MECHANICAL AND THERMAL PROPERTIES OF WASTE BIO-POLYMER COMPOUND BY HOT COMPRESSION MOULDING TECHNIQUE

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ABSTRACT

Demands for Bio-Polymer Compound (BPC) has attracted attention in various applications from industrial to medical. Thus, mechanical and thermal stability properties of recycling waste BPC from industrial are very important to be investigated. The waste BPC for this study, based on is the mixture of hydroxylated waste cooking oil with hardeners to produce Waste Bio-polymer Foam (WBF). The granulate of WBF were cast into the mould until all spaces evenly fill and compact into homogenous shape and thickness at 30 – 45 Bar for 2 hours using hot compression moulding. This method of BPC fabrication resultant in the tensile and flexural strength of 4.89 MPa and 18.08 MPa respectively. Meanwhile the thermal stability of BPC laminated was conducted by Thermal Gravimetric Analyzer (TGA) exhibited the first degradation occur at 263 °C of soft segment than subsequently the second degradation at 351 °C and last 416 °C.

Keywords: Bio-polymer compound; Hot compression moulding; Thermal stability.

INTRODUCTION

Due to environment and sustainability issues, this century has witnessed remarkable achievements in green technology in the field of materials science through the development of Bio-composites or Bio-Polymer Compound (BPC). The development of high-performance materials made from natural resources is increasing worldwide (Omar Faruk et al., 2012). Historically a predominantly aerospace material, natural fiber-reinforced composite structure have seen an increased application in other industries such as automotive, marine transportation, civil engineering, sporting goods, medical equipment and prosthetic devices. Natural fiber-reinforced composite structures provide high strength, high stiffness mechanical properties, unique flexibility in design capabilities, and ease of fabrication. Also, they are lightweight, corrosion resistant, impact resistant, and have excellent fatigue strength (Scott Robert et al., 2002). The greatest challenge in working with natural fiber reinforced plastic composites is their large variation in properties and characteristics. A Bio-composite such as WBC’s properties are inﬂuenced by a number of variables, including the temperature, pressure applied to moulding, processing methods, and type of resin that most popular matrices in Bio-composite based on petrochemical (Omar Faruk et al., 2012).
Bio-composites or WBC are composed of two or more materials which, when properly combined, form a different material with properties not available from the ingredients alone. Depending on the ingredients chosen and the method of combining them, a large spectrum of material properties can be achieved. A brittle material can be made more ductile (flexible) by adding a softer material; conversely a soft material can be made stiffer. Wood is a good example of a Bio-composite. The cellulose fibers provide the strength and are held together by the resin. Reinforced concrete is another example. The steel re-bars provide excellent tensile strength and the concrete provides compressive strength and transfers the load between the steel bars. Modern composites or FRP (Fiber reinforced polymers, or plastics) are the newest addition to the structural engineers toolbox. Although the materials have been available for decades, a reduction in cost, combined with newer understanding of the versatility and benefits of the material properties, has allowed composites to move into mainstream construction (Scott Robert et al., 2002).

Malaysia, being one of the largest producer and manufacturer of palm oil products, generates large amount of palm oil by-products, which can be recycled into bio-monomer. If this bio-monomer is put into good use, in this case as a main material in bio-polymer compound, then it will largely reduce the cost of high performance composite (M. Hilton Ahmad, 2007). At the same time, it will also reduce the amount of waste generated by the palm oil industry thus achieving a global aim of sustainable development. Not only it reduces the waste, it also preserves the nature by eliminating the need to harvest natural aggregates from natural sources. With the increased use of Bio-composite materials, there is a need to conduct serial of testing to predict the mechanical properties and behaviour of BPC materials and structures made of these materials under a variety of loading and environmental conditions.

Furthermore thermal stability of BPC has gained considerable attention because of their potential application in a number of areas. Many applications of BPC require materials that can resist a variety of external stresses such as heat or fire. However, BPC generally have low thermal stability at high temperatures and thermal degradation can begin to occur at processing temperatures above 180°C, depending on the parameters (D. Braun, 1981). The study of the decomposition of biopolymers is particularly difficult since they degrade with the formation of various gaseous products and a number of decomposition steps are typically observed in Thermal Gravimetric Analysis (TGA) experiments. The thermal stability of a material is defined by the specific temperature or temperature-time limit within which the material can be used without excessive loss of properties (Chattopadhyay DK et al., 2009). The main purpose of this study is to evaluate the degree of conversion and determine the thermal stability of biopolymer by using TGA with temperature of 25°C - 900°C at a rate of 10°C/min.

The exploration of this Waste Bio-polymer Compound (WBC) from waste palm cooking oil using hot compression technique is a good study to undertake. The preliminary study was to conducted base on the processing conditions that influences its mechanical properties and the thermal properties of WBC.
EXPERIMENTAL

Preparation Bio-Foam Compound (BFC)
Bio-Foam Granulate (BFG) was prepared (Anika Zafiah M. Rus. 2009) and cut into small size approximately 10 mm X 10 mm X 10 mm cube size and grained using rotor mill to form small particle, started with 6.00 mm, followed by 2.00 mm and 0.50 mm. This small granulate were cast into the mould until all spaces evenly filled and hot compress into homogenous shape and thickness at 30 – 45 bar with temperature of 40 – 55 °C for 2 hours. The sample was laminated with 10 gram of epoxy on top and bottom on both side of BPC.

Characterizations
Tensile and flexural strength of WBC was carried out by Universal Testing Machine (UTM) model Lloyd Instruments LR30K as according to standard BS EN ISO 527-2:1996 type 1A with 1.0 mm/min crosshead speed (BS EN ISO, 1996). The flexural (3 point bending test) is accordance to ISO 178:2010 with speed 0.10 mm/min (ISO 178, 2010). The specimens’ dimensions for tensile were 150 mm long, 10 mm wide and 4.0 mm thick meanwhile flexural was 80 mm long 10 mm wide and 4 mm thick. The Archimedes principle was used to obtained density of BFC and WBC. Scanning Electron Microscope (SEM) model JOEL JSM – 6380LA complete with Energy-dispersive X-ray spectroscopy (EDX) was used to examine the surface fracture morphology of the tensile specimens. The structure of specimen was coated with coating conductor material to allow electrons to flow through the specimen. The weight lost of WBC of a function of temperature was determined by using Linseis Thermo balance Simultaneous Thermal Analysis (STA) (TG + DTA). Sample weighing between 100-120 mg were placed in a crucible in a furnace and heated in nitrogen between 25°C - 900°C at a rate of 10°C/min.
RESULTS AND DISCUSSION

Mechanical properties of WBC
Figure 4 shows the relationship between molding pressure versus tensile strength and flexural strength. The tensile strength of WBC increases with increased molding pressure as well as the flexural strength. The highest the molding pressure revealed highest tensile strength of 4.89 MPa as well as flexural strength of 18.08 MPa for both sample of WBC. Meanwhile, the lowest molding pressure of 31 bar revealed the lowest tensile strength and flexural strength of 1.81 and 9.03 MPa of WBC respectively.

![Figure 4. Influence of molding pressure on tensile strength and flexural strength of WBC](image)

Figure 5 presents the relationship between tensile strength and density with increasing of molding pressure. This by increasing of the molding pressure, the density and the tensile strength were increased rapidly. The highest density of 44 bar molding pressure is 1.209 g/cm$^3$ with the highest tensile strength value of 4.89 MPa. This also resultant in the lower tensile value influences by the drop of density value to 0.857 g/cm$^3$ consequently. Figure 6 depicts the same and systematic pattern with Figure 4 and Figure 5 with the highest flexural of 18.08 MPa at 44 bar and 9.03 MPa at the lowest molding pressure of 31 bar.

![Figure 5. Influence of molding pressure on tensile strength and density of WBC](image)
Figure 6. Influence of molding pressure on flexural strength and density of WBC

**Morphology structure of WBC**

Mechanical properties of WBC were affected by internal defects such as voids as indicated by surface morphology with black area. This is in correlation with the finding of (Hitoshi Takagi, 2008). Consequently, the density usually serves as a good indicator for the WBC strength as refer to Figure 5 and 6.

Figure 7. SEM of morphology fracture surface at 30x magnification (A) molding pressure of 31 bar (B) molding pressure of 38 bar (C) molding pressure of 44 bar, with the red circle indicated void area

SEM micrographs of the fractured surface of the laminated WBC are shown in Figure 7. It can be concluded that at low molding pressure in Figure 7(A), shows debonding of granulate leave holes and void. The granulate have tendency to pull out than breakage indicating of weak adhesion between the granulate. At high molding pressure as shows in Figure 7(C) revealed absence of less holes and void due to improvement for the granulate adhesion. The granulate has covered the holes and void area thus better stress transfer between the granulate. In addition, the fractured surface also shows granulate breakage rather than pull out (Paul et. al, 2008). This is assumed due to increased interfacial shear strength for high molding pressure and good interfacial adhesion between the granulate and epoxy. The SEM pictures prove that high pressure molding set up enhances mechanical properties of the WBC as compared to low pressure molding.
Brittle fracture is observed as refer to the fracture surface of WBC, the identification of brittle fracture is due to the mode of fracture characterized by rapid crack propagation. This type of fracture have glassy smooth surface, flat, bright, shiny and having minimum plastic deformation as well as percentages of fracture with little yielding before the samples breaks. Figure 7 shows brittle fracture of sample (A), (B) and (C) with minimum strain percentage. Fracture surface for Figure 7 (C) shows grew voids as compared to (B) and (A) (Lubarda, V.A., 2001).

Thermal properties of WBC
The TGA weight loss curve displays 2 or 3 distinct regions that are reflected in the differential weight loss curve. Figure 8 shows the first curve of WBC occur at 74°C for volatile material such as gaseous (Y. M. Song, 1996) and usually this volatile material is not to be taken as first decomposition temperature. The first decomposition only occur on hard segment of WBC at 260°C and continues to 371°C for second decomposition indicated as the soft segment of WBC structure. The last decomposition occur at 415°C predicted as the byproduct of hard and soft segment structure. Meanwhile Figure 9 shows thermogram of epoxy material used to laminated BPC with hard segment decomposition at 351°C and volatile material with 1 distinct region.

Figure 10 of WBC laminated with epoxy shows only the decomposition started in hard segment at 263°C for the cross linking agent, second decomposition occur at 351°C for epoxy and third occur 416°C according to (Y. M. Song, 1996). The tabulated result of decomposition temperature is shows in Table 1.

![Figure 8. Thermogram of WBC](image)

Referring to Table 2, the onset degradation temperature, $T_{on}$ and maximum temperature, $T_{max}$ of WBC and WBC with laminated consist 3 step processes. For onset degradation temperature and maximum temperature for hard segment is $T_{1on}$-$T_{1max}$ of WBC is 220-280°C, and for laminated WBC is 230-280°C. The second $T_{2on}$-$T_{2max}$ for WBC is 340-380°C and laminated WBC is 330-360°C and last process $T_{3on}$-$T_{3max}$ is 400-455°C for WBC and 395-460°C for laminated WBC of soft segment.
The weight loss of WBC and laminated WBC during first degradation at is 3.00 % and 1.00 %. The second and third stage weight loss for WBC and laminated WBC is 12.00 % and 16.00 % for second stage, 18.00 % and 23.00 % for third stage. At last remaining weight losses are 67.00 % for WBC and 60.00 % for laminated WBC. The maximum epoxy weight loss is occur at temperature 385°C with 68.20% weight loss.

Figure 9. Thermogram of epoxy

Figure 10. Thermogram of laminated WBC with epoxy
Table 1. The degradation temperature of first, second and third decomposition

<table>
<thead>
<tr>
<th>Sample</th>
<th>First (°C)</th>
<th>Second (°C)</th>
<th>Third (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBC</td>
<td>260</td>
<td>371</td>
<td>415</td>
</tr>
<tr>
<td>Epoxy</td>
<td>351</td>
<td>385</td>
<td>-</td>
</tr>
<tr>
<td>Laminated with epoxy WBC</td>
<td>263</td>
<td>351</td>
<td>416</td>
</tr>
</tbody>
</table>

Table 2. Degradation temperature value of hard and soft segment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hard</th>
<th>Soft</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{1\ on}$</td>
<td>$T_{1\ max}$</td>
</tr>
<tr>
<td>WBC</td>
<td>220</td>
<td>280</td>
</tr>
<tr>
<td>Epoxy</td>
<td>330</td>
<td>385</td>
</tr>
<tr>
<td>Laminated with epoxy WBC</td>
<td>230</td>
<td>280</td>
</tr>
</tbody>
</table>

Table 3. Percentages of weight loss of WBC, epoxy and laminated WBC with epoxy from TGA

<table>
<thead>
<tr>
<th>Sample</th>
<th>WBC</th>
<th>Epoxy</th>
<th>Laminated with epoxy WBC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight Percentages (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>3.00</td>
<td>2.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>12.00</td>
<td>5.00</td>
<td>16.00</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>18.00</td>
<td>10.00</td>
<td>23.00</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>67.00</td>
<td>83.00</td>
<td>60.00</td>
</tr>
</tbody>
</table>
The Degree of Conversion \((\alpha)\)

The alpha value, \((\alpha)\) is calculated using equation:

\[
\alpha = 1 - \frac{w(t)}{w_o}
\]  

Where:
- \(\alpha\) = degree of conversion (alpha) = weight loss at given temperature
- \(w_o\) = initial weight
- \(w(t)\) = weight at any time
- \(t\) = during degradation

Referring to Table 4, the alpha \((\alpha)\) value of WBC show value 0.09 for hard segment and 0.22 for soft segment. Alpha \((\alpha)\) value for WBC laminated is 0.12 at hard segment 0.23 during degradation at soft segment. The value of degree of conversion for epoxy on hard segment is 0.42.

Table 4. Degradation temperature value for hard and soft segment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition Ratio</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hard</td>
<td>Soft</td>
</tr>
<tr>
<td>WBC</td>
<td>0.09</td>
<td>0.22</td>
</tr>
<tr>
<td>Epoxy</td>
<td>0.42</td>
<td>-</td>
</tr>
<tr>
<td>Laminated with epoxy</td>
<td>0.12</td>
<td>0.23</td>
</tr>
</tbody>
</table>

CONCLUSION

The experimental result shows the mechanical properties such as tensile strength and flexural strength were influences by the density, void area and molding pressure. In order to improve the compatibility of WBC granulated, more than 45 bar is suggested for the hot compression molding setup. Thus, the tensile and flexural strength of the WBC could be improved. For the thermal properties of WBC with and without laminated of epoxy weight loss shows slightly small different for example at temperature 400°C the WBC show 48.15 % and WBC laminated shows 48.00 %, it demonstrated that laminated with resin (epoxy) do not effected the decomposition WBC. Meanwhile SEM morphology where WBC with high pressured showed less voids and fiber pull out. This phenomenon indicates adhesion between granulate increases due to good interfacial adhesion between the granulated. Furthermore, the maximum tensile strength at highest compression parameter of pressure is 4.89 MPa with the highest density value.

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