Tensile and Water Absorption Properties of Biodegradable Composites Derived from Cassava Skin/Polyvinyl Alcohol with Glycerol as Plasticizer
(Sifat-sifat Tegangan dan Penyerapan Air oleh Komposit Biorosot daripada Kulit Ubi Kayu/Polvinil Alkohol dengan Gliserol sebagai Bahan Pemplastik)

DAYANGKU INTAN MUNTHOUB* & WAN AIZAN WAN ABDUL RAHMAN

ABSTRACT
Natural organic and abundant resources biopolymers received more attention due to their low cost, availability and degradability after usage. Cassava skin was used as natural fillers to the polyvinyl alcohol (PVA). Cassava skin/polyvinyl alcohol blends were compounded using melt extrusion twin screw extruder and test samples were prepared using the compression method. Various ratios of cassava skin and glycerol were investigated to identify suitable composition based on the water absorption and tensile properties. The water absorption of the cassava skins/PVA samples increased at higher composition of cassava skin due to their hydrophilic properties but decrease with glycerol content. The strength of the cassava skins/PVA samples increased with the higher composition of cassava skin up to 70 wt% while gradually decreased with the increasing composition of glycerol. The Young modulus increased with glycerol content but decreased with fibre loading up to 70 wt%. Elongation at break decreased with fibre loading and glycerol up to 70 wt% and 30 phr, respectively.

Keywords: Biodegradable; cassava skin; polyvinyl alcohol; tensile properties; water absorption

ABSTRAK

Kata kunci: Alkohol polivinil; biourai; kulit ubi kayu; penyerapan air; sifat-sifat tegangan

INTRODUCTION
Alternatives for petroleum based polymers have been much sought by researchers to replace non-degradable products that cause pollution and not environmental friendly, with polymers that can degrade. Biodegradable materials from renewable resources have been tested as an alternative to replace the usage of petroleum based materials. Biodegradable materials can be defined as polymers that are made by microbial system and polymers which been produced by chemical polymerization of biological starting materials (Glenn et al. 2001). Biodegradable composites derived from natural resources give great influence due to the environmental awareness. Natural biopolymers have been widely explored as the alternative to increase the biodegradability of the products.

In this study, cassava waste produced from cassava skin was used as the biodegradable fillers. Starch and fibre present as the constituents in the cassava skin. Cassava skins contain significant amount of starch and fibres. The use of starch in plastic production would greatly reduce the demand of petroleum as well as the negative impact on the environment caused by discarding non biodegradable materials (Lui & Peng 2005a). Starch can be obtained from corn, white potatoes, wheat, rice, barley, millet, cassava and sorghum (Carrabber 2008).

Polyvinyl alcohol (PVA) was selected as the blending combination to the cassava skin improved the properties of the products. PVA is the most readily biodegradable of vinyl polymers (Chandra & Rustgi 1998). This type of biodegradable and water-soluble polymers used in the textile processing, frequently for nylon and in fibre manufacture as a raw material for the production of PVA fibre (Lin & Ku 2008).
Glycerol was mostly used as the plasticizer for PVA based products as reported in previous studies (Alexy et al. 2004; Jang & Lee 2003; Preechawong et al. 2004, 2005). Alexy et al. (2004) studied on the effect of melt processing on thermo-mechanical degradation of poly vinyl alcohols. This study showed that the presence of glycerol as a plasticizer does not improve the processing stability of tested PVAs while its role is to decrease the internal viscosity of PVA processed at the same temperature as in the case of processing without glycerol. The relatively poor mechanical properties of starch-based materials have been tentatively modified by adding large amounts of plasticizers, such as glycerol or ethylene glycol, or by modifying the chemical properties of starch itself (Chiellini et al. 2003). Nevertheless, increasing amount of plasticizer content in the compound may lead to lower interaction between polymer chains and therefore the resistance to the shear flow decreased (Lin & Ku 2008).

There are many researchers reported on the application and potential utilization of starch as the biopolymer products for example, Bhatnagar & Hanna 1995; Cha et al. 2001; Ganjyal et al. 2003; Glenn et al. 2001; Glenn & Orts 2001; Lui & Peng 2005; Natar et al. 2006; Salgado et al. 2008; Tsivintzelis et al. 2007; Willett & Shogren 2002; Xu & Hanna 2005; Xu et al. 2005; Zhou et al. 2006, 2007.

The aims of this study were to investigate the physical properties of cassava skin/PVA-based composites with respect to the ratio of cassava skins, effects of varying the compositions of PVA and glycerol on the tensile properties.

**MATERIALS AND METHODS**

**MATERIALS**

Cassava skins generated from upstream cassava processing were used as the natural raw material. The cassava skins were dried under the sun for about a week. Dried cassava skins were ground and sieved to obtain powders with particle size approximately 100 µm. Fully hydrolyzed PVA resins, BF-17 manufactured from the Chang Chun company and glycerol manufactured by Fisons Scientific Equipment of 99.0% purity and molecular weight of 92.19 g/mol were used as thermoplastic component and plasticizer, respectively. Talc was added prior to extrusion as the nucleating agent and deionized water was used to regulate the viscosity and flow ability during extrusion (Willett & Shogren 2002).

**MIXING PROCESS**

Cassava powder, PVA, glycerol, talc and deionized water were premixed on the Chyau Long Machinery high speed mixer. Melt compounding method using the extrusion process on a twin screw extruder Brabender PL 2100 Plasticoder was conducted to form pellets at the processing temperature of 170ºC and 30 rpm of screw speed. Various formulations were prepared with varying composition of glycerol as the plasticizer. Table 1 shows the formulation used for the composite.

**TABLE 1. Formulations of cassava skin/PVA blend**

<table>
<thead>
<tr>
<th>Blend</th>
<th>PVA (wt%)</th>
<th>Cassava skins (wt%)</th>
<th>Glycerol (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90/10</td>
<td>10</td>
<td>90</td>
<td>20</td>
</tr>
<tr>
<td>80/20</td>
<td>20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>70/30</td>
<td>30</td>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td>60/40</td>
<td>40</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>50/50</td>
<td>50</td>
<td>50</td>
<td>20</td>
</tr>
</tbody>
</table>

**COMPRESSION PROCESS**

In order to produce the test samples, the final extrudates were compressed using the compression moulding technique. The compression temperature used was set at 180ºC with 5 min of preheating and 10 min for compression time. Test samples were cut to the specified dimension according to the required standard test method of ASTM D 638 Type IV. Five replicates were prepared for each test.

**TESTING AND CHARACTERIZATION**

**Tensile properties** The tensile properties of the composites were determined using the Lloyd Instrument EZ 2.5 kN at 25ºC, 50% humidity and cross speed of 5 mm/min. Test samples were in dumb bell shape Type IV with the dimension of 115 mm × 6 mm × 3.2 mm as in the procedure of ASTM D 638.

**WATER ABSORPTION TEST**

Water absorption test was carried out according to ASTM D 570. Test samples were dried in the oven for 24 h at 50ºC, cooled in a desiccator and immediately weighed for the conditioning steps. Water absorption tests were conducted for 1 h immersion and reconditioned with same conditioning step. The sample tests were reconditioned due to the presence of water-soluble matter in the composites.

**RESULTS AND DISCUSSION**

**TENSILE PROPERTIES**

**Tensile strength** Tensile strength is one of the common properties describing the strength of materials. Figure 1 shows the effect of glycerol content on the tensile strength. Tensile strength of the composite decreased sharply with the increasing amount of glycerol and gradually above 30 phr of glycerol content. Composition of plasticizer were varies from 20 to 40 phr. This is due to the effect of a plasticizer with respect to the fully hydrolyzed PVA is
larger than the partially hydrolyzed PVA below 40 phr of glycerol (Jang & Lee 2003).

The decrement of tensile strength corresponds to that observed by Torres et al. (2007). The study showed that the decreasing value in tensile strength which occurred at higher glycerol contents might be associated with the presence of free volume in the sample. These free volumes affected the tensile strength in the composites. Excessive composition of glycerol increased the mobility of mixture however it does not give much effect on the plasticizing process. Therefore tensile strength of the composite depends on the strength of the fibre components. The effect of fibre loading on the tensile strength is shown in Figure 2. Higher composition of fibre in the composites result in the increase in tensile strength up to 60 wt%. Tensile strength however decreased above 60 wt% of fibre loading.

The decrease in tensile strength might be due to the increase of filler content in the composite. According to Herald et al. (2002) higher filler content may lead to poor distribution of filler across the matrix which caused the stress in the continuous phase to increase and promote poor tensile strength. The decrease in tensile strength above 60 wt% can be explained by the imperfect distribution of the filler through the polymer matrix, as well as very poor adhesion between the matrix and filler (Buzarovska et al. 2008). Higher fibre loading needs higher content of glycerol in order to plasticize the materials. The poor adhesion results in phase separation between matrix and filler thus forces only act on the plasticized matrix PVA and starch.

**Elongation at break** Figure 3 illustrates the effect of glycerol on the elongation at break. Elongation at break decreased with the addition of glycerol up to 30 phr and then increased above 30 phr. The decrement was probably due to insufficient plasticizer in the compound that inhibits flexibility and continuity in the matrix chain. Samples without addition of filler or reinforcement tend to have poor mechanical and physical properties (Preechawong et al. 2004). However, above 30 phr of glycerol content, glycerol is able to adequately plasticize the composite and thus improved the chain flexibility and promote ductility both in PVA and cassava starch. More plasticizer content may lead to lower interaction between polymer chains (Lin & Ku 2008). Increasing amount of glycerol will increase the composite mobility but it will affect the mechanical properties by lowering the strength of the samples. Relatively poor mechanical properties of natural composites have been ameliorated by adding large amounts of plasticizers, such as glycerol or ethylene glycol or by modifying the chemical properties of raw materials itself (Chiellini et al. 2003).

**Figure 1.** Tensile strength at various glycerol content in cassava skins/PVA (70/30) formulation

**Figure 2.** Tensile strength at various cassava skin loading at 20 phr glycerol content

**Figure 3.** Elongation at break at various glycerol content in cassava skins/PVA at 70/30 formulation

**Figure 4** shows the effect of fibre loading on the elongation at break. This figure shows that elongation at break decrease with higher content of fibre loading up to 60 phr and gradually increases above 70 phr. This decrement was due to the fibre loading which promote brittleness and increase rigidity of the composite. The increment observed...
above 70 wt% fibre probably because of the plasticized PVA and starch which phase separate at high fibre content and results in forces acting only on the plasticized PVA. This is supported by the low tensile strength similarly observed in composite loaded with greater than 70 wt% fibre.

**Young Modulus**  Figures 5 and 6 show the trend of Young modulus with various glycerol content and fibre loading respectively. Figure 5 illustrates the effect of glycerol content in the composites. This plot shows that glycerol which function as plasticizer helps to gradually increase Young modulus in the formulations. This indicates that glycerol improve compatibility between cassava skin filler with PVA matrix. Figure 6 shows the effect of fibre loading to the composite. Young modulus declined with addition of fibre. Addition of cassave skin up to 90 wt% increased the rigidity of the samples hence lowering the Young modulus. Imperfect distribution of the fibre in the formulations also affected the Young modulus.

**WATER ABSORPTION**

Water absorption test is very important to determine the water absorptivity of the material. Figures 7 and 8 show the water absorption of the composites for different composition of cassava skin loading and the glycerol content. From these Figures, water absorption value of the composite increased with higher content of glycerol due to the properties of glycerol itself whereby glycerol is soluble in water and naturally hygroscopic. The increase in water absorption with respect to glycerol and fibre loading indicates that glycerol and fibre are highly hydrophilic. The presences of three hydroxyl groups in a glycerol molecule are responsible for the highest tendency for water absorption of glycerol-plasticized composite (Preechawong et al. 2005). Figure 8 shows that the water absorbed by the composite decreased as the cassava skin loading was increased. Addition of PVA in the composite helps to reduce the water uptake.

**CONCLUSION**

Addition of glycerol as plasticizer to the biodegradable composites helps to promote the mobility and increased mechanical properties. Elongation at break and Young modulus increased as the glycerol content increased. However tensile strength showed the opposite result. However, excessive amount of glycerol results in poor mechanical properties and water absorption due to the properties of glycerol itself. Increasing cassava skins to the compound disrupt extrusion processability, improved tensile strength but reduced Young modulus and elongation at break up to 70 wt% fibre. The filler and matrix underwent distinct phase separation.

**ACKNOWLEDGEMENTS**

The authors thank Universiti Teknologi Malaysia and Polymer Engineering Department for the laboratory facilities and technical support given throughout the research work. We also like to express our gratitude to MOSTI for providing research grants VOT 79284 and...
Research Management Center- UTM (UTM-RMC) for managing the fund.

REFERENCES


Lin, C.A. & Ku, T.H. 2008. Shear and elongation flow properties of thermoplastic polyvinyl alcohol melts with different


Department of Polymer Engineering
Faculty of Chemical Engineering and Natural Resources
Universiti Teknologi Malaysia
81310 Skudai, Johor D.T.
Malaysia

*Corresponding author; email: dkim_4585@yahoo.com

Received: 23 October 2009
Accepted: 25 October 2010