

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 Biosot daripada Kulit Ubi Kayu/Polivinil 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

Bahan organik semula jadi dan sumber biopolimer lebih mendapat perhatian disebabkan oleh kos yang rendah, mudah diperolehi dan mudah terurai. Kulit ubi kayu digunakan sebagai pengisi semula jadi kepada polivinil alkohol (PVA). Adunan kulit ubi kayu/PVA diadun menggunakan kaedah penyemperitan skru berkembar dan sampel disediakan melalui kaedah pemampatan. Gliserol ditambah sebagai bahan pemplastik untuk pemplastikan PVA dan menggalakkan kebolehergerakan adunan. Penyerapan air oleh adunan kulit ubi kayu/PVA meningkat apabila komposisi kulit ubi kayu yang tinggi digunakan disebabkan sifat hidrofilik bahan tersebut tetapi menurun dengan pertambahan gliserol. Kekuatan adunan kulit ubi kayu/PVA meningkat dengan pertambahan komposisi ubi kayu sehingga 70 wt% tetapi menurun dengan pertambahan komposisi gliserol. Modulus Young meningkat dengan pertambahan kandungan gliserol di dalam adunan tetapi menurun apabila kandungan kulit ubi kayu sehingga 70 wt%. Pemanjangan pada takat putus berkurangan dengan pertambahan kulit ubi kayu sehingga 70 wt% dan 30 phr gliserol.

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 (Carraher 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 2005a, 2005b; Nabar et al. 2006; Salgado et al. 2008; Tsvintzelis 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 170°C 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

| Blend | PVA (wt%) | Cassava skins (wt%) | Glycerol (phr) |
|-------|-----------|---------------------|----------------|
| 90/10 | 10 | 90 | 20 |
| 80/20 | 20 | 80 | 20 |
| 70/30 | 30 | 70 | 30 |
| 60/40 | 40 | 60 | 40 |
| 50/50 | 50 | 50 | 20 |

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 180°C 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 25°C, 50% humidity and cross speed of 5 mm/min. Test samples were in dumb bell shape Type IV with the dimension of 115 mm \times 6 mm \times 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 50°C, 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).

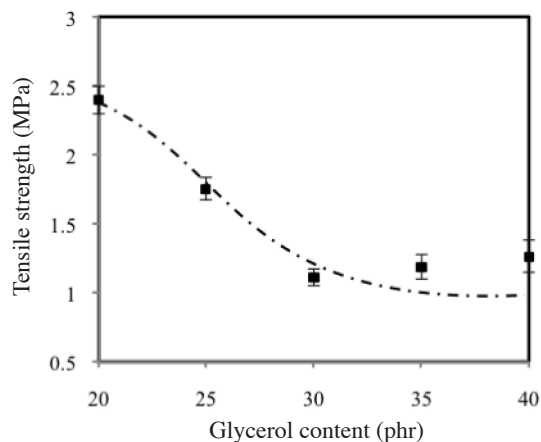


FIGURE 1. Tensile strength at various glycerol content in cassava skins/PVA (70/30) formulation

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

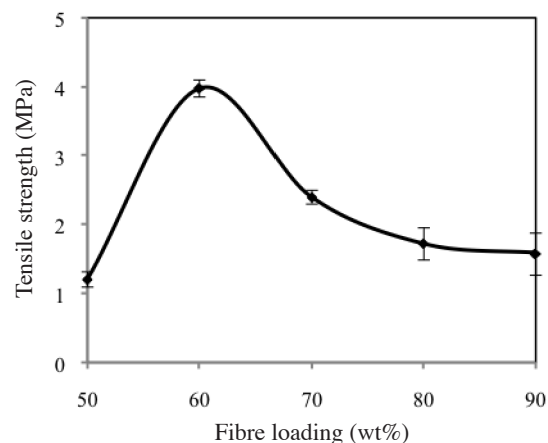


FIGURE 2. Tensile strength at various cassava skin loading at 20 phr glycerol content

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).

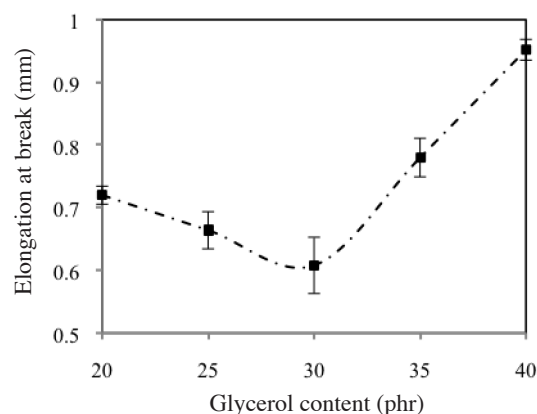


FIGURE 3. Elongation at break at various glycerol content in cassava skins/PVA at 70/30 formulation

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.

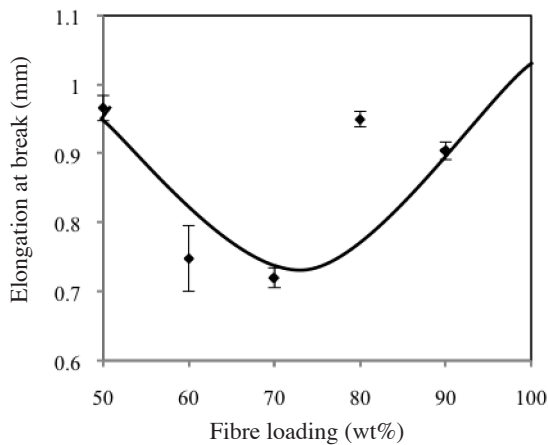


FIGURE 4. Elongation at break at various cassava skin loading in cassava skins/PVA at 20 phr glycerol

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 cassava 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.

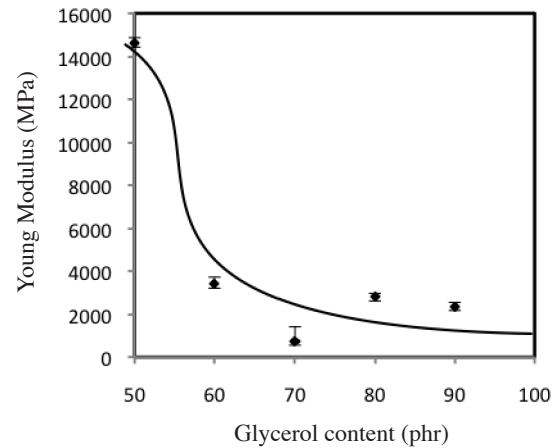


FIGURE 5. Effect of glycerol content on the Young modulus of cassava skins/PVA at 70/30 formulation

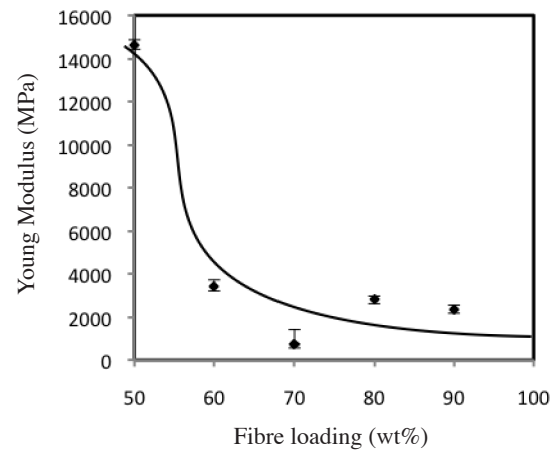


FIGURE 6. Effect of fibre loading to the Young modulus at 20 phr glycerol

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

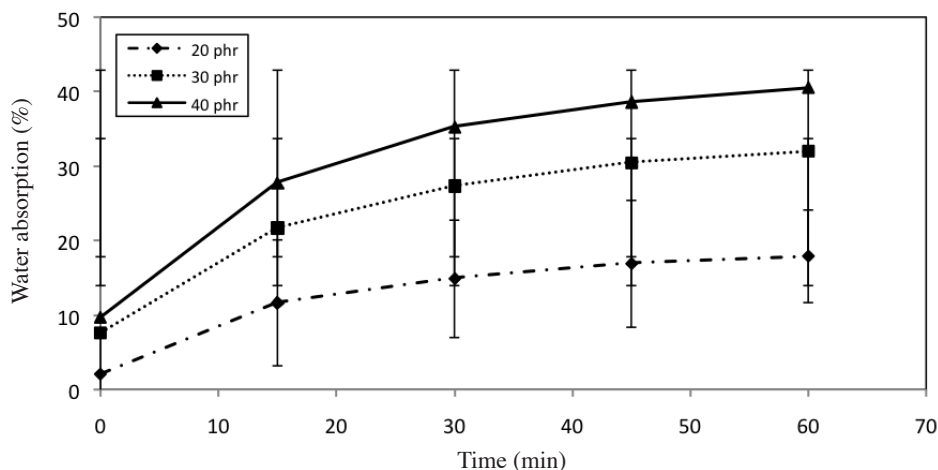


FIGURE 7. Effect of immersion time to the water absorption due to glycerol content

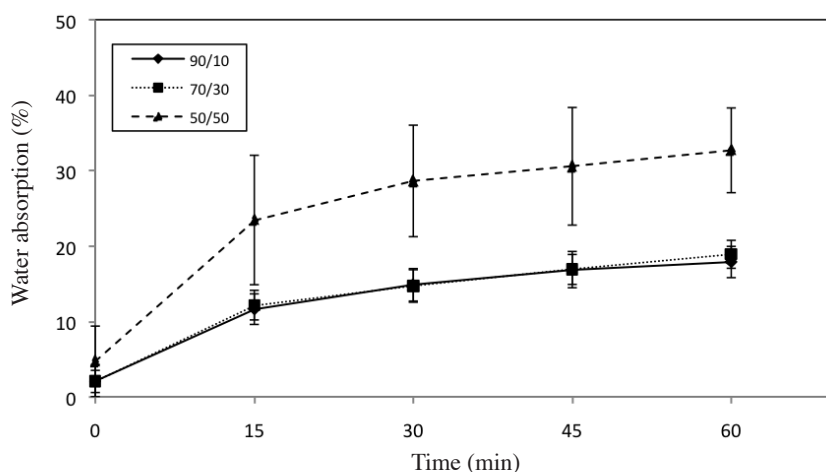


FIGURE 8. Effect of immersion time to the water absorption due to cassava skin loading at 20 phr glycerol

Research Management Center- UTM (UTM-RMC) for managing the fund.

REFERENCES

- Alexy, P., Lacík, I., Šimkovic, B., Bakoš, D., Prónayová, N., Liptaj, T., Hanzelová, S. & Várošová, M. 2004. Effect of melt processing on thermo-mechanical degradation of poly(vinyl alcohol)s. *Polymer Degradation and Stability* 85: 823-830.
- Bhatnagar, S. & Hanna, M.A. 1995. Properties of extruded starch-based plastic foam. *Industrial Crops and Products* 4: 71-77.
- Buzarovska, A., Bogoeva-Gaceva, G., Grozdanov, A., Avella, M., Gentile, G. & Errico, M. 2008. Potential use of rice straw as filler in eco-composite materials. *Australian Journal of Crop Science* 1(2): 37-42.
- Carragher, C.E. 2008. *Polymer Chemistry*. (7th ed). Boca Raton, FL: Taylor & Francis Group. pp 272-273.
- Cha, J.Y., Chung, D.S., Seib, P. A., Flores, R.A. & Hanna, M.A. 2001. Physical properties of starch-based foams as affected by extrusion temperature and moisture content. *Industrial Crops and Products* 14: 23-30.
- Chandra, R. & Rustgi, R. 1998. Biodegradable polymers. *Progress in Polymer Science* 23: 1273-1335.
- Chiellini, E., Corti, A.D., Antone, S. & Solaro, R. 2003. Biodegradation of poly(vinyl alcohol) based materials. *Progress in Polymer Science* 28: 963-1014.
- Ganjyal, G.M., Reddy, N., Yang, Y.Q. & Hanna, M.A. 2003. Biodegradable packaging foams of starch acetate blended with corn stalk fibres. *Journal of Applied Polymer Science* 93: 2627-2633.
- Glenn, G.M. & Orts, W.J. 2001. Properties of starch-based foam formed by compression/explosion processing. *Industrial crops and Products* 13: 135-143.
- Glenn, G.M., Orts, W.J. & Nobes, G.A.R. 2001. *In situ* Laminating process for baked starch-based foams. *Industrial Crops and Products*. 14: 201-212.
- Herald, T.J., Obuz, E., Twombly, W.W. & Rausch, K.D. 2002. Tensile Properties of Extruded Corn Protein Low-Density Polyethylene Films. *Cereal Chem.* 79(2): 261-264.
- Jang, J. & Lee, D.K. 2003. Plasticizer effect on the melting and crystallization behavior of polyvinyl alcohol. *Polymer* 44: 8139-8146.
- Lin, C.A. & Ku, T.H. 2008. Shear and elongation flow properties of thermoplastic polyvinyl alcohol melts with different

- plasticizer contents and degrees of polymerization. *Journal of Materials Processing Technology* 200: 331-338.
- Lui, W.B. & Peng, J. 2005a. Physical mechanical biodegradable properties and energy absorption behavior of corn grit-polyvinyl alcohol cushioning extrudates. *Journal of Food Engineering* 71: 73-84.
- Lui, W.B. & Peng, J. 2005b. Effects of operating conditions on degradable cushioning extrudates cellular structure and the specific heat. *Journal of Food Engineering* 70: 171-182.
- Nabar, Y., Narayan, R. & Schindler, M. 2006. Twin-screw extrusion production and characterization of starch foam products for use in cushioning and insulation applications. *Polymer Engineering and Science* 46: 438-451.
- Preechawong, D., Peesan, M., Supaphol, P. & Rujiravanit, R. 2004. Characterization of starch poly(ϵ -caprolactone) hybrid foams. *Polymer Testing* 23: 651-657.
- Preechawong, D., Peesan, M., Supaphol, P. & Rujiravanit, R. 2005. Preparation and characterization of starchpoly(L-lactic acid) hybrid foams. *Carbohydrate Polymers* 59: 329-337.
- Salgado, P.R., Schmidt, V.C., Ortiz, S.E.M., Mauri, A.N. & Laurindo, J.B. 2008. Biodegradable foams based on cassava starch, sunflower proteins and cellulose fibres obtained by a baking process. *Journal of Food Engineering* 85: 435-443.
- Shogren, R.L., Lawton, J.W., Tiefenbacher, K.F. & Chen, L. 1998. Starch-poly(vinyl alcohol) foamed articles prepared by a baking process. *Journal of Applied Polymer Sciences* 68: 2129-2140.
- Torres, F.G., Arroyo, O.H. & Gómez, C. 2007. Processing and mechanical properties of natural fibre reinforced thermoplastic starch biocomposites. *Journal of Thermoplastic Composite Materials* 20: 207-223.
- Tsivintzelis, I., Pavlidou, E. & Panayiotou, C. 2007. Biodegradable polymer foams prepared with supercritical CO₂-ethanol mixtures as blowing agents. *The Journal of Supercritical Fluids* 42: 265-272.
- Willett, J.L. & Shogren, R.L. 2002. and properties of extruded starch/polymer foams. *Polymer* 43: 5935-5947.
- Xu, Y.X., Dzenis, Y. & Hanna, M.A. 2005. Water solubility, thermal characteristics and biodegradability of extruded starch acetate foams. *Industrial Crops and Products* 21: 361-368.
- Xu, Y.X. & Hanna, M.A. 2005. Preparation and properties of biodegradable foams from starch acetate and poly(tetramethylene adipate-co-terephthlate). *Carbohydrate Polymers* 59: 521-529.
- Zhou, J., Song, J. & Parker, R. 2006. Structure and properties of starch-based foams prepared by microwave heating from extruded pellets. *Carbohydrate Polymers* 63: 466-475.
- Zhou, J., Song, J. & Parker, R. 2007. Microwave-assisted moulding using expandable extruded pellets from wheat flours and starch. *Carbohydrate Polymers* 69: 445-454.

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