESEM micrograph, which was obtained within this range of time upon voltage supply. It confirms that the drastic drop in current density is attributable to the Ti foil oxidation to form TiO\textsubscript{2} barrier layer for pH 1 sample. However, at 30 min, the current density rises to reach a maximum value of 65.3 mA/cm\textsuperscript{2}. It was due to chemical dissolution reaction of existing small pits have caused pits enlargement that was induced by F\textsuperscript{-} ions from the electrolyte as shown in Fig.1(ii). Beyond this point, current density drops slowly and became constant with increasing the anodizing time. This observation indicated the growth of nanotube structure. However, very small periodic fluctuation of current density was observed during this stage. This may be due to the competition between the growth and oxide layer dissolution to produce nanotubes. A self-alligned TiO\textsubscript{2} nanotubes with inner diameter of 64 nm and a length of 520 nm was formed after 1 hour of anodization (Fig. 1(iii)).

A relatively constant equilibrium state was maintained after current density drops slowly with increasing the anodizing time. This observation indicated the nanotube structure growth. However, very small periodic fluctuation of current density was observed during this stage. This may be due to the competition between the growth and oxide layer dissolution to produce nanotubes.

On the other hand, the drops in current density were less at pH 6 as compare with pH 1. The current density dropped specifically to 81.7 mA/cm\textsuperscript{2}. This indicated that the oxide layer formed in pH 6 (Fig. 1(iv)) is less dense as compared to that in pH 1. Less dense oxide layer mean low ohmic resistance, thus increase current density. The current density started to increase to a certain maximum (96.3 mA/cm\textsuperscript{2}) and could be ascribed to random pits drilling on the oxidized layer of Ti. This event was shown in Fig.1(v). After anodization of Ti for an hour at pH 6, the inner diameter and length of TiO\textsubscript{2} nanotubes produced was 47 nm.
(Fig. 1(vi)) and 720 nm, respectively. The inner diameter was smaller and longer nanotubes were formed due to chemical dissolution at the pore mouth was slower than drilling process by F- ions at pore bottom [9]. Fig.1 shows the current density in basic (pH 8) electrolytes during the anodization process. The current density decreases gradually with 15 min during the self-organization process to 85.9 mA/cm². The FESEM micrograph in Figs. 1(vi) and (vii) show the microstructure within 15 min anodization. High current density periodic fluctuation was observed between 85.9 mA/cm² and 104.0 mA/cm². This indicated that both the electrochemical etching rate at the tube bottom and chemical dissolution is higher to form stable nanotubes structure (Fig.1(ix)). In higher pH value (pH 8), the hydrolysis ability of the electrolyte was increased as compared to acidic electrolyte.

**Fig. 1** Lower pH value at the pore tip and higher pH value at pore mouth are necessary to obtain desired TiO₂ nanotubes length

Lower pH value at the pore tip and higher pH value at pore mouth are necessary to obtain desired TiO₂ nanotubes length. Kang et al. [10] reported that longer TiO₂ nanotubes could be achieved by controlling the TiO₂ dissolution rate, which is related to the pH value of the electrolyte. FESEM characterization was performed after an hour of Ti anodization in electrolyte with difference pH. As shown in Fig. 2, TiO₂ nanotubes can be grown in electrolyte within pH 1 to pH 9. The entire samples show formation of well-ordered TiO₂ nanotubes regardless to pH value.

Overall samples are free from debris and the surface was rough. An existence of uneven surface morphology caused uneven H⁺ distribution in the electrolyte or high H⁺ concentration fluctuation due to the relatively low ion diffusion [11]. Local acidification fluctuation had been considerably restrained by decreasing the original H⁺ concentration in the electrolyte. These results confirm that oxide dissolution rate is pH dependence. Lower pH value can accelerate TiO₂ dissolution.
However, it was found that the diameter and length of TiO$_2$ nanotubes changed with pH variation. The average inner diameter of the nanotubes produced in glycerol solution with initial pH value (pH 6) was ~47 nm. However, when anodized in acidic solution (pH 1-2), the inner diameter increase to ~59-64 nm. It is due to the high chemical dissolution rate of the anodized TiO$_2$ layer in the enhanced acidic condition. It also been noted that the inner diameter did not significantly change with increasing pH value (pH 7-9).

**Fig. 2** Microstructural topography at different electrolyte pH (a) pH 1, (b) pH 2, (c) pH 3, (d) pH 4, (e) pH 5, (f) pH 6, (g) pH 7, (h) pH 8 and (i) pH 9
Fig. 3 shows correlation of TiO$_2$ nanotubes length with regards of pH value. The nanotubes length increased significantly with the increase of the electrolyte pH value. In acidic electrolytes (pH 1), the TiO$_2$ layer was thinner compared to TiO$_2$ layer in neutral electrolyte (pH 6). The shortest TiO$_2$ nanotubes were achieved because chemical dissolution at the pore mouth was faster than drilling process by F$^-$ ions at pore bottom. As the low pH value induces a high chemical dissolution rate, the as-anodized nanotube tip is dissolved away gradually. This phenomenon prevents the TiO$_2$ nanotubes to grow longer.

![Graph showing correlation of TiO$_2$ nanotubes length with electrolyte pH](image)

**Fig. 3** Correlation of TiO$_2$ nanotubes length with regards of pH value

A relatively longer tube length of 1.98 μm could be obtained when the Ti foil was subjected to anodize in pH 8 electrolyte. By increasing pH of the electrolytes, chemical dissolution of TiO$_2$ was reducing. However, when increasing pH value to 9, the TiO$_2$ nanotubes became shorter. It is believed that with increasing pH, chemical dissolution rate was slow resulting slower growth kinetic for TiO$_2$ nanotubes formation. This process can also be expressed as electrochemical oxidation (Eq. 1) and chemical dissolution (Eq. 2) competition [12].

\[
\begin{align*}
\text{Ti} + 2\text{H}_2\text{O} & \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \\
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ & \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}
\end{align*}
\]

(1) \hspace{2cm} (2)

At the beginning, Ti oxidized to TiO$_2$ and then selectively dissolved by F$^-$ ion. Thus, the pore became deeper and deeper. The reason for this reaction is OH$^-$ in the bulk solution and H$^+$ produced via reaction process (Eq. 1) show lower diffusion rate in viscous electrolyte. The pH value at tube bottom controlled by self-acidification process (Eq. 1) and less influences by bulk electrolyte pH value. This effect prevents passivation at the pore bottom even in basic solution (pH 8). Generally, the chemical dissolution reaction (Eq. 2) is also occurring at the tubes mouth during the growth process. The pH value at the tubes mouth is controlled by the bulk solution. In basic electrolyte, the chemical dissolution reaction (Eq. 2) at the tubes mouth is extremely slow. This resulting, the as-formed TiO$_2$ nanotubes can survive for longer anodization period [12]. Therefore, longer TiO$_2$ nanotubes produced.

4. **SUMMARY**

The nanotubes length increased significantly with the increase of the electrolyte pH value and the longest TiO$_2$ nanotubes obtain at pH 8. Increment of pH value to 9, the TiO$_2$ nanotubes became shorter. Lower pH value at the pore tip and higher pH value at pore mouth are necessary to obtain desired TiO$_2$ nanotubes length.
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Morphological, Structural and Radon Concentration Properties of Two-Dimensional Titanium Carbide MXene, Ti$_3$C$_2$

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**ABSTRACT.** In this study, radon concentration of 2D Titanium Carbide MXene Ti$_3$C$_2$ was studied by using an established radon monitor. A layered MAX phase of Ti$_3$AlC$_2$ were synthesized through pressureless sintering (PLS) by the initial powder of TiH$_2$/Al/C without preliminary dehydrogenation under argon atmosphere at 1350 °C. An elegant exfoliation approach was used to eliminate Al from its precursor to form a layered-structure of Ti$_3$C$_2$. Morphological and structural properties of this 2D material also studied. SEM images show two types of morphology which is a layer of Ti$_3$C$_2$ and the agglomerates Al$_2$O$_3$ with graphite. XRD pattern reveals three phases in this material which is a rhombohedral Al$_2$O$_3$, rhombohedral graphite and rhombohedral Ti$_3$C$_2$ phases. Radon concentration for this material for five consecutive days explains the safety used of this material is under the maximum value from US Environmental Protection Agency (EPA).

**Keywords:** MAX phase, MXene, Two-dimensional materials, Ti$_3$C$_2$, Radon concentration;

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1. **INTRODUCTION**

Two-dimensional (2D) materials are materials with unique properties which can be defined as a material with single atomic plane, such as graphene, with have only 0.34 nm thick of one atomic layer of carbon [1]. The range of materials to be called as 2D materials are from 1 layer to 10 layers, where more than 10 layers is considered as 3D materials [2]. By far the most studied 2D material is graphene, which is comprised of atomically thin layers of sp$^2$-bonded carbon atoms connected by aromatic in-plane bonds. Since the outstanding electronic properties of graphene have been discovered, other alternative 2D materials have attracted much renewed attention.

A fascinating idea was proposed to prepared freestanding graphene-like carbides (and nitrides) from ternary layered MAX phases (known also as nanolaminates) [3], which includes various 2D-like layers of transition metal carbides (or nitrides) as building blocks [4]. These 2D materials are now known as 'MXenes'; this term denotes their genesis from MAX phases (with the loss of the A component) and their similarity to graphene [5].
MXenes is new 2D nanosheet materials and gaining so much attention from materials engineer because its properties and unique behaviour and has similar lamellar structure with graphene.

Generally, a 2D material is produced by removing A from MAX phases by chemical etching. MAX phases are ternary carbide or nitrides with the chemical formula of $M_{n+1}AX_n$, where M is an early transition metal, A is an A-group element and X is either carbon or nitrogen. The value of $n$ can be 1, 2 or 3 [3]. There is no research until recently was discussed about the radon-222 ($^{222}$Rn) concentration of MXene, and it is important to study since long term exposure to radon is associated with lung cancer risk and present a significant environmental health hazard. $^{222}$Rn is the heaviest gas element, nine times heavier than air and a noble radioactive gas. This element does not chemically react with other materials in air and was occurs naturally from U-238 decay process. Inhalation of $^{222}$Rn and $^{222}$Rn daughter products for human will increase the possibility of lung cancer due to the presence of alpha ($\alpha$) particles which have linear energy transfer (LET) and that affects the alveolus [6]. Measurements of radon are normally expressed as the concentration of radon in units of picocuries per liter of air (pCi/L) and the United States EPA recommendations are about 4 pCi/L or lower, which is the average or slightly above average for safety requirement in any applications [7].

The aims of this research are to study the significant radon concentration of 2D MXene Ti$_3$C$_2$ for future application in engineering and technology. In addition, morphological and structural analysis was also performed to investigate the microstructural and elemental properties of 2D MXene Titanium Carbide Ti$_3$C$_2$.

2. MATERIALS AND METHODS

Starting materials of titanium hydrate (TiH$_2$, 99%, 325 mesh, Alfa Aesar, United State), aluminium (Al, 99%, 200 mesh, Acros Organics, Austria) and graphite (C, 99%, 550 mesh, Acros Organics, Germany) were used in this research. The powder was weighed according to the stoichiometry ratio of 3:1.1:2, then mixed by using a planetary ball mill for 60 hours. The powder was then cold-pressed to form a pellet with diameter of 1 cm and thickness of 0.3 cm before sintered in tube furnace by using a pressureless sintering (PLS) technique. The heating rate was controlled at 10 °C/min and the sintering temperature was selected at 1350 °C for 2 hours in argon atmosphere. The pellet then was pulverized, immersed and stirred in hydrofluoric solution (HF, AR grade, 49%, Qrec, New Zealand) for 20 hours in fume hood. The resulted mixture was then placed in centrifuge tube and centrifugation process was run at 5000 rpm for 7 min. The mixture was then washed with deionized water for several times, until the pH of solution approaching 7. The resulting Ti$_3$C$_2$ was then dried in vacuum at 50 °C for 24 hours.

X-ray diffraction (XRD) analysis was performed using Bruker D2 Phaser at 2θ values of 20 - 60° with Cu Ka radiation to determine the corresponding peaks of the MXene. X’pert HighScore Plus software was used to match the corresponding peaks with the standard data from International Committee of Diffraction Data (ICDD) X-ray data file. Microstructure analysis was performed using Nova NanoSEM 450 to characterize surface morphology of MXene Ti$_3$C$_2$.

A pellet of MXene Ti$_3$C$_2$ together with the professional radon monitor model 05-240, thermometer and hygrometer were placed in closed, fabricated container to calculate the radon concentration by time. The small openings of the container were sealed by using modelling material. The build-up of Radon (Rn) inside the container was measured using the Rn monitor. Rn concentration (pCi/L) was recorded every hour for five consecutive days.

3. RESULTS AND DISCUSSION

The morphology of 2D MXene Ti$_3$C$_2$ shows the layered structure with the thickness of 1 μm due to the removal of Al during elegant exfoliation approach in 49% HF solution (Fig. 1). SEM images shows two types of morphology which are a layer of Ti$_3$C$_2$ (point A) and the agglomerates Al$_2$O$_3$ with graphite (point B). The images of layered Ti$_3$C$_2$ with the thickness of 0.1-1.0 μm confirms the successful exfoliation of Ti$_3$C$_2$ similar with reported exfoliation graphene [8]. Sonication of HF treated resulted the separation of 2D Ti$_3$C$_2$ MXene.
The agglomerates of Al₂O₃ and graphite may formed during sintering and because of the stability of this phase, it is impossible to etched during elegant exfoliation process [9].

![Fig. 1 SEM image of 2D MXene Ti₃C₂ after etching process in 49% HF solution](image)

The structural analysis of 2D MXene Ti₃C₂ shows there are three phases matches which is rhombohedral Al₂O₃, rhombohedral graphite and rhombohedral Ti₃C₂ phases (Fig. 2). This XRD result is also supported by other researchers [9-15] in this field based on the reactions of the HF solutions with Ti₃AlC₂ which include:

1. \[ Ti₃AlC₂ + 3HF \rightarrow AlF₃ + \frac{3}{2}H₂ + Ti₃C₂ \]
2. \[ Ti₃C₂ + 2H₂O \rightarrow Ti₃C₂(OH)₂ + H₂ \]
3. \[ Ti₃C₂ + 2HF \rightarrow Ti₃C₂F₂ + H₂ \]

The formation of Ti₃C₂ phase in XRD pattern instead of Ti₃C₂(OH)₂ in reaction (2) was attributed to the ultrasonication in methanol leads to exfoliation of MXene Ti₃C₂.

The radon concentration properties of 2D MXene Ti₃C₂ shows the rate of radon was slightly increase started from day 2 to day 5 (Fig. 3). Shaded region shows the concentration level is in between of maximum and minimum values for each days. The highest radon concentration was recorded at day 5 (1.2 pCi/L) which is lower that the suggested value by United State Environmental Protection Agency (EPA). Hence, it was experimentally proven that Ti₃C₂ could be an alternative material towards the development of new electronic technologies due to small radiation emission and considered safe for consumer usage.
4. SUMMARY

A layered of titanium carbide Ti$_3$C$_2$ MXene was synthesized by pressureless sintering (PLS) method using a starting powder of TiH$_2$, Al and graphite for two hours. A layered of Ti$_3$AlC$_2$ was successfully exfoliated and fabricates a layer of 2D Ti$_3$C$_2$ by using an elegant exfoliation approaches. This is happening since the relatively weak bonding of Al layer compared to the Ti-C bonds. The layers of 2D Ti$_3$C$_2$ is quite thin between 0.1-1.0 µm. There are three phases was detected by XRD after the treatment which is Ti$_3$C$_2$ and the agglomerates of C and Al$_2$O$_3$. SEM image shows the agglomerates of this phase at the side of Ti$_3$C$_2$ layers. Radon concentration for
this material for five consecutive days explains the radiation level of this material is under the suggestion value from US Environmental Protection Agency (EPA) which is 4 pCi/L.

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Fabrication and Characterization of Room Temperature Hydrogen Gas Sensor Using ZnO Nanocrystalline Fibers Prepared by Electrospinning

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ABSTRACT. Room temperature hydrogen gas sensor was successfully fabricated using ZnO nanocrystalline fibers prepared by electrospinning a precursor mixture of polyvinylpyrrolidone (PVP) and zinc acetate, followed by annealing at 500 °C for 4 hours in air. The ZnO nanocrystalline fibers were characterized by X-Ray Diffraction (XRD) which indicated that the fibers are single phase nanocrystalline ZnO. Surface morphology and chemical composition of ZnO nanocrystalline fibers were studied by Field Emission Scanning Electron Microscopy (FESEM) equipped with EDS spectroscopy. The sensitivity of the sensor towards hydrogen gas was about 4.9% in 2000 ppm.

Keywords: Hydrogen gas sensor, Electrospinning, ZnO;

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1. INTRODUCTION

As one of II-VI compounds, Zinc oxide (ZnO) has a wide energy band gap of 3.37 eV, and large exciton binding energy of 60 meV. It has a hexagonal wurtzite-type structure and is non-toxic and relatively cheap. ZnO in one-dimensional (1-D) nanostructures offer extra characteristics such as high aspect ratios, high electron mobility and possess both electrical and optical anisotropy [1,2]. These unique multiple characteristics make ZnO suitable for various applications including solar cell [3], gas sensor [4] and photodetector [5]. There are various methods reported in fabricating 1-D ZnO such as sol-gel, electrodeposition, solvothermal routes, vapor-solid, vapor-liquid-solid, solution-solid and electrospinning. Electrospinning is one of the simple and versatile methods among others. It is a method of producing fiber from polymer solutions with diameter ranging from nano to micro scale [6].

In this work, ZnO nanocrystalline fibers prepared by electrospinning were used to fabricate H₂ gas sensor. The main aim of this work is to demonstrate the sensing capability of ZnO nanocrystalline fibers toward H₂ gas at room temperature.

2. MATERIALS AND METHOD

1.5 M Zn(CH₃COO)₂.2H₂O was mixed with 10% PVP dissolved in ethanol with a volume ratio of 1:9 was used for electrospinning. The mixture was stirred for 1 hour and sonicated to remove any bubbles trapped in the solution. The solution was then loaded into a plastic syringe and connected to a high voltage power
A voltage of 16 kV was applied between the collector and the syringe separated at a distance of 16 cm. The solution flow rate was maintained at 0.03 ml/min.

A rotating steel wire drum was used as nanofibers collector. Fig. 1 shows the electrospinning setup. The fibers were transferred to SiO$_2$ coated Si wafers and annealing was performed in air at temperature of 500 °C for 4 hours to remove the organic constituents of the fibers and to obtain nanocrystalline ZnO phase. A Netzsch STA-449-F3 Jupiter was used for simultaneous TG-DSC analysis. Nitrogen gas with a constant flow rate of 20 ml/min and a heating rate of 10 °C/min was used in the analysis. Both the structures of PVP/zinc acetate and ZnO nanofibers were characterized by X-ray diffraction (XRD) using PANalytical XPert Pro MPD with Cu Kα irradiation. The morphologies of the nanofibers were examined by field emission scanning electron microscope (FESEM) Carl Zeiss GeminiSEM 500 equipped with an Oxford X-Max EDS detector.

Gas sensing tests were performed with gas flowing across the sensor chip in a sealed small acrylic glass chamber. Hydrogen was diluted at various proportions with dry air and the flow rates were regulated by mass flow controllers at 200 SCCM. Gas sensing data was acquired via a customized Labview program interfaced with a Keithley Series 2600B. A constant voltage of 1.4 V was applied. All experiments were carried out with the sensor chip first exposed to air to obtain the baseline resistance, followed by exposure to the desired concentrations of hydrogen gas before the air was flushed back to complete a cycle.

**Fig. 1** Schematic diagram of the electrospinning setup

### 3. RESULTS AND DISCUSSION

TG and DSC curves of PVP/zinc acetate fibers at N$_2$ atmosphere with temperature range RT-900 °C are shown in Fig. 2. The weight losses (~56%) found from TGA curves agree well with those estimated to the decomposition of PVP and zinc acetate and the formation of oxide. The TGA curve of PVP/zinc acetate fibers indicated three stages of decomposition. The first weight loss at around room temperature to 140 °C is attributed to the liberation of a small amount of water moisture. The second weight loss happens at around 220-320 °C due to loss of water of crystallization and melting of the polymer. The third stage is observed in a
range of 340-480 °C, which corresponds to the decomposition of organic phase. This was confirmed by the
sharp exothermic peak observed in the DSC curve at about 460 °C. When the temperature reaches about 500
°C, the curve becomes flat which indicates that the PVP/zinc acetate fibers has completely transformed into
inorganic oxide fibers. A broad exothermic peak appears between 520 and 900 °C, which probably due to ZnO
crystals growth. In our previous work [7], results showed that calcination at 500 °C can maintain the
structure of fiber while the fibers developed into segmented or dendritic structures after calcined at higher
temperatures. The effect of applied voltage and calcination temperature on the morphology and diameters of
the electrospun PVP/zinc acetate fibers has been investigated in the previous work also. Based on these
findings, 500 °C was chosen as the annealing temperature to obtain nanocrystalline ZnO fibers for H₂ gas
sensing application.

![Graph showing TG and DSC curves of PVP/zinc acetate precursor](image)

**Fig. 2** TG and DSC curves of PVP/zinc acetate precursor

Fig. 3 shows the FESEM micrographs and EDS spectrum of PVP/zinc acetate fibers obtained by
electrospinning. The as-spun PVP/zinc acetate fiber Fig. 3(a) give a smooth surface while Fig. 3(b), 3(c)
reveals that the surfaces of 500 °C annealed ZnO fiber consist of nanocrystallines which are connected to form
a high surface area fiber, the crystallites are less than 100 nm in size. After annealed at 500 °C for 4 hours, the
fibers remained continuous but the diameter becomes thinner, due to the decomposition of organic phase.
Fig. 3(d) shows EDS Spectrum of a fiber annealed at 500 °C for 4 hours, the results clearly indicate that
the presence of Zn in the fiber. The Si wafers were coated with SiO₂, which explains the reason of large
percentage of Si and O being detected.

Fig. 4 shows the X-ray diffractograms for as-spun and calcined fibers, it is found that the as-spun fibers
exhibited no apparent diffraction peaks, suggesting that the fibers were still in amorphous phase. On the
other hand, the results indicate that electrospun fibers annealed at 500 °C for 4 hours were successfully
converted to ZnO phase.

Fig. 5 shows the dynamic resistance response of the ZnO nanocrystalline fibers gas sensors as a function of
time exposed to a range of concentration of H₂ testing gas. In this H₂ gas sensing test, time interval for every
H₂ flow and air purging was set to 300 s. The volume of gas chamber used for gas sensing test was 12 cm³. Test results show that the sensor has good response to H₂ at room temperature. Sensitivity of the ZnO nanocrystalline fibers towards 2000 ppm of H₂ gas at room temperature is 4.92%. Lowest detection limit is 400 ppm H₂. It is observed that the gas sensor shows typical p-type sensing response to H₂, which the sensor resistance increased upon exposed to reducing gas.

The sensitivity (S) of the ZnO sensor towards H₂ gas was calculated using the following equation:

\[ S = \frac{R_g - R_0}{R_0} \times 100 \]  \hspace{1cm} (1)

where, R₀ and R₉ are the sensor resistance in the absence and presence of H₂ gas.

Fig. 3 FESEM morphology (a) as-spun fiber, (b, c) annealed fiber at different magnification and (d) EDS spectrum of annealed fiber
Fig. 4 X-ray diffractograms for as-spun and calcined fibers

Fig. 5 Dynamic resistance response of ZnO nanocrystalline fibers towards different concentration of H₂ at room temperature
4. SUMMARY

A room temperature hydrogen gas sensor was fabricated using ZnO nanocrystalline fibers. The fibers were prepared by electrospinning a precursor mixture of polyvinylpyrrolidone (PVP) and zinc acetate, followed by annealing at 500 °C for 4 hours in air. Annealed ZnO fiber consist of nanocrystallines which are connected to form a high surface area fiber, the crystallites are less than 100 nm in size. This work successfully demonstrated the sensing capability of ZnO nanocrystalline fibers toward H₂ gas at room temperature. Sensitivity of the ZnO nanocrystalline fibers towards 2000 ppm of H₂ gas at room temperature is 4.92% and the lowest detection limit is 400 ppm H₂.

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Characterization of Bio-Polymer Composite Thin Film Based on Banana Peel and Egg Shell

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ABSTRACT. This research study of xrd characterization analysis of organic filler comprise waste banana peel and waste egg shell as matrix and reinforcement in bio-composite thin film. Banana peel fibers exhibit good renewable material for the substitution of bio based composite. The banana peel and egg shell were separately cut into smaller pieces and boiled for 20 min before drying in oven at temperature 80 °C for 30 min. These pieces were then ground using mechanical blender into fine powder sizes ranging from 80 -100 µm. This bio-composite thin film will investigate by using X-ray diffraction (XRD) analysis to determine of crystallinity of a compound, distinguishing between amorphous and crystalline material and to quantification of the percent crystalline of a bio-composite thin film. shows that the sharp peaks on egg shell graph at 2θ = 28° and 42° which represent the CaCO3 and it has high crystallinity degree which is 82.9% compared to banana peel.

Keywords: Bio-polymer, Composite, Egg shell, Banana peel;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Vast amounts of food waste around the world can cause significant health and environmental problems that ultimately lead to economic world. However, most food wastes contain valuable minerals that could serve as raw materials for the production of glass, ceramics, and glass-ceramics. Organic waste typically has value in terms of energy, water content, and mineral content, but current methods of waste disposal do not utilize these resources. Instead, communities incur costs to store synthetic plastic thin film in landfills, where it emits uncontrolled greenhouse gases and poses risks to pollution. Recent government regulations regarding landfills, for example, those in Europe, lead to a direct economic stimulus to create value out of waste. Solutions to reduce the mass of landfills could be coupled with extraction of the resources they contain. Banana peel is a waste material with rich of starch. This characteristic makes them potential to produce bio-polymer thin film which is more environmentally friendly due to its biodegradable abilities compared to the conventional synthetic petroleum-polymer. In addition, banana peels are agricultural waste that discarded as useless material. This waste contributed to waste management problems although they have some compost
and cosmetics potentiality [1]. Banana peels are readily available, low cost and environmental friendly bio-
material. This agriculture waste is also inexhaustible, cheap, non-hazardous and specifically selective for
heavy metals and able to dispose easily by incineration [2]. For this reason, application of waste natural fiber
of bio-polymer are being investigate as good alternative resources. Natural fibers as reinforcement for
polymeric matrices have been studied due to it numerous of the advantages and their ideal environmental
performance when compared to inorganic fibers such as glass or carbon fibers [3]. The main advantages were
presented by these fibers are abundance and therefore low cost, biodegradability, flammability, flexibility
during processing, relatively high tensile and non-toxicity [4].

Banana (*Musa sapientum*) is the herbaceous plant that belongs to the family Musaceae. Bananas are the
most important tropical fruits in the world market and it is most eaten fruits in this world. Banana also
named as the World Healthiest Fruit. Banana peel (also known as banana skin) is the outer covering of
banana fruit. At present, the banana peels are not being used for any other purposes and generally removed
and dumped as solid waste at large expense. Therefore, a significant amount of organic waste is generated.
There are several utilizes of wasted banana peels such as it is used for water purification, as fertilizer and
used in the production of ethanol, cellulose and laccase. However, sometimes wasted banana peel is used as
feedstock typically in small farms for pigs, goats, rabbits, cattle and other several species [5].

Eggshells are litter and kitchen waste that can be collected in a large amount from many places such
housing areas, restaurants, hotels, food industries and even from the hatcheries and farm [6]. Eggshell
consists of 95% calcium carbonate (CaCO₃) as its main component and it is in the form of calcite. In the form
of calcium carbonate, calcite is the most stable which forms elongated structures called columns, crystalite or
palisade [7]. Besides that, there are remaining 5% of others inorganic material in the eggshell which are
calcium phosphate, magnesium carbonate, soluble proteins and insoluble proteins. Calcium carbonate is a
compound that brittle white stuff that limestone, chalk, sea shells, coral and pearls are made of [8].

Eggshell containing calcium carbonate (94%), calcium phosphate (1%), organic compounds (4%), and
magnesium carbonate (1%). The high contains of calcium in eggshells can be converted as a CaO catalyst by
calculations process at temperature around 800 ºC for 2 hours where the reaction takes place as exothermic
reaction.

 Nowadays, natural fibers have become attractive to those researchers, scientists and engineers as an
alternative reinforcement for fiber reinforced polymer composites. Natural fiber reinforced polymer matrix
got considerable attention in numerous applications due to its good properties and superior benefits of
natural fiber over synthetic fibers. Besides the advantages of eco-friendly and biodegradability, fiber
reinforced polymer are low weight, low cost, high specific strength, non- abrasive, fairly good mechanical
properties such as tensile modulus and flexural modulus, improved surface finish of molded parts composite,
renewable resources, flexibility during processing, being abundant, and also minimal health hazards [9].

2. MATERIALS AND METHODS

Banana peel was obtained from an available cafeteria at University Malaysia Kelantan (UMK) Jeli as solid
waste. Then, banana peel was cleaned with water to remove undesired materials. Banana peel was next left to
dry under sun light for 7 days, then it was dried in a drying oven at 70°C for 4 hours to remove water
content. Then, egg shells also were collected from the nearest UMK Jeli cafeteria. This eggshells were washed
with water to remove the dirt and membranes. Later, the cleaned eggshells were dried in the oven for an hour.
Then, dried eggshells were blended by using blender. The dried banana peels and egg shell were were
trimmed and crushed in simple crusher and sieved into particles with an average size of 0.725 mm.

Banana peels was boiled in water for 20 min to make it soft. The volume of water (ml) and weight of banana
peels (g) were in the ratio of 4:1. After 20 min, banana peels were blended with glycerol for 10 min. The
amount of glycerol were used is 15% w/w of the dried banana peels. Then, the blended mixture was boiled for 15 min at 70 °C.

Meanwhile, the mesh surface of the silkscreen was moistened with water. The boiled blended mixture was spread over the mesh using spatula. A roller was used to ensure the film surface to be more flat. Then, the mixture on silkscreen was placed in the oven at 80 °C for 3 hours for drying. Lastly, the dried bio-composite thin film was taken from the silkscreen. The thickness of the thin film was in the range of 0.10 mm to 0.15 mm.

The bio-composite films were ready to analyze the chemical elements presents in the bio-composites by using XRD analysis. The film samples were cut into small pieces (20 mm × 20 mm) and dehydrated in a desiccator with silica gel (∼0% RH) for 3 weeks before being characterized. The crystalline structures of the samples were determined using X-Ray Diffraction (XRD) technique. XRD analysis was carried out by using Bruker D8 Advance Powder XRD with CuK-α radiation (λ=1.5404 nm) and operated at a voltage of 40 kV with a current density of 30 mA. XRD data were collected within 2θ range of 10° to 40° at room temperature.

3. RESULTS AND DISCUSSION

The bio-composite thin film isolated from the banana peel and egg shell fillers presented homogeneous surface with no bubbles or cracks, as well as good handling characteristics. This means that the films could be easily detached from the plates without tearing, and that they were not sticky or too brittle. X-ray diffraction (XRD) of bio-composite thin film was analyzed the crystalline phases of the thin films. Banana peels are mainly composed of pectin, cellulose and hemicelluloses and the functional groups associated with these polymers as well as the proteinaceous matter may be involved. The patterns exhibited an intense peak at around 2θ = 30 ° (I200) for banana peel and egg shell fillers. XRD plots as shown in Fig.1 and 2. These types of peak represents the crystallinity region in samples. The XRD results analyzed using X’PertHighScore software shows in Fig. 1. The average crystallite size is determined from the full width at half maximum (FWHM) of the X-ray diffraction peak using Scherrer’s eq. 1:

\[
D = \frac{K \lambda}{B \cos \theta}
\]

Where D is the particle diameter, \( \lambda \) is the X-Ray wave length, B is the FWHM of the diffraction peak, \( \theta \) is the diffraction angle and K is the Scherrer’s constant of the order of unity for usual crystals.
Fig. 1. X-ray diffraction pattern for the banana peel waste sample

Fig. 1 shows that XRD pattern of amorphous of banana peel and it presence of containing copper, lithium and silicon has small number of crystallinity which is 29.1%. Amorphous or non-crystalline solid is a solid that lacks the long-range order characteristic of a crystal. The X-ray diffraction data indicate of broad peaks at an angle 2 theta of 24 and 44 degrees. Fig. 1 shows the X-ray diffraction pattern of amorphous materials of banana peel in bio-polymer thin films. Some sharp peak also exist in the thin film that indicated the existence of other elements that are crystalline characteristic [10].

Lignocellulocis fibers of waste banana fibers studied by Pereira et al. [11] shows the X-ray diffractograms pattern amorphous of the banana fibers. This peaks was observed for thin film samples at 2θ= 16° and 2θ = 22°, representing the cellulose crystallographic planes 1101 and 1002, respectively.

Fig. 2 X-ray diffraction pattern for the eggshell waste sample

Fig. 2 shows the result of XRD spectrum for egg shell waste sample. The peaks on the spectrum can be informative to estimate the crystallization. The mineral phase present in the as-collected eggshells was identified as calcite; no other crystalline species was detected. As shown in Fig. 1, the X-ray reflections correspond to the PDF files for calcite. The material obtained after drying process and thin film fabrication at 80 oC has a porous appearance, white color and fragile consistence. The corresponding X-ray diffraction pattern Fig. 2 shows reflections corresponding to PDF 010803276 files for (CaCO3); again no other species was found. It is confirms the presence of calcite (CaCO3) indicating CaCO3 is the main constituent in the egg shell. Calcite is the thermodynamically most stable form of CaCO3 at room temperature. X-ray diffraction (XRD) analysis was conducted with the aim of comparing XRD patterns of bio-composite thin film. than egg shell containing calcite with crystallinity of 82.9% as shown in Fig. 2.

It also clearly shows that the sharp peaks on egg shell graph at 2θ = 28° and 42° which represent the CaCO3 and it has high crystallinity degree which is 82.9%. The degree of crystallinity has a significant on hardness, density, transparency and diffusion.

4. SUMMARY
This paper discusses a technique for processing of bio-polymer thin film using waste banana peel and egg shell contains CaCO$_3$ which extracted from eggshell waste. XRD analysis confirmed that this thin film of bio-composite shows amorphous pattern of banana peel and it presence of containing copper, lithium and silicon has small number of crystallinity which is 29.1%. Other than that, it also reveal that eggshell particles were primarily composed of calcite (CaCO$_3$) with high percentage of crystallinity which is 82.9%. Calcite is the thermodynamically most stable form of CaCO$_3$ at room temperature. From Fig. 3, it is indicating that egg shell fillers have high crystalline which is 82.9% and confirms of presence calcite (CaCO$_3$). It can be indicated that egg shell characteristics (like commercial calcite and availability makes egg shell a potential source of filler for bulk quantity, inexpensive, lightweight and low load-bearing composite application.

**ACKNOWLEDGEMENT**

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**REFERENCES**


Comparison of Different Types of Dispersing Agent on Zeta Potential and Particle Size Analysis of Sago Starch Dispersion as Bio-filler for Natural Rubber Latex Films

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\textbf{ABSTRACT.} The incorporation of sago starch into the latex compound will act as bio-filler to accelerate the degradation process of natural rubber (NR) latex based product including latex gloves. However, well-dispersed of sago starch in NR latex compound is necessary in order to have a better biodegradation of the latex products. In this study, sago starch dispersion was prepared with different types (anchoid and nonyl phenol) and loading percentages (4, 5 and 6 wt.\%) of dispersing agent. Results of sago starch dispersion with 5 wt.\% loading of anchoid as dispersing agent shown highest zeta potential value (-34.8 mV) and the smallest particle size (531.2 nm). The addition of the anchoid sago starch dispersion into NR latex compound also produces better NR latex films mechanical properties (tensile strength: 21.72 MPa; elongation at break: 1269.5\%; tear strength: 63.76 MPa) compared to NR latex films with nonyl-phenol sago starch dispersion. These results support the potential of anchoid as dispersing agent for NR latex bio-filler.

\textbf{Keywords:} Dispersing agent, Zeta potential, Particle size, Sago starch, Natural rubber latex;

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1. INTRODUCTION

Disposable products such as natural rubber (NR) latex gloves is one of the world highest consumable products as it is designed for disposal after single use [1]. This scenario caused the volume of rubber solid waste disposal increase each year. Furthermore, the disposed gloves normally take few years to degrade in the natural environment due to the presence of inorganic materials such as antioxidants and sulphur crosslinks that make NR latex films resistant to microbial infections [2]. Thus, the combination of rubber system with bio-materials is a feasible option. Misman and Azura [3] had proven that the incorporation of sago starch as biodegradable natural filler in NR latex films was able to accelerate the degradation process of NR latex films. The degradation of NR latex films occurred due to the breakdown of glucosidic linkages of amylose and amylopectin by means of enzymatic hydrolysis by microorganism which consumed the sago starch as source of nutrients [2].

In order to have a better and accelerated biodegradation, well-dispersed of sago starch in NR latex is a necessity. This is achieved by preparing the sago starch bio-filler in aqueous form which mixed with dispersing agent, stabiliser, and water. However, there are different types of dispersing agent (or surfactant) with a different stabilisation mechanism can be used to prepare the dispersion. According to Moore and Spencer [4], the most common physical property used in classifying the surfactants is ionic: anionic, cationic, non-ionic and amphoteric/zwitterionic. Usually, in the NR processing, surfactants that are either anionic or non-ionic in nature are added to improve the stability [5]. Due to their amphiphilic nature [6], the hydrophilic part of the surfactant molecule will tend to interact with the aqueous media, whereas the hydrophobic part will adsorb itself onto the rubber particle, therefore enhancing the stability of the particles against
flocculation and coagulation. The general mechanism of interaction of anionic and non-ionic surfactant with the aqueous phase as shown in Fig. 1.

Considering the above factor, this study will be focusing on the effect of using anionic (anchoid) and non-ionic (nonyl phenol) surfactants as well as their loading percentages on the sago starch dispersion; prepared by using ball milling. Ball milling is selected due to the capability of this technique to reduce crystalline region and modify the particle size of filler [7]. The stability of the dispersion will be characterised by zeta potential and particle size analysis. Besides, the mechanical properties of both anchoid and nonyl phenol-loaded NR latex films will also be determined and compared.

Fig. 1 Interaction of anionic and non-ionic surfactant with the aqueous phase. The Stern layer consists of adsorbed (bound) counterions, while the diffuse layer contains free ions involved in Brownian motion [8]

2. MATERIALS AND METHODS

NR latex was purchased from Zarm Scientific and Supplies Sdn. Bhd. with the initial properties of dry rubber content (DRC) of 60.00%, total solid content (TSC) of 61.52%, mechanical stability time (MST) of 970 s, and volatile fatty acid number (VFA no.) not exceeding 0.2. Meanwhile, sago starch was obtained from Sago Link Sdn. Bhd. Other compounding ingredients such as diethyldithiocarbamate (ZDEC), zinc oxide (ZnO), potassium oleate, potassium hydroxide (KOH), antioxidant and sulphur were obtained from Bayer (Malaysia) Sdn. Bhd.

2.1 Preparation of sago starch dispersion and NR latex films. The dispersed sago starch was prepared by mixing sago starch with different types (anchoid and nonyl phenol) and loading percentages (4, 5 and 6 wt.%) of dispersing agent, stabiliser and distilled water. The mixture was then stirred using a mechanical stirrer (Wise Stir HS-120A, Korea) and transferred into the ball mill jar and left mixing at 35 rpm for 18 hours. The sago starch dispersion was then used as filler to NR latex compound as per listed in Table 1 in order to produce biodegradable NR latex films. Zeta potential and particle size analysis: The particle size distributions of NR latex and sago starch dispersions were measured using Malvern™ (Worcestershire, UK). The sample used was 1 g of NR latex or sago starch dispersion which was pre-dispersed in 10 ml of deionised water.
Table 1 Formulation for sago starch filled NR latex compound

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Dry weight (pphr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR latex (60 wt.%)</td>
<td>100.00</td>
</tr>
<tr>
<td>Sago starch dispersion (25 wt.%)</td>
<td>10.00</td>
</tr>
<tr>
<td>KOH (10 wt.%)</td>
<td>0.30</td>
</tr>
<tr>
<td>Potassium oleate (20 wt.%)</td>
<td>0.25</td>
</tr>
<tr>
<td>Antioxidant (50 wt.%)</td>
<td>0.50</td>
</tr>
<tr>
<td>ZnO (50 wt.%)</td>
<td>0.25</td>
</tr>
<tr>
<td>ZDEC (50 wt.%)</td>
<td>0.75</td>
</tr>
<tr>
<td>Sulphur (50 wt.%)</td>
<td>0.50</td>
</tr>
</tbody>
</table>

*** Sago starch dispersion prepared with anchoid and nonyl phenol

2.2 Films mechanical properties tests. Tensile and tear tests were carried out according to ASTM D412 and ASTM D624 respectively by using Instron Machine (Model 3366, USA) with the crosshead speed of 500 mm/min. The films were cut into dumbbell and crescent shapes (die type C). The results are based from the average of 5 samples.

3. RESULTS AND DISCUSSION

3.1 Zeta potential and particle size analysis. Zeta potential was the key indicator of stability of the dispersion. It was a measure of the magnitude of the electrostatic or charge repulsion/attraction between sago starch particles. For a stable dispersion, the value of zeta potential should be above +30 mV or below -30 mV. If the value is within -30 mV to +30 mV, the dispersion is considered as not stable [9]. Zeta potential and particle size analysis of sago starch dispersion for each type of dispersing agents are shown in Fig. 2.

For the sago starch dispersion containing anchoid dispersing agent, loading of 4 wt.% showed results of zeta potential -15.2 mV which indicating as not stable dispersion, while for 5 and 6 wt.% loading, the zeta potential value showed -34.8 and -31.5 mV respectively. Although both 5 and 6 wt.% loading dispersing agents showed a stable dispersion, 5 wt.% loading anchoid dispersion was more stable than 6 wt.% loading dispersion based on highest value obtained. Besides, the particle size of each dispersion was 595.8, 531.2 and 714.9 nm for 4, 5 and 6 wt.% loading anchoid respectively. For 5 wt.% anchoid loading, the dispersion has the smallest particle size. This size of particle was the nearest to the size of NR latex, which was 482 nm, where more homogenous compound can be achieved. Thus, 5 wt.% anchoid loading can be concluded to be the optimum loading of dispersing agent in sago starch dispersion. While for 4 wt.% loading, the lack of amount of dispersing agent gave lesser stabilizing effect for the sago dispersion. Extra dispersing agent in 6 wt.% loading dispersion resulted in reversing effect due to the agglomeration of particles.

For nonyl phenol, the similar percentages of dispersing agent are used which were 4 to 6 wt.%. The zeta potential for all these three dispersion falls within the range of non-stable dispersion which were -11.00, -7.84 and -7.92 mV for 4, 5 and 6 wt.% loading respectively. Meanwhile, the particle size of dispersion obtained were 356.0, 795.7 and 3560.0 nm for 4, 5 and 6 wt.% loading, respectively. The particle size of dispersion with 6wt% surfactant loading was very big compared to 4 and 5 wt.% loading dispersion. This phenomenon can be said as flocculation. In the similar volume of dispersion, too much surfactant might cause the collision between particles and thus lead to particle flocculation. The particles flocculation acts as a stress concentration point reduced the tensile strength of the NR latex films [10].
Nonyl phenol was non-ionic surfactant which, according to Shegokar and Müller [11], the hydrophobic parts of the dispersing agent adsorb on the particle surfaces as the "anchor chain", while the hydrophilic parts pull out from the surface to aqueous medium, creating a stabilizing layer. Zirak and Pazeshki [12] also reported that the addition of non-ionic surfactant caused increasing of particle size indicating the coalescence of fillers. This is due to the weak steric repulsion forces exerted on each particle surface caused a low frequency of collisions between the particles. During collision, particles are moving actively and thus prevent the particles to coalesce and combine with each other.

3.2 Mechanical properties. Table 2 showed the comparison of mechanical properties between anchoid-loaded and nonyl phenol-loaded NR latex films 5 wt.% loading of dispersing agent. Based on Table 2, both types of NR latex films showed quite similar values of tensile modulus. However, for tensile strength, elongation at break (EB) and tear strength, the anchoid-loaded NR latex films always possessed greater value than nonyl phenol-loaded NR latex films. The tensile strength, EB and tear strength of NR latex films at 5 wt.% loading of anchoid were 21.72 MPa, 1269.5% and 63.76 MPa respectively. Meanwhile, with the same loading percentage, nonyl phenol-loaded NR latex films showed the tensile strength, EB and tear strength were respectively 19.85 MPa, 1248.0% and 51.87 MPa.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Anchoid</th>
<th>Nonyl phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>21.72</td>
<td>19.85</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>1269.5</td>
<td>1248.0</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(M100)</td>
<td>0.7611</td>
<td>0.8340</td>
</tr>
<tr>
<td>(M300)</td>
<td>1.3035</td>
<td>1.3980</td>
</tr>
<tr>
<td>(M500)</td>
<td>2.1230</td>
<td>2.1230</td>
</tr>
<tr>
<td>Tear strength (N/mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>63.76</td>
<td>51.87</td>
</tr>
</tbody>
</table>

This phenomenon might due to the better and stronger dispersion of filler in the anchoid-loaded NR latex films. It is well known that the dispersion stability is related to high zeta potentials [9]. If the particles have a
large zeta potential, they will repel each other. Hence, the higher the zeta potential, the more stable the dispersion obtained. It is known that the NR latex always preserved in basic condition to prevent destabilisation. Therefore, NR latex particle surface is surrounded by negatively charged. It is considered that the negatively charged of anchoid adsorbed to the sago starch particle surface, enhances the negative potential between NR latex and sago starch filler particles.

4. SUMMARY

In summary, 5 wt.% anchoid loaded sago starch dispersion can be concluded as an optimum composition to be introduced in NR latex system. When the stability of the sago starch dispersion was high and good enough which can be indicated by zeta potential, it can help to improve the mechanical properties of the NR latex films as the filler was well-dispersed in the films.

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Influence of Epoxidized Palm Oil on Polyhydroxyalkanoates Tensile Properties

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**ABSTRACT.** These papers focus on the influence of epoxidized palm oil (EPO) on polyhydroxyalkanoates (PHA) tensile properties. Previous researchers has found a thermoplastic polymer polyhydroxyalkanoates (PHA) that exhibit biodegradable properties and produced from renewable materials such as sugar and molasses. However, pure PHA are brittle materials. A modification on the mechanical properties of PHA can be done by introducing plasticizer to the materials. In this study, (EPO) was used as plasticizer to PHA with varied composition of EPO content range 1 wt.% to 5 wt.%. The blend was prepared by mixing the two components using internal mixer at 175 °C. The mechanical property of each sample was determined by tensile test. Result shows that the Young's modulus of PHA was improved with 3 wt.% optimum plasticizer loading while lowest tensile strength which indicates the rigidity of PHA/EPO at this composition is optimized.

**Keywords:** Plasticizer, EPO, Mechanical properties, PHA;

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1. INTRODUCTIONS

Plastics waste is a part of main problem in environmental issues. Developments of biodegradable plastics become a concern in solving this issue. Researchers has discovered a polymer known as polyhydroxyalkanoates (PHAs) that can be produced from renewable and bio-waste resource by bacteria fermentation [1,2]. Numbers of studies did focus on the PHA synthesis methods [3-5]. The biodegradability of PHA was good in solving the plastics packaging waste issues. However, pure PHA is a brittle material due to re-crystallization with ageing at room temperature. Thus, the mechanical properties of PHA change with time. It is reported that the mechanical properties of PHA can be modified by adding plasticizer [6]. Addition of plasticizer enhances the molecular motion and reduces the glass transition temperature of the materials hence change the thermal properties of biopolymer [7-9]. Numbers of research done including modified the mechanical properties of PHA by adding various plasticizer such as soybean oil, epoxidized soybean oil, dibutyl phthalate and triethyl citrate [10-16]. However, few number of research if any done on EPO as the plasticizer for PHA. Development of PHA blend with natural plasticizer like EPO is very interesting as the blend will be completely biodegradable in environment and epoxidized palm oil (EPO) source is available in this country hence will increase the utilization of EPO. The objective of this paper is to investigate the effect of local produced EPO to the mechanical properties of PHA.

2. MATERIALS AND METHODS

Polyhydroxyalkanoates (PHAs) used was in pellets form supplied by Shenzen Bright China Industrial Co. Ltd., China with density of 1.23 g/cm$^3$. The yellowish PHA palette was dried for 5 hours at 50 °C to remove any moisture before blended with EPO. The EPO used supplied by Budi Oil Holding Sdn Bhd was in semi-solid
state at room temperature. The PHA and EPO was blend using the internal mixer Hakee Internal Mixer Rheomix 600 p at 175 °C with speed 50 rpm for 15 min. The blend composition was varied as summarized in Table 1. After been cold, the blend was crushed into size from 1 mm to 10 mm. The blend then molded into dumbbell shape tensile sample by hot pressing at 165 °C for 5 min.

**Table 1** Composition of PHA/EPO blend

<table>
<thead>
<tr>
<th>Blend</th>
<th>Polyhydroxyalkanoates (wt.%)</th>
<th>Epoxidized Palm Oil (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>B1</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>B2</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>B3</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>B4</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>B5</td>
<td>95</td>
<td>5</td>
</tr>
</tbody>
</table>

The tensile properties were determined by testing 4 samples for each composition using Universal Testing Machine based on ASTM D638. The tensile test was run at constant speed 5 mm/min with similar storage time. The break surface of the sample then was observed by The Field Emission Scanning Electron Microscope (FESEM) (JSM 6700F, JEOL) at the break surface.

**3. RESULTS AND DISCUSSION**

The tensile properties of plasticized PHA were compared to pure PHA. Fig. 1 shows the effect of EPO content to the Young's modulus of PHA. The Young's modulus of PHA increase from 420 MPa to 890 MPa with 3 wt.% of EPO introduced to the composition. At this point, the EPO composition was optimum followed by 5 wt.% EPO (515 MPa), 2 wt.% EPO (467 MPa), 1 wt.% EPO (428MPa) and 4 wt.% EPO (344 MPa). High Young's modulus exhibited by rigid materials which more stress required for deformation to occur.

For tensile strength shows in Fig. 2, the trend was decreased as the EPO loading increase. The trends of increasing of Young's modulus while decreasing in tensile strength as EPO loading increased indicate that the strain range was wider. The interaction between PHA and EPO makes the blend more rigid. However at 4 wt.% of EPO the tensile strength drop to the lowest. This may results by non homogenous
blend due to excessive content of EPO. FESEM analysis was done to study the homogenity and breaking behaviour of the samples.

Fig. 2 Effect of EPO on tensile strength of PHA

Fig. 3 illustrate the FESEM image of the tensile sample fracture surface of the optimum blend with 500x magnification. In this figure, it shows good compatible morphologies and smooth fracture surface indicate that the miscible of EPO in the blend. It is also show good adhesion between the PHA matrix and plasticizer as there are only one phase produce. Fig. 4 shows the morphology of fracture surface for 4 wt.% EPO with similar magnification. The presence of voids can be observed clearly indicating region of accumulate EPO in PHA matrix. The voids formed due to inhomogeneous dispersion between PHA and EPO which contribute to low Young’s modulus. Therefore better dispersion of EPO in PHA at lower EPO loading compare to high EPO.

Fig. 3 FESEM image for 3wt% EPO in PHA blend

Fig. 4 FESEM image on fracture part of sample with 4 wt.%

4. SUMMARY

The optimum composition for EPO is 3% with Young’s modulus of 890 MPa and low value of tensile strength. The efficiency of EPO loading as plasticizer was higher in order 3 wt.% > 5 wt.% > 2 wt.% > 1 wt.% > 4 wt.%. The tensile strength of PHA decrease as the composition EPO increase and at 3 wt.% EPO content, the tensile strength lower compared to neat PHA. The relation of Young’s modulus to tensile strength indicate wide range of elastic region for PHA at this composition. This indicates high rigidity of PHA with 3 wt.% EPO.
REFERENCES


Plasticizer for Liquid Polymeric Membrane of Ion Selective Electrode Based on Thiazole Derivatives as Ionophore

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ABSTRACT. Ion selective electrode (ISE) is an electrode that has been designed to identify heavy metal ion in a solution. In this experiment, thiazole-4-carboxamide (Th) is used as ionophore and sodium tetraphenylborate (NaTPB) as an additive. Polyvinyl chloride (PVC) was used as a polymeric matrix in the membrane selective electrode. Different type of commonly used plasticizers is analysed to choose the one with the best response. There are four types of plasticizer used; dioctyl phthalate (DOP), dibutyl phthalate (DBP), benzyl acetate (BA) and nitrobenzene (NB). The ratio (w/w)% used for all plasticizers Th:PVC:NaTPB:Plasticizer is 5.0:30.0:2.0:63.0. ISE is used in a sample solution with different concentration to figure out the best plasticizer. Ion selective membrane using BA gives the best response with 19.3±1.4 slope value, while ion selective membrane using DOP gives the least response with 11.3±0.7 slope value.

Keywords: Plasticizer, Polymeric membrane, Ion selective electrode, Ionophore;

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Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Ion Selective Electrode (ISE) has been widely used in many types of research for years. ISE is a sensor with a membrane that has potential to select specific ion and known as specific ion electrode. It indicates the activity of the ion dissolved in a solution and converts it into an electrical potential. There are four types of ISE which are glass membrane electrode, solid state electrode, liquid membrane electrode and gas sensing electrode. Liquid membrane electrode is designed using ion selective membrane as a main part of the electrode. The advantages of using liquid membrane are due to its high selectivity, efficient and effective.

In addition, specific molecular recognition can be achieved with the aid of suitable ion carriers for the transport mechanism [1]. Fig. 1 shows the components of ISE consist of four parts, which are the body, the electrode, inner solution and at the bottom which is the main part, the liquid membrane.

The liquid membrane is made of four components; polymeric matrix, ionic additive, ionophore, and plasticizer. It is generally accepted that the components of the membrane, such as the carrier, ionic additives, and plasticizer influence the response and lifetime of the electrode [2]. Table 1 shows all of the membrane's component and its function.
Fig. 1 Ion Selective Electrode (ISE)

Table 1 The component of the liquid membrane and its function

<table>
<thead>
<tr>
<th>Component</th>
<th>Compounds</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric membrane</td>
<td>Polyvinyl chloride (PVC)</td>
<td>To provide elasticity properties in the membrane</td>
</tr>
<tr>
<td>Ionic additive</td>
<td>Sodium tetraphenylborate (NaTPB)</td>
<td>To induce a selective response when there is insufficient ionophore amount is present [1]</td>
</tr>
<tr>
<td>Ionophore</td>
<td>Thiazole-4-carboxamide (Th)</td>
<td>As an ion exchanger</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>Diocetyl phthalate (DOP), Dibutyl phthalate (DBP), Benzyl acetate (BA), Nitrobenzene (NB)</td>
<td>To increase the plasticity or fluidity of the membrane</td>
</tr>
</tbody>
</table>

Fig. 2 shows a structure of thiazole-4-carboxamide (Th) that act as ionophore in this experiment. The ideal plasticizer should have the following properties: softens the PVC membrane, solubilizes the ionophore, insoluble in water, and is inert with respect to ion exchange [3]. The plasticizers must have plasticity or fluidity properties to be physically compatible with the polymer, so as to give a homogeneous organic phase [4]. In contrast, the plasticizer must have solubility properties to be compatible with the chosen ionophore. These plasticizers must be fulfilled the four criterias such as high lipophilic, soluble with no crystallize formed,
no exudation and give a better selective behavior of ISE [5]. The appropriate plasticizer to use in the sensor membrane specifies that the lipophilicity of the plasticizer should be as close as possible to that of the ionophore [3].

![Fig. 2 Structure of thiazole-4-carboxamide (Th)](image)

![Fig. 3 The structure of plasticizer (a) Dioctyl phthalate (DOP), (b) Dibutyl phthalate (DBP), (c) Benzyl acetate (BA) and (d) Nitrobenzene (NB)](image)
DOP is an ester of phthalic acid that appears as a light colored, odorless liquid and is used as a plasticizer for many resins and elastomers. DOP has good stability to heat and ultraviolet light, excellent resistance to hydrolysis and has a broad range of compatibility. DOP also insoluble in water and can be used as softening agent, because of its good plasticizing properties; can make long polymers molecules to slide against one another. DBP is in the same phthalate group with DOP, which is an ester and light colored, odorless liquid. DBP has the same properties with DOP; insoluble in water and can be used as softener mainly in adhesives, lacquers, varnishes and printing inks. DBP appears to have relatively low and chronic toxicity.

BA is an ester formed by condensation of benzyl alcohol and acetic acid. It from Benzylolcarboxyls family; organic compounds that containing a carbonyl group substituted with a benzylolxyl group. BA can be found naturally in many flowers. It appears as a colorless liquid with an odor of pears and has a very low solubility in water. Whereas NB that emits toxic fumes of nitrogen oxides upon combustion is a yellowish, oily, aromatic nitro-compound with an almond-like odor. It's very slightly soluble in water but freely soluble in ethanol, ether, acetone and benzene. Fig. 3 shows the structure of each plasticizer. All these plasticizers are used in the experiment to choose the most suitable plasticizer for ISE. Although the rate ion exchange of plasticizer is small compared to the rate ion exchange of ionophore, the plasticizer is important in the membrane as it does not just soften the membrane but it also helps to increase the selectivity of ISE without interfering with ion exchange of ionophore. The plasticizer in the membrane also had a large effect on sensitivity, selectivity and usable service life [3]. The objective of this study is to select the best plasticizer from a various range of plasticizers (dioctyl phthalate (DOP), dibutyl phthalate (DBP), benzyl acetate (BA) and nitrobenzene (NB)) for ISE with thiazole-4-carboxamide (Th) as an ionophore using Cd(NO₃)₂ solution as analyte.

2. MATERIALS AND METHODS

2.1 Electrode Preparation. A 100 mg liquid membrane is prepared with a ratio 5.0:30.0:2.0:63 for Th:PVC:NaTPB:plasticizer. All of the components are measured respectively in 100 ml of beaker before completely dissolved in 5 ml of THF. Then, a PVC tube is dipped in the solution until a nontransparent membrane is formed at the bottom of the tube. The tube was kept for 24 hours at room temperature before finally conditioned it in the sample solution for 20 hours or until it gives a stable reading [6].

The membrane is conducted in cell assembly Ag/AgCl| KCl (3 mol/L)| internal solution (1.0 × 10⁻¹ mol/L Cd(NO₃)₂)| membrane| sample solution| reference electrode to measure the potential difference of the electrode. An Extech EX420: 11 function professional multimeter was used to measure the potential at 21±1 °C.

2.2 Sample Preparation. 7.71 g of Cd(NO₃)₂ powder is dissolved using deionized water in a 200 ml beaker and diluted to 250 ml volumetric flask labelled as A (1.0 × 10⁻¹ mol/L Cd(NO₃)₂ solution). Pipette 25 ml solution A before diluted with deionized water in 250 ml volumetric flask and labelled as B (1.0 × 10⁻² mol/L Cd(NO₃)₂ solution). The dilution process is accordingly to 1.0 × 10⁻³ mol/L Cd(NO₃)₂ solution, 1.0 × 10⁻⁴ mol/L Cd(NO₃)₂ solution, 1.0 × 10⁻⁵ mol/L Cd(NO₃)₂ solution, 1.0 × 10⁻⁶ mol/L Cd(NO₃)₂ solution, and 1.0 × 10⁻⁷ mol/L of Cd(NO₃)₂ solution and labelled as G.

3. RESULTS AND DISCUSSIONS

Four sensors have been prepared using same ratio and ionophore for the membrane, each sensor gives a different response behavior. The typical composition of solvent polymeric membranes is 30-33% (w/w) PVC and 60-66% of a plasticizer [1,4]. The sensitivity and selectivity of the ion selective electrodes depend significantly on the membrane compositions [7]. Addition of appropriate amount of plasticizer leads to
improve the electrochemical properties of conventional ISEs [6]. The right plasticizer leads to a better polymeric membrane and can form a high selectivity ISE. Fig. 4 shows a graph of the potential difference of ISE against log concentration of sample solutions.

![Graph of E/mV vs log concentration](image)

**Fig. 4** Graph of E/mV vs log concentration

The graph shows four different slopes; DOP, DBP, BA and NB. The potential difference between the liquid membrane and the sample solution were plotted in the graph. The slope indicates the reaction of ion in the sample solution with the liquid membrane. Different slopes are patterned as a different content of liquid membrane are used. All ISE used was labelled as Sensor No.1 for Th:PVC:NaTPB:DOP; (5.0:30.0:2.0:63.0), Sensor No.2 for Th:PVC:NaTPB:DBP; (5.0:30.0:2.0:63.0), Sensor No.3 for Th:PVC:NaTPB:BA; (5.0:30.0:2.0:63.0) and Sensor No.4 for Th:PVC:NaTPB:NB; (5.0:30.0:2.0:63.0) in Table 2. The slope value and linear range are recorded.

<table>
<thead>
<tr>
<th>Sensor No.</th>
<th>Composition [wt.%]</th>
<th>Slope [mV/decade]</th>
<th>Linear range [M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVC:30 DOP:63 NaTPB:2 Th:5</td>
<td>11.3±0.7</td>
<td>1.0 \times 10^{-6} to 1.0 \times 10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>PVC:30 DBP:63 NaTPB:2 Th:5</td>
<td>11.7±0.8</td>
<td>1.0 \times 10^{-6} to 1.0 \times 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>PVC:30 BA:63 NaTPB:2 Th:5</td>
<td>19.3±1.4</td>
<td>1.0 \times 10^{-6} to 1.0 \times 10^{-2}</td>
</tr>
<tr>
<td>4</td>
<td>PVC:30 NB:63 NaTPB:2 Th:5</td>
<td>12.4±1.2</td>
<td>1.0 \times 10^{-7} to 1.0 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Sensor No.3 has the highest slope compared to others sensor. The highest slope is 19.3±1.4 with 1.0 \times 10^{-6} to 1.0 \times 10^{-2} of working range. While Sensor No. 1 has the lowest value, 11.3±0.7 with 1.0 \times 10^{-6}...
to $1.0 \times 10^{-4}$ of working range. As the highest slope indicates the high response in the sensor, Sensor No.3 which is BA has the best response compared with other sensors.

The result clearly shows the effect of the plasticizer in ISE. When a plasticizer is added, the free volume of the polymeric chain is expanded, making penetration of an analyte easier, increasing its interaction with the sensing phase [8]. The nature of plasticizer affects the response characteristics of the electrode, due to its influence on the dielectric constant of the membrane phase, the mobility of ionophore molecules and the state of the ligand [4].

4. SUMMARY

A sensor that made up with a membrane containing ionophore is adequate to form a sensor that works properly. However, choosing a compatible plasticizer is important to get the best selective sensor. From the experiments, it is found that BA is the best plasticizers as it responded well as compared to the other plasticizers.

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Preliminary Development of Laminated Nanocomposite from Nanocellulose-Kevlar for Military Application

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\textbf{ABSTRACT}. Generally, aramid fibre used in industries reportedly possesses high mechanical strength with high modulus, toughness and thermal stability. There is a high demand for eco-friendly, renewable and low cost materials. The demand also affects the production of Kevlar within Kevlar based industries. Previous studies found that cellulose has the capability to improve the performance of a composite. The objective of this study is to investigate the mechanical strength of cellulose micro or nano fibres (CMNF) in laminate cellulose or Kevlar reinforced epoxy resins. The composite material was fabricated manually using hand lay-up technique. The nanocomposite laminates were made using plain fibre (Kevlar 29). The laminates contained a minimum of 80% fibre with 1 wt.% CMNF powder loading in an epoxy resin. Tests were conducted on two types of sample: Kevlar/Epoxy (KE), and Kevlar/CMNF/Epoxy (KEC). The laminated composite material was found to have the highest stress-strain in Kevlar/CMNF/Epoxy (KEC). The material strength and tensile behaviour of the two types of sample are different where KEC (559.34 MPa) > KE. This study is a part of the exploration on potential applications of laminated composite in military applications.

\textbf{Keywords}: Kevlar 29, Kevlar 29 reinforced epoxy, Laminate composite, Nanocellulose;

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\textbf{DOI}: 10.30967/ijcrset.1.S1.2018.566-570

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1. \textbf{INTRODUCTION}

Aramid fibre is a synthetic polyamide made up by the linkage of an amino group of one molecule and a carboxylic acid group of another. Nylon is an example of many synthetic fibres available in the market. Aramid is a super strong material which can stop bullets and knives from going through. The strength of aramid is five times stronger than steel at the same weight. Technically, aramid fibres are long-chain synthetic polyamides. These fibres have extremely high tensile strength, which is why they are commonly used in armor and ballistic protection applications.

Generally, aramid is mostly used in composite material form. It is mostly applied in the production of products such as sports equipment, vehicle parts, building materials, safety apparatus and military equipment. The various composite materials can be classified using several methods based on their usage. Several studies that focused on the type of composite materials have been conducted, such as the study on fibre-reinforced polymer composites, in which continuous thin Kevlar 29 as the aramid fibre are embedded.
in a polymer matrix [1]. The reinforcement is carried out to enhance the strength, stiffness, fatigue strength, resistance, or strength to weight ratio by incorporating strong and stiff fibres in a softer, more ductile matrix.

Based on previous studies, many researches were carried out on the usage of fibre reinforced polymer composite to improve the mechanical properties of the composite [2,3]. However, there is a lack of published information of cellulose reinforced fibre composites used in military applications. The objective of this paper is to uncover the mechanical properties of nanocellulose combined with Kevlar to be applied in the production of military helmet. In most of the previous studies, multiple layers of Kevlar were used in the helmet, making it heavy. The performance of the composite can be optimized and the behaviour of the sample can be enhanced using laminate or hybrid composites [4,5]. Hand lay up technique is used in the characterizations of the laminate. There are several studies available on the characterization of Kevlar or carbon combination fibre in sandwiched composite [6], cellulose nanofibres or epoxy composite [7], and woven jute or green epoxy composites [8]. Jabbar et al. [8] reported that nanocellulose has the potential in military applications because it can improve the performance of the composite thus increasing its mechanical properties.

2. MATERIALS AND METHODS

2.1 Materials. The materials employed in this study are nanocellulose prepared from rice straw (similar to our previous work [9]), Kevlar 29 fabrics and epoxy resin supplied by Oriental Option Sdn. Bhd. The cellulose and fabric used are shown in Figs. 1 and 2.

![Cellulose from rice straw](image1)

*Fig. 1 Cellulose from rice straw*

![Fabric of Kevlar 29](image2)

*Fig. 2 Fabric of Kevlar 29*

2.2 Preparation of Nanocellulose.

The micro or nano cellulose is extracted from rice straws which were collected from a local paddy field in Ulu Derdap, Perak, Malaysia. The rice straw sample is cut into small pieces of approximately 5 cm chips. The sample is weighed wet to ascertain its moisture content and dried in a vacuum oven at 30 °C for 24 hours. The extraction procedure involved swelling, acid hydrolysis, alkaline treatment and bleaching to obtain the final nano or micro cellulose.
2.3 **Preparation of Nanocomposite Laminated Sample.** The composite is prepared by hand lay up method. The polymer resin used is epoxy; the epoxy and hardener are mixed in a ratio of 2:1 by weight, according to the manufacturer’s recommendations for hand lay up process. The nanocomposite laminate are made using plain fibre (Kevlar 29) and laminated with epoxy or nanocellulose matrix. The laminate comprised a minimum of 80% by weight of fibre and the nano or micro cellulose loading is 1 wt.%. The fabric is then cut into pieces of 200 mm x 200 mm in size to produce the composite laminate. The micro/nano cellulose are mixed with epoxy by using mechanical stirrer less than 1 hour before lay up at the fabric of Kevlar fibre. The laminated composite will hardened at least 24 hours.

2.4 **Tensile test setup.**

Tensile test is performed following the ASTM D3039 test standard on a 160 mm x 25 mm x t (thickness of the laminate) sample, with a gauge length of 60 mm. The test is performed at a crosshead speed of 3 mm/min with 50 kN load. Five bone shaped samples are prepared for each composite laminates and each sample is tested in vertical direction.

3. **RESULTS AND DISCUSSION**

3.1 **Laminated Composite.** Two types of sample were prepared. The first type consists of Kevlar 29/Epoxy/micro-nanocellulose, and the second type is Kevlar 29/Epoxy, acting as a reference sample. The laminated composites are shown in Fig. 3.

3.2 **Tensile test.** The engineering stress-strain response of a material is shown in Fig. 4 and the tensile properties of the different composite laminates are given in Table 1 and Table 2. It showed that KE has lower tensile modulus compared to KEC. From the different types of composite laminate materials used, it was found that the composite reinforced with nanocellulose improved the strength of the laminate. It was proven in previous studies that even a minimal amount of cellulose is able to increase the mechanical performance of a composite [10].

![Fig. 3 Laminated composite](image)

**Table 1** Thickness of both fabricated composite laminates
<table>
<thead>
<tr>
<th>Composite laminate</th>
<th>No. of layer</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 29/Epoxy (KE)</td>
<td>1</td>
<td>0.44</td>
</tr>
<tr>
<td>Kevlar 29/Epoxy/1%CMNF(KEC)</td>
<td>1</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 2 The mechanical strength of both fabricated composite laminates

<table>
<thead>
<tr>
<th>Composite laminated</th>
<th>Tensile strength (MPa)</th>
<th>Elastic modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KE</td>
<td>316.51</td>
<td>425.10</td>
</tr>
<tr>
<td>KEC</td>
<td>559.34</td>
<td>776.02</td>
</tr>
</tbody>
</table>

Fig. 4 The stress-strain curve composite laminates: Kevlar 29/Epoxy/micro-nanocellulose (KEC), and Kevlar 29/Epoxy (KE) The strength of various Kevlar 29 samples with varied composition matrix used in this study is shown in Table 2. It was observed from Fig. 4 that KEC showed the highest mechanical strength of 559.34 MPa tensile strength; and 776.02 MPa elongation at break. This is because the sample contained 1 wt. % of CMNF powder, which improved its strength compared to KE. By adding approximately 1 wt.% of CMNF powder in the KEC sample, the mechanical or tensile strength of the composite improved up to 559.34 MPa compared to the KE sample (without the addition of cellulose) with tensile strength value of 316.51 MPa. The tensile strength of the Kevlar 29 reinforced sample is 60% higher than non-reinforced samples. It is because of the CMNF powder as filler are fulfill the gaps between of the particles and fill in the porosity. From Table 2, it can be seen that laminated composite with CMNF has higher elasticity. It also shows the elastic modulus of KEC increased by 45% compared to the KE laminated composite.

In addition, the laminated composite materials can be differentiated by the crack length of its sample. The crack length of KE is 0.5 mm while KEC is 2.2 mm. Thus, it is proven that Kevlar 29 laminated composite reinforced resin can increase the time and displacement of the laminated composite crack.

Furthermore, for the nano or micro cellulose wt.% loading, the composite strength increases with decreasing particle size. Smaller particles have a higher total surface area for a given particle loading. This indicates that the strength increases with increasing surface area of the filled particles through a more efficient stress transfer mechanism.

4. SUMMARY

In conclusion, this study discovered that the inclusion of cellulose micro or nano fibres in laminated cellulose or Kevlar 29 reinforced epoxy improved the mechanical properties of laminate composite.
study explores the potential application of the laminated composite in high velocity impact applications. This research can also be directed to optimize the mechanical properties of the composite, making it higher in strength yet light in weight. The lay-up technique was used for the composite reinforcement sorting to obtain the most optimized result. In comparison with the other materials used, this research demonstrated the favorable potential usage of nanocellulose in a composite as the stress-strain result showed that it has improved the performance of the laminated composite.

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This research is carried out in collaboration with Universiti Pertahanan Nasional Malaysia (UPNM), and members of UPNM X-Ray research group. The authors would also like to acknowledge the financial support by The Ministry of Higher Education under the Niche Grant Scheme (NRGS), NRGS/2013/UPNM/PK/P1.

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Effects of Banana Skin Powder on Properties of Jackfruit Seed Starch/Poly(Vinyl Alcohol) PVA Film

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ABSTRACT. Biodegradable jackfruit seed starch (JFSS)/poly (vinyl alcohol) (PVA) films reinforced with different amount of banana fruit skin powder (BSP) were produced via solution casting method. This study aims to investigate the effect of BSP on the properties of JFSS/PVA films. The blend ratio between JFSS and PVA was fixed at 4:3 wt.% while the composition of BSP was varied from 1 to 2.5 wt.%. The mechanical and physical properties of the composite films were investigated. From the analysis, the optimum blend ratio of JFSS/PVA is achieved at maximum tensile strength 10.90 MPa with 1 wt.% BSP. The results of mechanical properties were supported by scanning electron microscope (SEM) in which the banana skin powder is properly wetted by the JFSS/PVA blend, thus indicates the good interaction within the blend. The reinforcement of BSP into JFSS/PVA blend films has also resulted in the existence of hydrogen bonding interaction evidenced by Fourier transform infrared spectroscopy (FTIR) spectra and increase the percent weight loss of the film over time through soil burial test, hence, proved its biodegradability.

Keywords: Starch/PVA blend, Banana reinforcement, Biodegradable, Composite films;

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1. INTRODUCTION

One third of the plastics produced today are used for packing purposes which will be quickly discarded. The plastics will be accumulated in landfills and causes threat to the environment [1]. From the environment point of view, biodegradable materials have been rapidly developed in the past years. PVA is one of the biodegradable synthetic polymers commonly used, but, its degradation rate is slow. As an alternative to reduce the plastic waste and accelerate the degradation process, PVA frequently blended with other natural polymers to improve its biodegradability. The natural polymer such as starch has high potential in enhancing PVA biodegradability by blending both components. Starch is renewable, inexpensive, biodegradable and abundantly available especially from agriculture field [2]. The usage of starch extracted from agriculture wastes such as jackfruit seed is quite promising, since it does not interrupt food chain and may add value to the starch as well [3]. The blend of starch extracted from fruit seeds and PVA is assumed able to increase biodegradation rate of composite film formed. Adding starch to PVA, however, may reduce its original mechanical properties, hence, the film is reinforced with fruit skin powder as filler to further improve its properties. Currently, natural fibers are gaining so much attention to act as filler or reinforcement in a matrix material because they are eco-friendly, low in cost, abundantly available resources and renewable. In this study, banana skin is utilized as it is considered as one of agricultural waste. Having said that, this natural fiber can be easily obtained from banana skin as the reinforcement for composite material in order to improve its mechanical properties [4].
Therefore, the main objective of this study is to develop biodegradable composite film of poly (vinyl alcohol) (PVA) blended with jackfruit seed starch (JFSS) and reinforced with banana fruit skin powder (BSP) for packaging applications via solution casting method. The relationship between the amount of reinforced fruit skin powder with starch/PVA in composite film on mechanical and physical properties was evaluated. Finally, biodegradability studies through soil burial test were performed to investigate the effect of incorporating reinforcement of BSP in the films degradation.

2. EXPERIMENTAL METHOD

2.1 Preparation of Starch/PVA Reinforced Banana Skin Composite Film. The starch/PVA blend films were prepared via solution casting method proposed [5] with minor alteration. The ratio of starch to PVA was fixed at 4:3 wt.%, while the amount of BSP were varied from 1 to 2.5 wt.% with total mass of the system is 100 g. First, 3 wt.% PVA was dissolved in distilled water was heated up to 95 °C. Then, 4 wt.% starch was added to the mixture and stirred continuously at about 70 °C to ensure the solution is homogeneous. Finally, the films solution was casted over an acrylic plate and oven dried at 35 °C for 24 hours. The films were peeled off and stored in the desiccator maintained at 23 °C and 30% relative humidity prior to characterization. The steps were repeated by adding different weight percent of banana skin powder. Table 1 illustrates the ratio of PVA, jackfruit seed starch and banana skin powder in sample preparation.

2.2 Tensile Test. The mechanical properties of the composite films such as tensile strength and percent of elongation were evaluated using universal testing machine (Shimadzu; Material Testing System) based on ASTM Standard D882-02 at 20 mm/min of speed under load of 5 kN. Samples of composite film with dimension of 70 mm × 10 mm were cut according to ISO-527.

2.3 Scanning Electron Microscope (SEM) Test. The surface structures of the JFSS, BSP, starch/PVA film with and without reinforcement of BSP were observed using a scanning electron microscope (JEOL, Model JSM 5600 SEM; JEOL Ltd., Tokyo, Japan). The samples were sputter coated with carbon (Polaron SC515) and observed under the SEM at a voltage of 5 kV and 10 kV.

2.4 Fourier Transform Infrared Spectrometry (FTIR) test. Fourier transform infra-red (FTIR) spectra of the BSP, PVA film, starch/PVA film with and without reinforcement of BSP were recorded on FTIR spectrometer (Spectrum 100 FTIR; Perkin Elmer, United States). Measurements were obtained between 4000 cm⁻¹ to 600 cm⁻¹ at a resolution of 4 cm⁻¹ with average of 32 scans per sample.

2.5 Soil Burial Test. Biodegradability of the starch/PVA blend films with and without reinforcement of BSP were investigated through soil burial method [6] with slight modifications. Samples were cut to dimension of 20 mm × 20 mm and the initial mass are recorded. Then, the samples covered with plastic net and placed in...
pots containing soil for 20 days with exposure to natural weathering. Each sample are taken for measurement at interval of 5 days for 20 days, dried and weighed on the electronic mass balance. The weight loss of the sample over time was calculated using Eq. 1.

\[
Weight\ loss\ (\%) = \frac{w_i - w_d}{w_i} \times 1
\]

where \( w_i \) is the initial weight of the sample and \( w_d \) is the weight of the sample after 5 days.

3. RESULTS AND DISCUSSION

The addition of BSP as reinforcement greatly affect the tensile strength (TS) and elongation at break (E%) of starch/PVA film. Fig. 1 shows the effect of increasing BSP on mechanical properties of starch/PVA films.

![Graph](image)

**Fig. 1** Effect of increasing banana skin powder content on tensile properties of starch/PVA films

Reinforcement of starch/PVA films with 1 wt.% BSP improves both TS and E%. The TS of film increased by more than 4% which is from 10.45 MPa to 10.90 MPa. At the same time, the E% significantly increased by 59% with addition of 1 wt.% BSP which is from 2.28% to 3.63%. This is because the banana fiber gives strong adhesion between the phases in starch/PVA, thus, provides better intermolecular interactions between starch molecules and fiber or fiber and PVA [5]. However, further addition of BSP more than 1 wt.% deteriorated both TS and E% of starch/PVA film. This is probably due to the agglomeration of the banana fiber, thus, reduce the attachment between the fibers and the starch/PVA that causes by the reduction of wettability of the fiber [7]. The results obtained are supported by morphological structure observed under SEM. The morphology of JFSS granules and BSP (magnification of 1000x), PVA, starch/PVA and reinforced BPS starch/PVA films (magnification of 100x) were presented in Fig. 2. Fig. 2(a) revealed the starch granules have varied round and irregular shape with smooth surface [8]. Meanwhile, Fig. 2(b) revealed the BSP has long entangled structure of fiber with rough surface which is expected to provide strong adhesion when reinforced to starch/PVA blend [9]. Fig. 2(c) shows morphology of unfilled PVA film is smooth and
transparent without any addition of starch. As a result from blending starch with PVA, Fig. 2(d) demonstrates good interactions between starch and PVA. The blend is well dispersed, less agglomerate and no formation of voids occur. Fig. 2(e) illustrates the addition of 1 wt.% BSP result in properly wetted fiber with starch/PVA film, hence gives good interaction between the fiber and starch/PVA. Adding more than 1 wt.% BSP promotes formation of voids and agglomeration of the granules as shown in Fig. 2(f-g). When 2.5 wt.% of BSP is added, formation of crack can be observed. This is due to more fiber for film reaction and bigger void is formed due to pull out from agglomerated BSP as shown in Fig. 2(h).

Fig. 2 SEM micrographs of (a) jackfruit seed starch, (b) banana skin fiber, (c) PVA, (d) S-PVA, (e) S-PVA-BSP1, (f) S-PVA-BSP1.5, (g) S-PVA-BSP2 and (h) S-PVA-BSP2.5

The FTIR spectra of BSP, PVA, S-PVA and S-PVA-BSP1 are shown in Fig. 3(a-d), respectively. Fig. 3(a) shows the broad peak at 3274.02 cm\(^{-1}\) correspond to O-H stretching related to intramolecular hydrogen bonds of cellulose while the small peak at 2917.83 cm\(^{-1}\) represents C-H bond stretching in cellulose and hemicellulose of the banana skin. The peak of 1732.21 cm\(^{-1}\) and 1012.06 cm\(^{-1}\) indicate the C=O stretching and O-H bond, respectively. The results of FTIR spectrum obtained for BSP is in agreement with the study reported [9] which confirmed that banana skin is one of the cellulosic fibers.

Furthermore, all spectra in Fig. 3(b-d) exhibit the characteristic absorption bands of pure PVA which are 3274, 2919, 1732 and 1243 and 1087 cm\(^{-1}\) which correspond to O-H stretching, C-H stretching, C=O stretching, and C-H wagging of PVA, respectively. These peaks also existed in the FTIR spectra of starch/PVA.
blends shown in Fig. 3(c), indicating the success of blending of PVA with starch. Fig. 3(b,c) show the peak intensity reduce with incorporation of starch in PVA. The peak was shifted from 1732.21 to 1715.94 cm\(^{-1}\) and from 1087.95 to 1019.88 cm\(^{-1}\) which means that the C-O in C-O-H group of starch and C=O stretching was involved in the hydrogen bond formation, respectively. This can be concluded that the FTIR analysis for starch/PVA blend showed that more stable hydrogen bond can be formed.

Furthermore, incorporation of banana fiber reinforcement in starch/PVA blend in Fig. 3(d) shifted the characteristic peak from 1715.94 to 1732.52 cm\(^{-1}\) was wider and less intense with incorporation of starch and banana fiber. This indicated that there is O-H that is more easily vibrate, hence more O-H forming hydrogen bond. The change in peak intensity at 3274 cm\(^{-1}\) confirmed the number of the hydroxyl groups rises due the interaction of fiber with starch/PVA blend [10]. It is believed that the formation of hydrogen bond based on the FTIR spectra is correlated with the mechanical properties and biodegradability rate of film.

![FTIR spectra](image)

**Fig. 3** FTIR spectra for (a) banana skin powder, (b) PVA, (c) starch/PVA and (d) reinforced starch/PVA films

The biodegradability behavior of non-reinforced and reinforced starch/PVA loss and macroscopic appearance shown in Fig. 4(a,b), respectively. The degradation behavior of the films is dependent on the presence of banana fiber reinforced in the starch/PVA blend. The graph shows that, starch/PVA blend has the highest biodegradability rate than reinforced starch/PVA blend films. The blend films incur the highest weight loss at 27.42% probably due to the hydrophilic nature of starch itself. Hydrophilicity increase water absorbability, hence, increase degradation. It is believed that the white spot on the surface of the samples are the microorganisms since starch is their source of food, hence, causing the biodegradability behavior of the samples. In fact, the degradability also can be related with its appearance which is diminished in size which contributed to the weight loss of the samples. Moreover, addition of BSP reinforcement improved properties of the starch/PVA blend film as a whole. Both banana skin and starch are hydrophilic and polar. Incorporation of both components is believed to resist water due to formation of hydrogen bonding between starch and banana skin fiber evidenced by FTIR analysis. Thus, better hydrogen bonding reduced susceptibility of blend film to water [10]. It can be concluded that the weight loss of the starch/PVA films at 20 days proved that they are biodegradable.
Fig. 4 Biodegradation of non-reinforced and reinforced starch/PVA films (a) weight loss, and (b) macroscopic appearance after buried in soil for 20 days

4. SUMMARY

This study has shown that banana skin powder effectively reinforced jackfruit seed starch/PVA blend film. Reinforcement of 1 wt.% banana skin powder has achieved the maximum strength of 10.90 MPa. The morphological structure of the film revealed the banana skin powder is well distributed within the blend by the appearance of peak indicating hydrogen bond. In addition, the composite films showed their degradability in soil environment, but considerably decreased the weight loss as reinforcement is incorporated.

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Characterization and Preparation of Polyvinyl Alcohol (PVA) as Inhibitor in Formation of Hydrates
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ABSTRACT. The thermal properties of PVA with different degree of hydrolysis (DH) was studied by preparation of aqueous polymer solution, followed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The DSC result showed the typical partially crystalline materials, showing some phases of separation are characterized by a glass transition ($T_g = 25$-$26 \degree C$) related to the amorphous part of the material, followed by two endothermic peaks related to the melting point ($T_m = 185$-$225$) of the crystallites. Due to the same material (PVA) used, the main composition temperatures are close to each other (for peak I between 320 K and 350 K, and for peak II between 429 K and 430 K). Finally, FTIR confirmed that between the three materials P 100, P 87 and P 85, there were distinctness in the band absorbed between fully hydrolysed PVA, P 100 and partially hydrolysed PVA, P 85 and P 87.

Keywords: Poly(vinyl alcohol), Degree of hydrolysis, Polymer characterization, Kinetic hydrate inhibitor;

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1. INTRODUCTION
Gas hydrate is an ice-like crystal composed of light gases such as methane, nitrogen and carbon dioxide, and it can be formed at a specific temperature and pressure condition. The formation of these hydrates can cause serious plugging inside the oil and gas pipeline [1]. Conventional method of removing hydrates is called thermodynamic hydrate inhibitor (THI) and this method uses a large dosage of chemical to shift the hydrate equilibrium curve to lower the temperature. Meanwhile, the alternative method for THI is the low dosage hydrate inhibitor (LHDI), whereby it is developed and the dosage intake is below 1 wt.%. There are two types of LHDI, which are kinetic hydrate inhibitor (KHI) and anti-agglomerant (AA). KHIs function is to inhibit and delay the nucleation of hydrate formation, whereas AAs keep the hydrate particles agglomerated in small particles. Previously tested KHIs polymers in several other researches are polyvinylcaprolactam (PVCap), polyvinylpyrrolidione (PVP), polyacrylamide (PAM) and more. Despite the abundance of research done on KHIs, the mechanisms of hydrate inhibition are not fully understood. Only several mechanisms [2-4] have been proposed. It is necessary to fully understand the properties of the polymer first in terms of molecular
organisation and composition to predict the interaction between the hydrate and inhibitor. In this way, the significant knowledge gap can be filled [5], where the general ideas of hydrate inhibition is known to be by the KHI’s polymers absorbing onto the hydrate surface crystals to prevent the complete formation of hydrate. Poly(vinyl alcohol) (PVA) is extensively used in industries in diverse applications such as biopolymer film, coating industry, food processing, medical industries, and it has also been used as hydrate inhibitor in oil and gas industries. PVA is a synthetic water-soluble polymer. Its backbones are composed only of carbon atoms, which are biodegradable [6-9] under both aerobic and anaerobic conditions. In order to study the KHIs polymer adsorption process, it is important to look on the pendant group existing on the polymer itself. For example, some of the previous studied KHIs such as PVP and PVCap show a strong KHI performance associated with the amide pendant group, whereby it is prone to adhere because of its hydrophilic properties [10,11]. Similar process goes with PVA. PVA is prepared via hydrolysis of polyvinyl acetate. There are two types of PVA, fully hydrolysed and partially hydrolysed. Different degree of hydrolysis (DH) of PVA is the result of incomplete hydrolysis reaction of PVA. Through several methods of characterisation, the behaviour of KHIs polymer adsorption can be predicted. For these reasons, PVA was chosen as inhibitor to study the effect of different degree of hydrolysis (DH) of PVA and what it may contribute through the polymer-water interaction. Therefore, in this research paper, characterization methods such thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) were used to predict the structural behaviour and interaction of the PVA inhibitor.

2. MATERIALS AND METHODS

Polyvinyl alcohol, fully hydrolysed (degree hydrolysis of 99%, molecular weight MW = 145,000 g/mol), polyvinyl alcohol, partially hydrolysed (degree hydrolysis of 87%, molecular weight MW = 70,000 g/mol), polyvinyl alcohol, partially hydrolysed was acquired from Merck Millipore Singapore. Distilled water was used to prepare the aqueous solution. The solution concentration is in weight per hundred (%). A total of 10 samples of varying concentration (wt.%) were prepared from 0.1-1.1%.

| Table 1 Sample composition and molecular weight (Mw) |
|-----------------|-----------------|-----------------|
| Samples class   | Degree of hydrolysis (%) | Molecular weight (Mw) |
| P 85            | 85               | 70,000          |
| P 87            | 87               | 70,000          |
| P 100           | 100              | 145,000         |

2.1 Fourier transforms infrared spectroscopy (FTIR). A Perkin Elmer Spectrum One FTIR spectrometer equipped with Spectrum software was used to perform the FTIR analysis. The samples were scanned over the range 14000 to 2100 cm⁻¹ with the best resolution of 0.5 cm⁻¹.

2.2 Thermogravimetric analysis (TGA). Thermal stability analysis was run on a Perkin-Elmer Thermoanalyser in a nitrogen atmosphere. The temperature ranges used were between 0 to 530 °C. The heating rate applied throughout the process was 10 °C/min.

2.3 Differential scanning calorimetry (DSC). The thermal properties of polyvinyl alcohol were performed by the Metler Toledo instrument model DSC1/700. The heating scans were carried out at a heating rate of 10 °C/min from 0 to 530 °C.

3. RESULTS AND DISCUSSION

3.1 Differential scanning calorimetry (DSC).
The DSC thermograms obtained showed 3 peaks. The first peak was not very significant, it presented dehydration of water that were used as solvent. It also showed a glass transition (Tg) occurring between 20 to 27 °C (Table 2), related to the amorphous part of the material. The second peak refers to the melting of the crystalline phase which is in relation to the melting temperature (Tm) of the crystals. The last peak referred to the decomposition of residual acetate group. Fig. 1 shows the DSC results of pure PVA at different degree of hydrolysis (DH). The melting temperature of P100, P87 and P85 were found to be 225 °C, 192.41 °C and 185.08 °C, respectively. Other studies showed that Tm of pure PVA occurred around 191 °C [12]. The melting temperatures of PVA at different DH are found to have increased with an increasing in DH number. At P100, the melting temperature is higher compare to P85 and P87, this is due to more orderly structure of P100 as fully hydrolysed PVA have a symmetrical structure. Whereas, for PVA with lower DH, the lower melting point is due to the less orderly structure of PVA that allow the bond to break easily. From the result, it showed that the same polymer with different DH can produce a different melting temperature range. These different behaviors of PVA from the same group of polymer bring the conjecture that the sample of PVA with different DH are constituted of several fractions of different pendant groups such as acetyl and hydroxyl [13]. These can be proved through FTIR studies, which will be shown in next section.

<table>
<thead>
<tr>
<th>Code</th>
<th>Melting temperature, Tm (°C)</th>
<th>Glass transition, Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P85</td>
<td>185.08</td>
<td>25.86</td>
</tr>
<tr>
<td>P87</td>
<td>192.41</td>
<td>28.75</td>
</tr>
<tr>
<td>P100</td>
<td>225.00</td>
<td>26.02</td>
</tr>
</tbody>
</table>

Fig.1 DSC curves of P100, P87 and P85

3.2 Thermogravimetric analysis (TGA).

The results from TGA are presented in Fig. 2. The deflection temperatures are shown in Table 3. All three results of PVA, P100, P87 and P85 had a slight weight loss in the early stage of thermal analysis, which could be in regards to the loss of moisture and the trapped and adsorbed water by PVA [14]. All samples of PVA with different DH also show the same trend of roughly 2 step of degradation in the whole range of testing temperature. For P 85, the two peaks were observed with a maximum temperatures at 328.56 °C and 429.38
°C. Whereas at P 87, the two peak of maximum temperature were at 328.56 °C and 432.28 °C meanwhile, for P100 are at 356.62 °C and 429.94 °C. The first temperature can be assigned to the side chain of the PVA while the second temperature can be related to a decomposition of the main chain of PVA. The first degradation is corresponding to the dehydration of PVA chains and formation of polyene structure, and the other step was relative to the degradation of the polyene chain [15]. The result showed that higher DH of PVA shows a slightly better thermal stability. It is expected from PVA with a DH higher than 88%. They hardly dissolves in water without added heat compared to the one with a lower degree of hydrolysis [16]. The decrease in number of hydrophobic acetate groups (decrease of DH) increases inter and intra chain hydrogen bonding. Hence, it increases degree of hydrogen bonding between the PVA chains and water molecules that contributed to higher thermal stability with increasing DH.

**Table 3** Degradation temperature of P100, P87 and P85 at peak I and II

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tpeak I (°C)</th>
<th>Tpeak II (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 85</td>
<td>328.56</td>
<td>429.38</td>
</tr>
<tr>
<td>P 87</td>
<td>333.49</td>
<td>432.28</td>
</tr>
<tr>
<td>P 100</td>
<td>356.62</td>
<td>429.94</td>
</tr>
</tbody>
</table>

**Fig. 2** Thermal stability analysis (TGA) curves of (a) P85, (b) P87 and (c) P100

### 3.3 Fourier transforms infrared spectroscopy (FTIR).

Table 4 shows the most evident characteristic band of PVA and their respective assignment. Fig. 3 shows the FTIR spectrum of P100, P87 and P85. All major peaks related to hydroxyl and acetate group were observed. The large bands observed between 3550 and 3200 cm⁻¹ are linked to the stretching O-H from the intermolecular and intramolecular hydrogen bonds (region (a) in Fig. 3). The vibrational band observed between 2840-3000 cm⁻¹ refers to the stretching C-H from alkyl groups (region (b) in Fig. 3) and the peaks between 1720 - 1705 cm⁻¹ (region (c) in Fig. 3) are due to the stretching of carbonyl, C=O from acetate group remaining from PVA. Also in Fig. 3, the FTIR spectrum is only shown for P85 and P87. The intensity of the
1720 - 1705 cm$^{-1}$ is weak for PVAs with high DH, indicating that only a few acetate groups are present in the polymer chain and, whereas the intensity is very strong for PVAs with low DH. For P100, there is no signal in the region of 1720 - 1705 cm$^{-1}$. This might be due to P100 is a highly hydrolysed grades PVA and have a symmetrical PVA molecular structure. These resulted in no change in dipole moment when the carbon-carbon double bond stretches. Meanwhile, the peaks observed between 1260 - 1000 cm$^{-1}$ (region (e) in Fig. 3) belong to the C=O in the carboxylic group. The peak for P85 appears to be increased by twofold compared to P87 due to hydrogen bonding [17]. The C-H group in phenyl ring of P100 is 828.11 cm$^{-1}$, and for P85 and P87, the band shifted towards higher value, suggesting that this is due to asymmetric stretching in CH$_3$ [18].

![FTIR spectra of P 100, P 87 and P 85](image)

**Fig. 3** FTIR spectra of P 100, P 87 and P 85

**Table 4** Chemical group present through analysis

<table>
<thead>
<tr>
<th>No</th>
<th>PVA spectrum</th>
<th>Wave number cm$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>PVA spectrum</td>
<td>Wave number cm$^{-1}$</td>
<td>References</td>
</tr>
<tr>
<td>1</td>
<td>PVA – OH from inter and intra hydrogen bonds</td>
<td>V 3550 – 3200</td>
<td>3265.09</td>
</tr>
<tr>
<td>2</td>
<td>PVA from alkyl groups C – H</td>
<td>V 2840 – 3000</td>
<td>2907.80</td>
</tr>
<tr>
<td>3</td>
<td>PVA, C = O (H bonded) carbonyl</td>
<td>V 1720 – 1705</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>PVA C – O asymmetric stretch</td>
<td>V 1260 - 1000</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>PVA C – O – C ether</td>
<td>V 1150 – 1085</td>
<td>1086.77</td>
</tr>
<tr>
<td>6</td>
<td>PVA CH$_2$</td>
<td>V 1461 – 1417</td>
<td>1419.10</td>
</tr>
<tr>
<td>7</td>
<td>PVA C-H phenyl ring</td>
<td>V 870 – 675</td>
<td>828.11</td>
</tr>
</tbody>
</table>

### 4. SUMMARY

In this study, the thermal properties of PVA was investigated with different degree of hydrolysis (DH) (P100, P87 and P85) at different concentrations (0.1-1.1 wt.%). The DSC measurement showed that the melting temperatures of PVA at different DH were found to have increased with an increasing in DH and increasing concentration. The melting temperature range of PVA at different DH did not show much distinction because the result came from the same polymer, although it was with different DH. As for TGA measurement, it showed the same trend where the lower DH of PVA showed a slightly better thermal
stability. Degree of hydrolysis is associated with different number of acetate groups within the PVA itself. The increase in number of hydrophobic acetate groups reduced the interchain and intrachain hydrogen bonding, which explained the higher stability of PVA with decreasing DH. FTIR analysis showed in the region between 1720 - 1705 cm⁻¹, belongs to carbonyl group (C=O) stretched from the acetate group in PVA. For P87 sample (with high DH), the intensity of carbonyl stretching was weak, whereas for P 85 (with low DH) the intensity was strong. This proved that the number of acetate group in PVA had affected their interaction. Thus, it can be concluded that different of DH can affect the thermal properties of PVA.

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Effect of Single Walled Carbon Nanotube Addition to the Physical Properties of Monolithic Alumina

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ABSTRACT. The effect of single-wall carbon nanotube (SWCNT) addition on the physical properties of alumina (Al2O3) ceramic composite were studied in this paper. The SWCNT and Al2O3 nanocomposite samples were prepared using wet mixing with 5 different compositions of SWCNT. The nanocomposite samples were confined inside alumina sagger with high purity graphite packing powder and were sintered using pressureless sintering at 1600°C. The hardness shows an optimum values at 0.1 wt% of SWCNT, 20.13 GPa. However, further addition of SWCNT then reduced the properties values of the Al2O3.

Keyword: Al2O3, Hardness, SWCNT, Density;

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1. INTRODUCTION

Al2O3 is a well-known ceramic because of its exceptional properties which makes it suitable for wide range of application[1-9]. Al2O3 has magnificent hardness around 15-22 GPa[10], good flexibility [11] high melting point where the value is 2000°C [12] and also has great wear resistance material with high electrical resistivity and corrosion resistance [10]. Al2O3 suitable for cutting tool application because it more stable when operating at high temperature condition, which it resistant to chemical reaction when operated at high working temperature [13]. However, Al2O3 experiences the characteristic of low toughness, around 3-4 MPa.m1/2[14], which may lead to premature failure in applications that are related to load-stress. So, in order to increase the toughness, Al2O3 can be reinforced with many type of material either metal like Fe, Ni and Mo or ceramics such as SiC, ZrO and MgO [15]. Recently, nanotechnology industrials have emerged along with some new nanomaterials that have extraordinary properties. It is suggested that the composite may be able to be integrated with these nanomaterial as it can improve the properties of ceramics. Nanomaterials are materials that have particles size smaller than 100 nm in at least one dimension [16]. Carbon nanotubes (CNT) are widely used as they exhibit excellent mechanical properties such as stiffness up to 1.5 TPa and tensile strength above 100 GPa [17]. Types of CNTs can be categorized into two classes, which are Single-
Walled Carbon Nanotubes (SWCNT) and Multi-Walled Carbon Nanotubes (MWCNTs). In this study, SWCNT is preferred because are more malleable than MWCNT and also capable of generally self-assemble into bundles as in order to minimize surface energy [18]. The SWCNT are described by strongly bonded by covalent bond, unique one-dimensional (1D) structure and also nanometer size which give astonishing properties, such as magnificent tensile strength more than 100 GPa [17] good resilience, Young Modulus of up to 1 TPa [19], great electrical conductivity [20] and excellent thermal conductivity, almost 3500 Wm⁻¹K⁻¹ with length and diameter of 2.6 μm 1.7 nm, respectively [21]. Al₂O₃ ceramics were fabricated and studied to ascertain the effect of a mixture of SWCNT on the fracture behavior, hardness, density and microstructure.

Many studies had been done to test the effect of reinforced Al₂O₃ with SWCNT. For example, from researched that was conducted by Zhan [10], it has been reported that a fracture toughness of 10 vol% SWCNT/Al₂O₃ fabricated by spark-plasma sintering technique is 9.7 MPa.m¹/₂ compared to pure Al₂O₃ which is only 3.7 MPa.m¹/₂. Thomson et al. [22] have questioned the effectiveness of the Vickers method to evaluate the hardness in 10 vol.% SWCNT/Al₂O₃ composites that was fabricated by Wang et al. [23] as the surface finishing was not acceptable. He disagreed with Wang and said that the presence of large pores impedes indentation measuring. The aim of this study is to investigate the effect SWCNT addition to the physical properties of Al₂O₃.

2. MATERIALS AND METHODS

The raw materials (SWCNT and Al₂O₃) were weighed using AND EK 300-I according to different composition of SWCNT which are 0, 0.05, 0.1, 0.3, and 0.5 wt.% of SWCNT. The compositions of SWCNT were varied between 0-0.5 wt.% The total weigh for each composition is 15g. Table 3.2 illustrates the composition of the raw materials used.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SWCNT (wt.%)</th>
<th>Al₂O₃ (g)</th>
<th>SWCNT (g)</th>
<th>Total (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>15.0000</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
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<td>0.0075</td>
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</tr>
<tr>
<td>3</td>
<td>0.1</td>
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<td>0.0150</td>
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<td>0.0450</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>14.9250</td>
<td>0.0750</td>
<td>15</td>
</tr>
</tbody>
</table>

After the weighing process was done, then, continued with mixing process. Each of the mixture of Al₂O₃ with SWCNT were put into a beaker and carefully dispersed with 40ml ethanol with ultrasonic agitation for 2 hours. The ethanol here acts as a binder for the mixtures. Then, the mixtures were dried in an oven with temperature of 100°C for 24 hours. Then, the dried mixtures were then grounded using agitate mortar. Samples powder then were sieved using 75 micron size siever. The mixtures were uniaxially pressed at pressure of 17.93 MPa in a disk (steel die) using hydraulic hand press (Carver) and then hold for 5 minutes which then produced green compact samples with diameter of 11mm. The compacted samples were confined into alumina sagger with high purity graphite packing powder, and then sintered at 1600°C for 1 hour.

There are three of characterization to be observed in this study, density, firing shrinkage and Vickers hardness. For density observation, each composition was tested 10 times using electronic densitometer. For Vickers hardness, samples were first prepared by grinding and polishing until the surface was able to be seen under optical microscope and no scratches on the polished surfaces. Grinding machine used was Mecapol P 260. The hardness of the samples was determined using Micro-Hardness Tester 401 MVA and Buehler
Omnimet software. Load used was 10 kgf to produce the indentation on the sample for 15 s. Measurement of bulk density was done according to Archimedes method.

3. RESULTS AND DISCUSSION

From Fig. 5, it is shows that the percentage of shrinkage for the ceramics is increase from 8.95% of 0 wt.% SWCNT to 9.29% and 10.03% at composition of 0.05 and 0.1 wt.%, respectively. However, with further addition of SWCNT, the value of shrinkage dropped to 9.7% at 0.3 wt% of SWCNT and 8.6% at 0.5 SWCNT wt.%. Generally, the addition of SWCNT will affect the shrinkage of Al$_2$O$_3$ during sintering. Good dispersion of SWCNT inside Al$_2$O$_3$ will be resulting high shrinkage percentage values, and vice versa. High shrinkage percentage means that the density of the ceramic is also high, which related to the densification.

During sintering, the particle become close to each other. As the sample shrink, the grain size become smaller. Small grain size will result in porosity reduction. Thus, results in denser ceramics. However, from the graph, we can see that the trend drop at the composition of 0.3 and 0.5 wt.% SWCNT. This is because of the SWCNT agglomerations. At 0.01wt.% SWCNT, although the amount of SWCNT inside the Al$_2$O$_3$ is small, the decrease in the shrinkage percentage may due to the poor dispersion of the SWCNT, which lead to agglomeration. At 0.3 and 0.5 wt.% SWCNT, the drop on shrinkage percentage value is because the amount of SWCNT is exceeding optimum, because it tends to agglomerate more.

![Fig.4. Density of Al$_2$O$_3$ with different different composition of SWCNT](image)

Hardness is defines as the resistance of a solid material toward plastic deformation due to compression. Vickers Hardness is chose as a test method because it is preferable for hard materials. Fig. 6 shows the Al$_2$O$_3$ of alumina with addition of SWCNT, varies from 0 to 0.5 wt% of SWCNT addition. From the graph, it can be seen that the hardness of the Al$_2$O$_3$-SWCNT composite increase from 16.07 GPa to 17.09 and 20.13 GPa with the addition of 0.05 and 0.1 wt% SWCNT, respectively. However, the trend dropped with further addition of SWCNT, to 18.08 GPa at 0.3 wt% and 11.97 GPa at 0.5 wt% of SWCNT.
Based on previous studies by Arsecularatne and Zhang [24] and Lopez et al. [25], proved that the addition of SWCNT will reduce the Al₂O₃ hardness. This is because of the poor dispersion of the SWCNT inside the Al₂O₃ matrix. Poor dispersion of SWCNT cause the agglomerated SWCNT, which make the interfacial cohesion of SWCNT with Al₂O₃ matrix is deteriorate. With the inhomogeneous dispersion of SWCNT inside Al₂O₃ matrix, the grains of Al₂O₃ composite are unable to be refined during sintering process. This will cause the cancellation of mechanical improvement at room temperature, as the hardness will only increase with grain refinement. Besides that, the agglomeration of SWCNT will reduce the matrix-SWCNT bonding (interfacial), thus the only small amount of load will be transfer from matrix to the SWCNT. However, in this study, the hardness of A Al₂O₃ ceramic increases with the addition of 0.05 and 0.1 wt% of SWCNT, while decrease with other compositions of SWCNT. Increasing in hardness of this ceramic is due to the good dispersion of SWCNT inside the A Al₂O₃ matrix, which caused a strong bonding between SWCNT and A Al₂O₃ [3]. Hence, load will be effectively transfers to the SWCNT from Al₂O₃ matrix, thus increase the hardness of Al₂O₃.
4. SUMMARY

In this paper, the effect of adding SWCNT on Al₂O₃ properties was thoroughly studied. The used of SWCNT as an additive into Al₂O₃ can increase the properties of Al₂O₃. With addition 0.05 and 0.1 wt.% SWCNT, the properties of the composite is increase, meanwhile the further addition of 0.3 and 0.5 wt.% of SWCNT into Al₂O₃ matrix reduced the composite properties. Increase of the Al₂O₃ properties with addition of SWCNT is due to excellent dispersion of SWCNT inside the Al₂O₃ matrix lead to strong interfacial bonding of SWCNT with the Al₂O₃ matrix. However, poor dispersion of SWCNT reduced the properties of the composite, as agglomeration of SWCNT happen which lead to weak interfacial bonding between SWCNT and the Al₂O₃ matrix. In Summary, all properties achieved highest value at composition of 0.1 wt.% of SWCNT, where the density and hardness have the values of 3.63 g/cm³ and 20.13 GPa respectively. This mean, at this composition, the SWCNT disperse excellently.

ACKNOWLEDGEMENT

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Deposition and Characteristics of Sputtered Coated CCTO Thin Layer on Silicon Wafer

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ABSTRACT. In the present study, the calcium copper titanate (CCTO) thin layer has been coated onto Si wafer at 300°C using a CCTO target by Radio Frequency (RF) magnetron sputtering in argon atmosphere. The surface morphology crystal structure was examined by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively. The CCTO layer revealed polycrystalline nature with characteristic peaks of (0 2 2), (2 2 4), and (0 2 4) at 34.19°, 54.75° and 61.29°. The average grain size and pore size of porous sputtered CCTO were determined as 20 nm and 15.70 nm, respectively.

Keywords: CCTO thin layer, RF magnetron sputtering, Silicon wafer;

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1. INTRODUCTION

CaCu3Ti4O12 (CCTO) is perovskite-like compound, which possesses high dielectric constant ($\varepsilon_r \leq 10^5$) over a wide range of temperature from 100 to 600 K. This unprecedented characteristic makes it suitable for microelectronic applications. There are several methods for the deposition of CCTO thin including sol-gel process [1-2], pulsed laser deposition (PLD) [3-6], sputtering [7], and metal organic chemical vapor deposition (MOCVD) [8,9]. The RF magnetron sputtering has noticeable advantages over the other methods; it needs a very simple apparatus, high deposition rate, as well as deposition on a large area. Most of the CCTO studies have focused on the preparation of bulk materials such as ceramics or single crystals using chemical methods and the identification of the possible mechanism regarding to its unique properties [10,11]. However, thin layer have shown advantages over the bulk material for electronic applications [12-14]. The CCTO porous thin layer has been fabricated for different application such as humidity and gas sensor, dielectric constant applications [13,14]. It was reported that the properties of CCTO is dependent on the synthesis method as well as experimental conditions [15,16].

There are few studies available in the literature focusing on the fabrication of CCTO thin layer via RF magnetron sputtering process [12-14] to study the dielectric constant of gas sensors. However, the structural and physical properties of RF sputtered CCTO thin layer on Si wafer has not been discovered. The aim of this study is primary investigation of the crystallite structure and surface morphology of CCTO thin layer on Si wafer via RF magnetron sputtering.

2. MATERIALS AND METHODS
**CCTO thin layer preparation.** The CCTO thin layer with the 400 nm thickness have been coated on Si wafer via RF magnetron sputtering technique with the target (CCTO, 99.9% purity) (76 mm in diameter and 5 mm in thickness). The Si wafer carefully washed by hydrochloric acid (HCl), hydrogen peroxide (H₂O₂) and deionized water prior to coating process in order to eliminate surface impurities. The base pressure was set as 30×10⁻⁵ mbar in the coating chamber and CCTO target was pre-sputtered for ∼300 s at 30 WRF power to eliminate pollution on the surface. The layer was coated at 1.23×10⁻² mbar pressure, 10 sccm argon gas flow rate, and 150 W of RF power. The temperature of the substrate was retained at 300°C during coating process to enhance the layer crystallinity [17]. In order to analysis phase, surface topography and morphology of the CCTO thin layer, X-ray diffraction (XRD Bruker, D8 Advance system, Cu Kα irradiation, λ = 1.5405 Å), atomic force microscope (AFM) (Nano Navi, SPA 400) and scanning electron microscope linked with energy dispersive X-ray spectroscopy (SEM-EDX, Zeiss Supra™35VP) was used.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the RF sputtered CCTO thin layer on the silicon wafer with 400 nm thickness. The characteristic peaks indicated body centered cubic perovskite structures (ICDD data card no. 98-006-9415) with space group of Im-3 [18]. Five peaks centered at 2θ = 34.19°, 54.75° and 61.29° were matched to diffraction planes of (0 2 2), (2 2 4) and (0 2 4), respectively. The characteristic peaks at 2θ=47.21°, 56.27°, 69.23° and 76.61° confirmed the crystalline structure of Si wafer (ICDD data card no. 98-002-2990). The peak at 69.14° of high intensity was ascribed to reflection lines of silicon wafer. Nevertheless, not all of the expected peaks for CCTO thin layer were observed in the XRD pattern. This may be attributed to the small quantity of deposited CCTO thin layer on the substrate.

![XRD patterns of the sputtered CCTO thin layer on silicon wafer](image)

The surface characteristic and size distribution of the CCTO thin layer was investigated by AFM analysis (tapping mode) at ambient condition. Fig. 2 depicts the 2D and 3D topography images of the porous CCTO thin layer with the 400 nm thickness. The roughness (Ra) and root mean square (RMS) of the roughness were calculated by using the scan area of 10 × 10 μm². Ra and RMS values obtained were 5.6 nm and 7.1 nm, respectively. The microstructure of CCTO layer consisted of small and large grains. The pore size was estimated around 15.7 nm by variations of surface profile as shown in Fig. 2(c).
**Fig. 2.** Atomic force micrographs of CCTO thin layer (a) 3D image, (b) 2D image and (c) the corresponding average profile line

**Fig. 3** SEM micrographs of CCTO thin layer (a) topside, (b) cross section and (c) EDX analysis
The surface morphology of the CCTO thin layer is shown in Fig. 3. The SEM images of CCTO thin layer exhibited a uniform surface morphology. The average distributed grain size on the layer surface was nearly 20 nm as shown in Fig. 3(a). It is obvious that CCTO thin layer have a porous intergranular structure. The cross-section of thickness related to CCTO thin layer is shown in Fig. 3(b). In addition, the chemical composition was quantitatively determined from EDX as in Fig. 3(c). The observed Si peak in the EDX table was belonged to the substrate.

4. SUMMARY

The CCTO thin layer with the 400 nm thickness was successfully coated on the surface of Si wafer via RF magnetron sputtering process at substrate temperature of 300 °C with 150 W power. The surface morphology and crystal structure were evaluated by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The results demonstrated the uniform intergranular porous microstructure of CCTO thin layer. The average grain size and pore size were also found to be 20 nm and 15.70 nm, respectively.

ACKNOWLEDGMENTS

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Dielectric Resonator Antenna of Nd-doped BaTiO$_3$ for X-Band Applications

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ABSTRACT. In this paper, dielectric resonator antenna (DRA) fabricated using neodymium (Nd) doped on barium titanate powder (Ba$_{(1-x)}$Nd$_x$TiO$_3$) with x values varying from 0, 0.01, 0.03, 0.05, 0.07 and 0.10 via sol-gel process was investigated. Ba$_{(1-x)}$Nd$_x$TiO$_3$ in cylindrical shape with high dielectric constant and low loss tangent was used. A simple microstrip line was utilized as a feeder to ease the fabrication process. A comparative study of the various dope values of Nd with the same dimensions in terms of resonant frequency, return loss, bandwidth as well as radiation pattern were analyzed. Operational frequency of DRA was found to be tunable using different values of doped Nd, but the radiation patterns of the DRA were not very different. This antenna is suitable for use in X-band applications.

Keyword: Dielectric resonator antenna, Barium titanate, Neodymium, X-band;

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1. INTRODUCTION

The field of microwave communication has gone through exceptional growth for the last two decades. This is driven by the latest trend of technology miniaturization which demands the enhancement of technology versatility to accommodate various technological constraints. The dielectric resonator antenna (DRA) is seen as the most adaptable antenna which can be integrated with any applications [1]. One of the most attractive features of DRA is its adjustability in terms of shape, dimensions and permittivity of dielectric resonator [2-4]. As permittivity increases, the size of DRA decreases since both parameters are inversely proportional to each other. Additional advantages are various feeding methods which is strongly associated with modes being excited, wide range of dielectric constant from different dielectric materials, as well as lightweight and low loss characteristics [1,3,5,6].

Adjustability the resonant frequency is critical in DRA design. This offers a certain degree of freedom to incorporate DRA with tunable devices. A metallic plate attached to the dielectric resonator provides significant effect in varying the resonant frequency of the DRA [1,7,8]. The biggest the metallic plate on top of the DRA, the larger the shift of resonant frequency which can be obtained [9]. Besides changing the diameter
of the metal plate, varying its height can also allow changes in frequency [10]. Moreover, the height of the metal plate has greater effect towards resonant frequency of the DRA compared to the diameter. Resonant frequency of the DRA is a function of material permittivity as well as structural parameters. A set of different resonant frequencies is generated from dielectric resonators (DR) having different permittivity [11]. Adding an additive to the dielectric resonator will modify the dielectric properties of DR. In previous work [12-15], the presence of additive in BaTiO$_3$ was reported to affect the permittivity and loss tangent of DR. This in turn, influences the DRA’s resonant frequency.

The common practice in producing dielectric resonators for antenna application is through the conventional solid state reaction process [16-18]. Kumazawa and Masuda [19] reported the fabrication of barium titanate thin film using sol-gel techniques. Bijumon et al. [20] reported an integrated DRA for system-on-chip applications by sol-gel composites. None were purely fabricated from sol-gel since the bulk dielectric resonator was made using wet mixing process. The sol-gel process is preferred due to its inherent advantages such as high homogeneity and purity, lower processing temperature, and fine particle size, as compared to the co precipitation and wet mixing methods [21]. However, there are very little reports about the characteristics of DRA fabricated using the sol gel method. Hence, in this paper, the compact and low profile DRA fabricated from BaTiO$_3$ material through sol gel process is reported. The effect of Nd dopant on the BaTiO$_3$ DRA performance was also investigated.

2. MATERIALS AND METHODS

A pellet was prepared from pure and Nd doped BaTiO$_3$ using the sol gel method. The value of the Nd additive was varied from 0, 0.01, 0.03, 0.05, 0.07, 0.10 and 0.13. BaTiO$_3$ powders were derived using the sol-gel method instead of the conventional method which involved mixing and milling processes. The solid state reaction of BaTiO$_3$ DR was studied by means of XRD and SEM. HP4291B RF Impedance Analyzer (1 MHz -1.8 GHz) was used to determine dielectric properties of the sample. The fabricated pellet was later attached to the grounded dielectric substrate for the completion of the DRA. The antenna structure is shown in Fig. 1. It consists of cylindrical pellets which are of radius = 10.07 mm and thickness = 1.2 mm. The pellets were placed on the 50 Ω microstrip line of length = 40 mm and width = 1.9 mm. The dimension of the microstrip line was calculated using an impedance calculation tool in the computer simulation technology (CST) software. For modeling purposes, a CST software which contains a frequency and time domain solver was used. The preferred feeding technique in this design is microstrip line due to its simplicity and direct excitation to DRA. The microstrip line had a 50 Ω impedance which was printed on a grounded substrate of permittivity $\varepsilon = 3.38$ and size of 50 mm $\times$ 40 mm $\times$ 0.813 mm. The positions of both DR and 50 Ω microstrip line were centered on the substrate board. To obtain optimum coupling, the position of each DR was varied provided that HEM$_{11d}$ mode excitation was not disturbed. Once fabricated, DRA must be attached to the substrate. The air gap surface between the DRA and substrate can affect the measurement results. To do so, a nonpermanent adhesive i.e. a silicon sealant was used to bond the DRA in place. The level of this silicon sealant should be as thin as possible. The 50 Ω microstrip line is soldered to the compatible subminiature version A (SMA) connector. The measurements on resonant frequency return loss and bandwidth of DRA was done using HP8720D Network Analyzer (50 MHz to 20 GHz). Radiation patterns for both pure BaTiO$_3$ DRA and Nd doped BaTiO$_3$ DRA were also measured using Agilent Spectrum Analyzer 8565E. The first part of the measurement deals with the investigation on the pure BaTiO$_3$ pellet in DRA. The measurement consists of the modeling design, and a comparison of measurement results to highlight the potential of BaTiO$_3$ pellet synthesized via sol-gel in DRA application. Later, the same measurement used on the DRA was repeated for the Nd doped BaTiO$_3$. The amount of additive was varied and a comparison on the effect of the additive was done.
Field characteristics inside the cylindrical DRA can be analyzed using a magnetic wall model [22]. The normal mode excitation for the cylindrical DRA with direct microstrip coupling is HEM_{11d} mode. Consequently, the resonant frequency of the cylindrical DRA can be predicted from the separation equation as shown in Eq. 1 [1,22].

\[ k_r^2 + k_z^2 = \varepsilon_r \left( \frac{2\pi f}{c} \right)^2 \]  

(1)

where \( c \) is the velocity of light in free space and \( f \) is frequency. \( k_r \) and \( k_z \) are the wavenumbers inside the cylindrical DR in \( r \) and \( z \) directions, respectively. The equation is as below:

\[ k_r = \frac{X_{vp}}{a} \]  

(2)

\[ k_z = \frac{(2m+1)\pi}{2d} \]  

(3)

After rearrangement of Eq. 1, the resonant frequency of mode \( f_{vpm} \) is given as:

\[ f_{vpm} = \frac{c}{2\pi\sqrt{\varepsilon_r}} \sqrt{k_r^2 + k_z^2} \]  

(4)

and when both Eqs. 2 and 3 are substituted into Eq. 4, the theoretical resonant frequency is given as Eq. 5:

\[ f_{vpm} = \frac{c}{2\pi \sqrt{\varepsilon_r}} \sqrt{\frac{X_{vp}^2}{2d} + \left( \frac{\pi a}{2d} (2m+1) \right)^2} \]  

(5)

where \( X_{vp} \) is the root satisfying the characteristic equation.

3. RESULTS AND DISCUSSION

In order to analyze the performance of a BaTiO\(_3\) pellet as the dielectric resonator in a DRA application, measurements of several parameters of the antenna were done. Fig. 2 shows simulated and measured input impedance on the Smith chart for the pure BaTiO\(_3\) DRA. The range of frequency starts from 8 GHz to 10 GHz. It is noted that both impedance loops are close to the prime center of the Smith chart which represents 50 + j 0 Ω. The simulated result has an input impedance of 54.30 - j 1.70 Ω, while the measured input impedance is 48.27 - j 2.64 Ω. This shows that the DRA which utilizes the pure BaTiO\(_3\) pellet has good impedance matching with the simulated one. This is because the value of measured input impedance is the closest to the prime center of the Smith chart. It shows that pure BaTiO\(_3\) pellet fabricated using the sol-gel process can have good impedance matching in real antenna applications.

In correlation with the Smith chart, return loss curves are given in the Fig. 3. It shows measured and simulated return loss as a function of frequency for the DRA which uses pure BaTiO\(_3\) pellet. As can be clearly
seen, the measured DRA attained a return loss of -31.18 dB at a frequency of 8.71 GHz. It gives a -15 dB bandwidth of 700 MHz or 8.03%, whereas the simulated resonant frequency shifted to the lower frequency at 8.99 GHz with -21.64 dB. The impedance bandwidth is around 380 MHz or 4.22%. As can be concluded from the curves, the significant dissimilarity between these two DRA is the impedance bandwidth.

![Fig. 3 Input impedance of pure BaTiO$_3$](image)

The measured bandwidth of BaTiO$_3$ DRA is double that of the simulated bandwidth. In terms of return loss, the result shows that both measure lower than -20 dB, indicating that both DRA have low power loss. This can be related to the Smith chart as the lower the S11 curve, the closer the impedance loop to the prime center of the Smith chart. Generally, both the simulated and fabricated DRAs have different bandwidths due to tolerance of the dielectric properties and possession of different frequency resonances. Based on the S11 curves, it is proven that the BaTiO$_3$ pellet functions as a resonant structure with a specific resonant frequency. This is triggered from the internal reflections of electromagnetic waves between the air and pellet boundary. This in turn confines the energy within, and in the vicinity of the pellet, therefore forming a resonant structure [21].

![Fig. 4 Return loss of pure BaTiO$_3$ DRA](image)

Fig. 4 shows the input impedance of pure and dopant BaTiO$_3$ DRA. All the loops are almost at the center of the Smith chart which indicates good matching for the DRA. However, it can be clearly seen that by adding dopant (Nd) into BaTiO$_3$ DR, the level of matching was improved. The loop which represents pure BaTiO$_3$ DRA is the farthest from the circle of the Smith chart, showing that it has the worst matching level with input.
 impedance of 48.27 - j 2.64 Ω at 8.71 GHz. However, for x = 0.03 and x = 0.05, the DRA has better matching. For x = 0.03, the input impedance is near to 50 Ω with 49.95 – j 0.02 Ω. It is almost equivalent to the 0.05 dopant BaTiO$_3$ DRA with 50.1 – j 0.02 Ω. Hence, it is proven that by introducing the additive Nd into BaTiO$_3$ DRA, the impedance matching of DRA can be improved.

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**Fig. 4** Measured input impedance of doped BaTiO$_3$ DRA with (a) 0, 0.01, 0.03 Nd and (b) 0.05, 0.07, 0.10 Nd

The effect of Nd doped BaTiO$_3$ on the DRA in terms of return loss is shown in Fig. 5. It can be noted that different values of Nd as dopant resulted in different resonant frequencies. The lowest frequency belongs to the pure BaTiO$_3$ DRA at 8.71 GHz while the highest operational frequency is triggered at 9.27 GHz for 0.07 Nd BaTiO$_3$ DRA. This can be explained by the effect of permittivity values for each sample. The higher the permittivity, the lower the resonant frequency. According to our previous work [12], pure BaTiO$_3$ pellet has the highest permittivity compared to Nd doped BaTiO$_3$ pellets where the lowest permittivity was measured in the (x = 0.07) pellet. With regards to return loss, all the curves have values lower than -30 dB. It shows that all DRA achieved good matching levels at the respective frequencies where pure BaTiO$_3$ and Nd doped BaTiO$_3$ DRA performed successfully as antenna elements. The return loss for pure BaTiO$_3$ DRA is the highest with -31.18 dB, whereas all dopant BaTiO$_3$ DRA measured lower than that. In terms of bandwidth, pure BaTiO$_3$ DRA possesses the largest impedance bandwidth with 8.03%, while the x = 0.07 pellet exhibited the lowest impedance bandwidth of 3%. As expected, the presence of Nd dopant increases tan loss of BaTiO$_3$ DRA while at the same time lowers the dielectric constant. Generally, the presence of the additive Nd in BaTiO$_3$ pellet has improved the reflection coefficient of DRA, altering the resonant frequency and reduced the bandwidth of DRA.

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**Fig. 5** Measured return loss of BaTiO$_3$ DRA with different Nd doped
4. SUMMARY

DRA using BaTiO₃ ceramic was designed, fabricated by means of sol-gel process and analyzed. Both simulated and measured results were presented, and it was proved that Nd-doped BaTiO₃ synthesized using the sol-gel process is suitable for DRA applications. The results of resonant frequency show that BaTiO₃ pellet is a resonant structure with HEM₁₁∂ mode excitation. Good impedance matching and quasi omni directional type radiation pattern was exhibited. The presence of the additive Nd in the BaTiO₃ DRA changed the resonant frequency. Therefore, the BaTiO₃ DRA fabricated via the sol-gel process was successfully proven to be applicable in DRA.

REFERENCES


