

# Effect of Lignin Derivatives in the Bio-Polyols from Microwave Liquefied Bamboo on the Properties of Polyurethane Foams

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Bamboo residues were subjected to a microwave-assisted liquefaction process for the production of crude bio-polyols (CBP). The fractionated bio-polyols (FBP) were obtained by the removal of lignin derivatives from the crude bio-polyols (CBP) using a simple method. Polyurethane (PU) foams were successfully prepared from both CBP and FBP. The object of this study was to evaluate the effect of lignin derivatives in bio-polyols on the physical properties, thermal stability, and microstructure of PU foams. The results revealed that the PU foam made from CBP had a higher density and superior thermal stability compared to that made from FBP; however, they were also much more fragile. Scanning electron microscope (SEM) images indicated that the lignin compounds in the CBP had impact on the structure of the PU foam.

*Keywords:* Bamboo; Liquefaction; Microwave; Lignin derivatives; Polyurethane foam

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## INTRODUCTION

Polyurethane (PU) foams have been widely used for insulation and transportation, packaging, furniture cushioning, building construction, and more. Commercially, the raw materials for the preparation of PU foams are polyols and isocyanates, which are derived from fossil fuel resources. In recent years, with increasing concern for the depletion of fossil fuels, global warming, and other environmental impacts from petroleum-based products, the technologies for the production of renewable chemicals, such as bio-polyols and phenolic products, have been receiving increasing attention.

Pyrolysis and liquefaction are two common pathways for the conversion of lignocellulosic biomass. Compared to pyrolysis, liquefaction with organic solvents has great potential to produce value-added bio-products because of its mild reaction conditions (low temperatures). As an efficient method, liquefaction has been applied in the conversion of solid lignocellulosic biomass into liquid products, and the liquid products have become attractive alternatives for the PU industry. A great number of forest and agricultural residues, such as wood waste (Bai and Gao 2012; Li *et al.* 2012), wheat straw (Chen and Lu 2009; Chen *et al.* 2012), bagasse (Xie and Chen 2005), soybean straw (Hu *et al.* 2012), and kenaf core (Juhaida *et al.* 2010; Bakarudin *et al.* 2012), have been successfully subjected to liquefaction processes, and their liquefied products exhibit promising properties for the preparation of PU foams and adhesives/resins. Due to the fact that microwave energy penetrates and produces a volumetrically distributed heat source, microwave energy has recently been applied in

polymer chemistry and lignocellulosic biomass conversion (Krzan and Zagar 2009; Xiao *et al.* 2011; Pan *et al.* 2012; Hayden *et al.* 2013).

In general, the high content of cellulose and hemicellulose in woody materials contributes to the generation of hydroxyl-rich bio-polyols from liquefaction, and the resulting high-quality bio-polyols possess excellent properties for the production of PU foams (Xu *et al.* 2012). However, the main components of woody materials, *i.e.*, cellulose, hemicellulose, and lignin, have all been converted into small liquid molecules through complete liquefaction. Thus, the undesired lignin derivatives usually lack hydroxyl functionalities, leading to low activity during the reaction with isocyanate. On the other hand, lignin is composed of phenylpropane units, which are a rich source of phenolic compounds upon thermal degradation. Several studies concerning the production of phenols from biomass feedstocks have been published (Amen-Chen *et al.* 2001; Effendi *et al.* 2008). Therefore, it is necessary to separate the lignin derivatives from enriched hydroxyl bio-polyols and evaluate their potential utilization for other valuable products.

From previous results, bamboo was found to be composed of about 42% cellulose, 22% hemicellulose, and 20% lignin (Qi *et al.* 2013). These components are chemically known to have a great potential for the production of hydroxyl-rich bio-polyols through liquefaction. Moreover, glycerol is a by-product of the transesterification process to manufacture bio-diesel. With the increase in global bio-diesel production, the price for this crude glycerol has crashed, and the commercial utilization of this compound has become a challenge. Thus, to address latent problems concerning glycerol waste disposal, resource waste, and commercial costs, a new microwave-assisted liquefaction system was previously optimized using glycerol as a solvent, and a simple method to separate the liquefied products was developed (Xu *et al.* 2012). In the present study, bamboo residues were subjected to the liquefaction process, and the liquefied bamboo was fractionated to obtain lignin derivative-free bio-polyols. The bio-polyols both before and after the lignin removal process were applied in the preparation of PU foams. The aim of this study was to evaluate the effect of lignin derivatives in liquefied biopolyols on the density, thermal stability, and microstructure of PU foams.

## EXPERIMENTAL

### Materials and Chemicals

Bamboo residues used in the experiments were collected from central Louisiana, USA. The weight percentages of alcohol-toluene extractive, hot water extractive, cellulose, and lignin matters in the raw material were 7.24, 10.53, 41.72, and 20.91%, respectively, and were defined in accordance to ASTM methods (D1107-96, D1110-96, D1103-60, and D1106-96). The air-dried residues were reduced to pass through a 40-mesh sieve using a Wiley mill, followed by oven drying at 80 °C for further use. All the reagents used in this study were of analytical grade and obtained from commercial sources.

### Liquefaction Reaction

Microwave-assisted liquefaction of bamboo was performed in a Milestone MEGA laboratory microwave system (Ethos EX, 1200 W microwave extractive system). The liquefaction reaction was carried out using optimized conditions in a previous study (Xie

*et al.* 2014). Glycerol and methanol were used as solvents at a solvent-to-bamboo ratio of 4/1 (w/w), and sulfuric acid was used as the catalyst. A typical reaction mixture consisting of 2 g of bamboo particles, 8 g of solvent, and 0.14 g of sulfuric acid was loaded into Teflon vessels and thoroughly pre-mixed. The Teflon vessels were then placed on a rotor tray inside the microwave cavity. The liquefaction temperature was increased from room temperature to 150 °C at a heating rate of 32.5 °C min<sup>-1</sup> and maintained for 3 min. The vessels were then allowed to cool before opening, normally below 50 °C.

### Preparation of Lignin Derivative-Free Bio-Polyols

The liquefied materials were dissolved in 150 mL of methanol under constant stirring for 4 h. The liquefied solutions were then vacuum-filtered through Whatman No. 4 filter paper. The conversion yield was calculated as follows:

$$\text{conversion yield (\%)} = \left(1 - \frac{\text{weight of residue}}{\text{weight of raw material}}\right) \times 100 \quad (1)$$

The average conversion yield (liquid product) for the optimized liquefaction process was 94.2%. The filtrated liquid was evaporated at 45 °C under vacuum to remove methanol, the obtained black liquid was designated crude bio-polyols (CBP), and then distilled water (10/1, w/w) was added to the black crude bio-polyols. The mixture was stirred thoroughly with a glass rod. Afterwards, the mixture was centrifuged at 5000 rpm for 10 min. Fractionated bio-polyols (FBP) were obtained by the removal of water from the supernatant fluid using a rotary evaporator. The lignin derivatives (precipitate) were dried at 30 °C for 12 h. The hydroxyl numbers for the FBP and CBP were 824 and 564 mg KOH/g, respectively and measured according to ASTM D 4274-05.

### Preparation of PU Foams

PU foams were prepared using a one-step method. A typical mixture of CBP/FBP (3.5 g), PEG-400 (0.5 g), catalyst (dibutyltine dilaurate, 0.1 g), blowing agents (water, 0.3 g), and surfactant (Dow corning 193, 0.1 g) was premixed thoroughly in a beaker with a mechanical stirrer for 15 s. Afterwards, isocyanate (MDI, 7 g) was added to the pre-mixture and the combination was stirred with a high-speed agitator at a stirring speed of 3600 rpm. Immediately afterwards, the resultant mixture was poured into an open cylindrical mold and was allowed to freely rise at room conditions. The obtained foams were allowed to cure at room temperature for 1 h. All foams were conditioned for 48 h at room conditions. The foams were cut into 50 mm × 50 mm × 50 mm specimens for the measurement of density (ASTM D 1622-08), and five replicates were measured for each foam formulation.

### Analysis Methods

#### *Fourier transform infrared spectroscopy (FT-IR)*

The FT-IR analysis was performed using a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. A small amount of sample was applied directly on the diamond crystal. Data collection was performed with a 4-cm<sup>-1</sup> spectral resolution, and 32 scans were taken per sample.

#### *Gas chromatograph-mass spectrometer (GC-MS)*

The general profile for the FBP was obtained using electron ionization mass spectrometry (EI-MS). Analysis of the product was conducted on a mass spectrometer (Agilent 5975C VL MSD), and the products were separated into their components using a gas chromatograph (Agilent 7890A) equipped with a fused capillary column (HP-5, L=30 m, i.d. 0.32 mm, film thickness 0.25  $\mu\text{m}$ ) with 5% phenyl and 95% dimethylpolysiloxane as the stationary phase. The carrier gas was helium at a flow rate of 1.8 mL/min.

Condition for analysis: injection mode was split at split rate 35; the column was held at 50  $^{\circ}\text{C}$  for 2 min and then heated to 250  $^{\circ}\text{C}$  at the rate of 10  $^{\circ}\text{C}/\text{min}$ , while the injector temperature was 250  $^{\circ}\text{C}$ . The identification of the product components was confirmed using total ion chromatograms as well as fragmentation patterns.

#### *Thermogravimetric (TG) analysis*

TG/DTG analysis of the bamboo residues was conducted with a thermal analyzer, TGA (Q50), to simultaneously obtain thermogravimetric data. About 2 mg of sample was analyzed by the thermal analyzer. Pyrolysis was terminated at 800  $^{\circ}\text{C}$  with a heating rate of 20  $^{\circ}\text{C}/\text{min}$  under a 60-mL/min flow of nitrogen gas.

#### *Scanning electron microscope (SEM) analysis*

The structure and surface morphology of polyurethane foams were observed using a scanning electron microscope (SEM, JCM-5000). Test samples were coated with gold using a vacuum sputter coater before being subjected to the SEM analysis.

## RESULTS AND DISCUSSION

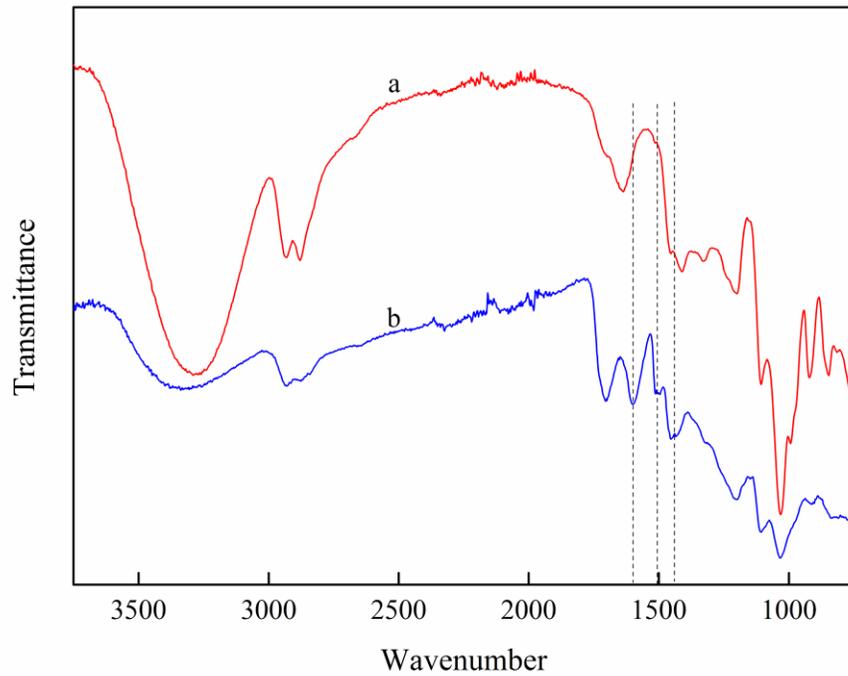
### Chemical Analysis of Fractionated Bio-Polyols

#### *FT-IR spectra*

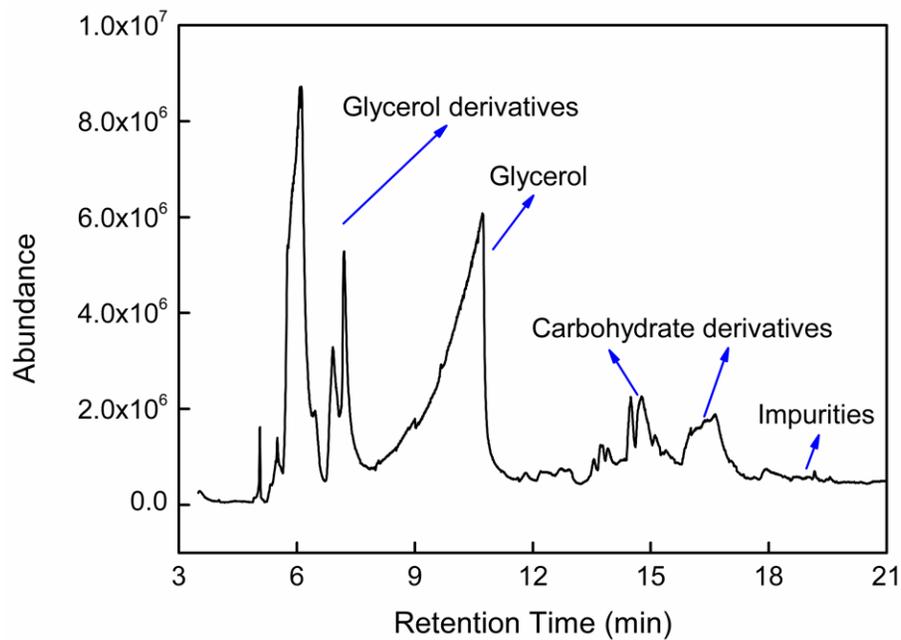
FT-IR was conducted to determine the differences in chemical functional groups present in the fractionated polyols and precipitated lignin derivatives. The fractionated bio-polyols (spectrum a) showed enriched hydroxyl groups, as indicated by the bands at 3320, 1028, 1108, 920, and 845  $\text{cm}^{-1}$  that were assigned to cellulose, glycerol, and its derivatives. The lignin bands (1596, 1506, and 1456  $\text{cm}^{-1}$ ) disappeared, indicating that lignin derivatives were removed. However, the lignin bands were present in the spectrum of precipitates (spectrum b). The results revealed that the fractionated bio-polyols primarily contained carbohydrate-degraded fragments and glycerol/methanol blended solvents. This was further evidenced by the GC-MS results for fractionated bio-polyols, discussed later.

#### *GC-MS analysis*

The fractionated bio-polyols in this study were analyzed by GC-MS (Fig. 2), and the identified compounds are presented in Table 1. It can be seen that, except for the unreacted glycerol solvent, carbohydrate derivatives having more than two hydroxyl groups were identified. The results shown in Table 1 also demonstrated that large quantities of glycerol derivatives, such as 1,2-propanediol, 3-methoxy-, and 1,2,4-butanetriol were produced with the degradation of carbohydrates. The most interesting finding for the GC-MS results was that no phenolic compound was identified, indicating that the lignin derivatives were successfully removed.



**Fig. 1.** FTIR spectra of (a) fractionated bio-polyols and (b) precipitated lignin derivatives



**Fig. 2.** GC-MS analysis of the fractionated bio-polyols

**Table 1.** Hydroxy Compounds in the Fractionated Bio-Polyols Identified by GC-MS

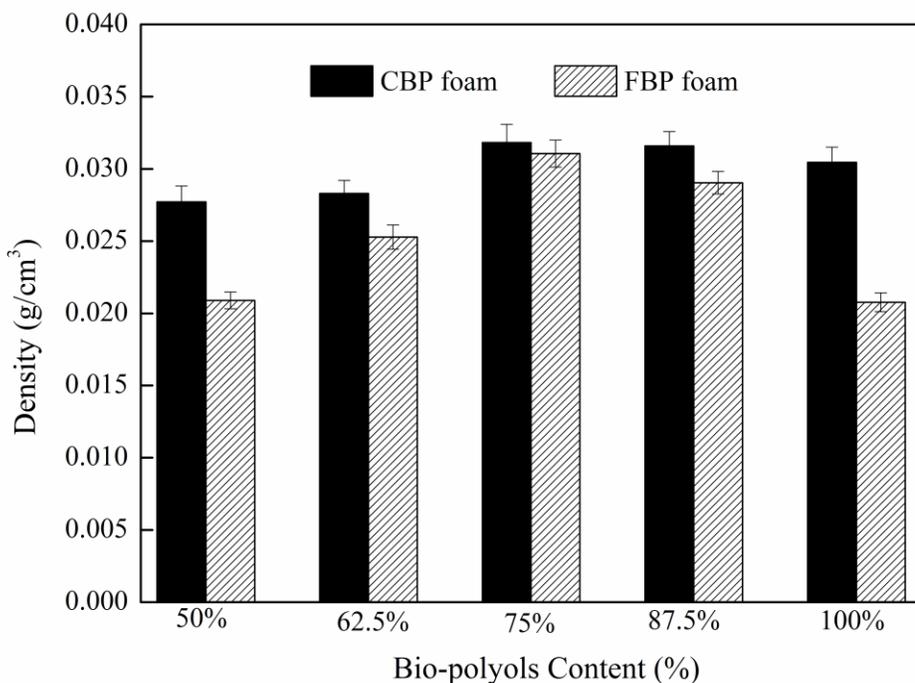
Component	Proportion
Glycerol derivatives (1,2-Propanediol, 3-methoxy-; 1,2,4-Butanetriol; Oxirane, (methoxymethyl)-; 1,1,3-Trimethoxypropane)	12.99%
Glycerol	70.80%
Carbohydrate derivatives ( $\alpha$ -D-Glucopyranoside, methyl; $\beta$ -D-Glucopyranoside, methyl; Propanoic acid, 3-hydroxy-; 3, 4-Altrosan)	8.42%
Impurities	7.79%

## Properties of PU Foams

### Density

In this study, the CBP and FBP were used directly to produce PU foams. The densities of the CBP and FBP foams with respect to the bio-polyols content in polyols are shown in Fig. 3. The density of CBP and FBP foams varied between 0.028 and 0.032 g/cm<sup>3</sup> and 0.021 and 0.031 g/cm<sup>3</sup>, respectively. As can be seen in Fig. 3, the density of CBP foam is higher than that of FBP foam at various bio-polyols content, indicating that the lignin derivatives in the CBP could lead to denser foams. However, it was also found that the CBP foam was quite fragile and was easy to smash into powder. Figure 3 also shows that, with increasing bio-polyol content, the density of CBP and FBP foams first increased and then decreased. The density reached a maximum value when the bio-polyols content was 75%.

According to the literature, increasing the content of bio-polyols in polyol components could result in increasing PU foam density because of the increase in wood components in the bio-polyols (Liu 2010). However, in this study, when the bio-polyols content was high enough (75 to 100%), the foam density showed a decreasing trend. Therefore, the effect of bio-polyols and their chemical compositions on foam density is rather complex and difficult to thoroughly understand. To clarify the effect of bio-polyols content on the foam density, it is necessary to investigate the reaction pathways between each bio-polyols component and isocyanate. Such experimentation is under consideration.



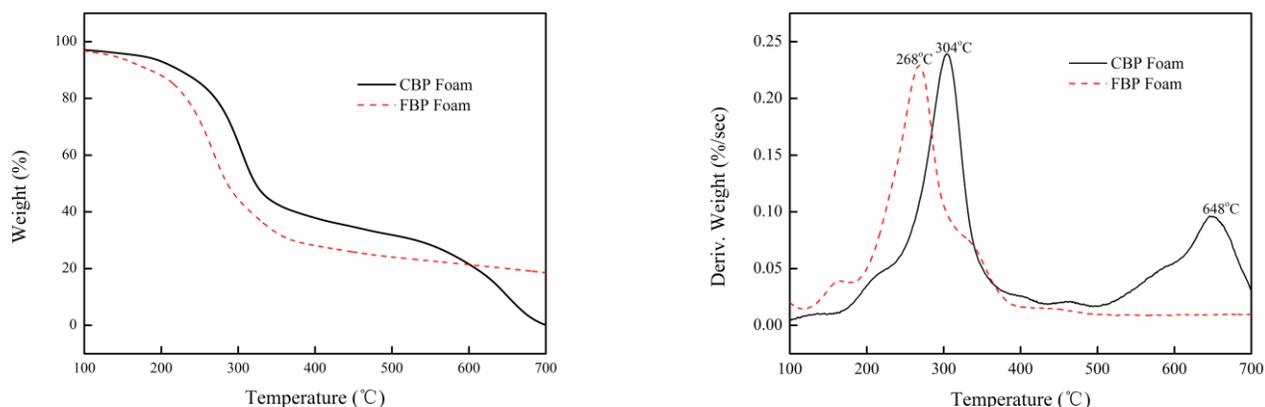
**Fig. 3.** Density of PU foams with respect to bio-polyols content in polyols (foam formulation: polyol (CBP/FBP+PEG-400), 4.0 g; catalyst, 0.1 g; blowing agent, 0.3 g; surfactant, 0.1 g; MDI, 7.0 g)

#### *Thermal stability*

The thermal decomposition behaviors of PU foams are presented in Fig. 4. According to the TG and DTG curves, no apparent weight loss for the CBP foam was found under 200 °C. The thermal decomposition of the CBP foam proceeded primarily via two main stages, at temperatures of 304 and 648 °C. In general, polyurethane is thought to be relatively thermally unstable primarily because of the presence of urethane bonds (Chen and Lu 2009; Zhang *et al.* 2013). Thus, the first decomposition stage (200 to 304 °C) can be attributed to the decomposition of urethane segments and isocyanate. The second stage (500 to 648 °C) may be attributed to the decomposition of lignin and other contents that are difficult to decompose. The thermal decomposition behavior of CBP foam was similar to those reported for PU foams prepared from other liquefied lignocellulosic biomasses (Zhao *et al.* 2012; Gao *et al.* 2010).

There was only one region of major weight loss in the thermal decomposition curves of FBP foam. A similar result was found in a study of PU foams made from liquefied paper waste (Lee *et al.* 2002). The FBP foam was found to decompose under 150 °C and lost 12% of its initial weight at 200 °C. This may be due to the higher content of glycerol derivatives in the FBP, which leads to high volatility at lower temperatures. For comparison, the peak corresponding to the maximum decomposition rate of FBP foam was shifted to the low-temperature side compared to that of CBP foam, indicating that the removal of lignin compounds in bio-polyols could decrease the thermal stability of the PU foams. This may be attributed to the fact that lignin has superior thermal

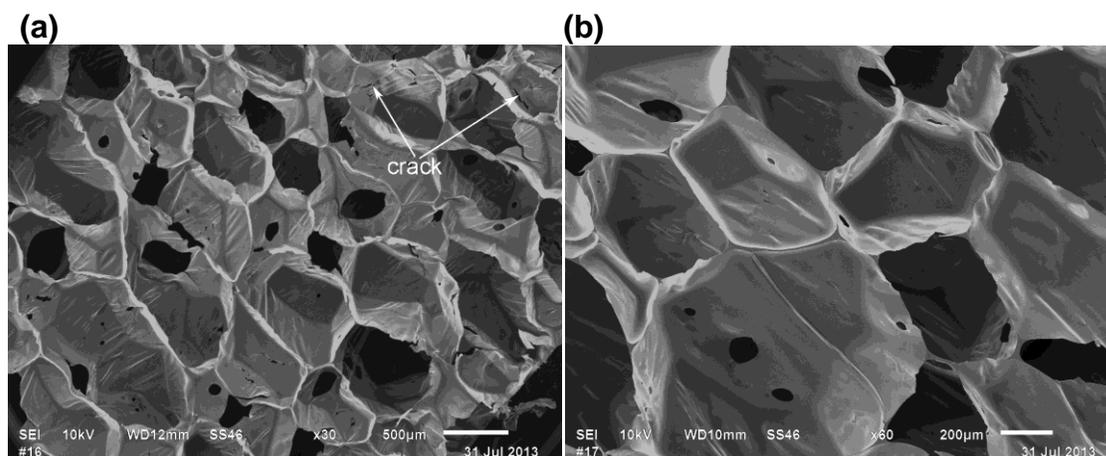
stability compared to other components in woody materials (Niu *et al.* 2011; Qi *et al.* 2013).



**Fig. 4.** TG and DTG curves of PU foams prepared from CBP and FBP (foam formulation: CBP/FBP, 2.0 g; PEG-400, 2.0 g; catalyst, 0.1 g; blowing agent, 0.3 g; surfactant, 0.1 g; MDI, 7.0 g)

#### *Microstructure of polyurethane foams*

Representative SEM images of PU foams made from both CBP and FBP are shown in Fig. 4. All the PU foams exhibited a honeycomb skeleton coated with a thin film, indicating that both the CBP and FBP have acceptable capability for the preparation of PU foams. As shown in Fig. 5, a few more wrinkles were found on the foams made from CBP when compared to those from FBP, and cracks were observed on its thin film. The lignin derivatives, which lack hydroxy functionalities, could lead to low activity during the reaction with diisocyanate. Thus, the presence of lignin compounds in CBP resulted in the inhomogeneous surface and irregular pore shape of the foams.



**Fig. 5.** SEM images of PU foams (a, CBP foam, 30x; b, FBP foam, 60x) (foam formulation: CBP/FBP, 2.0 g; PEG-400, 2.0 g; catalyst, 0.1 g; blowing agent, 0.3 g; surfactant, 0.1 g; and MDI, 7.0 g)

## CONCLUSIONS

1. Bio-polyols were generated from the microwave-assisted liquefaction of bamboo, and the lignin derivatives in the crude bio-polyols (CBP) were successfully removed by the addition of water, as evidenced by FT-IR and GC-MS analyses.
2. Both the crude bio-polyols (CBP) and fractionated bio-polyols (FBP) showed acceptable quality in the preparation of PU foams.
3. The PU foam made from CBP had a higher density than that made from FBP. Lignin derivatives in CBP contributed to the denser foams.
4. A significant difference was found in the thermal stability of PU foams made from crude bio-polyols (CBP) and those made from fractionated bio-polyols (FBP). The PU foam made from CBP showed superior thermal stability compared to that made from FBP.
5. The presence of lignin derivatives in CBP affected the formation of PU foam, resulting in irregular pore shapes with cracks and more wrinkles.

## ACKNOWLEDGMENTS

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## REFERENCES CITED

- ASTM D 1103-60 (1971). "Standard test method for alpha-cellulose in wood," American Society for Testing and Materials.
- ASTM D 1106-96 (1996a). "Standard Test Method for acid-insoluble lignin in wood," American Society for Testing and Materials.
- ASTM D 1110-96 (1996b). "Standard test method for water solubility of wood," American Society for Testing and Materials.
- ASTM D 1107-96 (1996c). "Standard test method for ethanol-toluene solubility of wood," American Society for Testing and Materials.
- ASTM D 4274-05 (2005). "Standard test method for testing polyurethane raw materials: Determination of hydroxyl numbers of polyols," American Society for Testing and Materials.
- ASTM D 1622-08 (2008). "Standard test method for apparent density of rigid cellular plastics," American Society for Testing and Materials.
- Amen-Chen, C., Pakdel, H., and Roy, C. (2001). "Production of monomeric phenols by thermochemical conversion of biomass: A review," *Bioresource Technology* 79(3), 277-299.
- Bakarudin, S. B., Zakaria, S., Chia, C. H., and Jani, M. (2012). "Liquefied residue of kenaf core wood produced at different phenol-kenaf ratio," *Sains Malaysiana* 41(2), 225-231.

- Bai, Y. M., and Gao, Z. H. (2012). "Water-resistant plywood adhesives prepared from phenolated larch bark in the presence of various combination catalysts," *Journal of Applied Polymer Science* 126(S1), E373-E382.
- Chen, F. G., and Lu, Z. M. (2009). "Liquefaction of wheat straw and preparation of polyurethane foam from the liquefaction products," *Journal of Applied Polymer Science* 111(1), 508-516.
- Chen, H. Z., Zhang, Y. Z., and Xie, S. P. (2012). "Selective liquefaction of wheat straw in phenol and its fractionation," *Applied Biochemistry and Biotechnology* 167(2), 250-258.
- Effendi, A., Gerhauser, H., and Bridgwater, A.V. (2008). "Production of renewable phenolic resins by thermochemical conversion of biomass: A review," *Renewable and Sustainable Energy Reviews* 12(8), 2092-2116.
- Gao, L. L., Liu, Y. H., Lei, H. W., Peng, H., and Ruan, R. (2010). "Preparation of semirigid polyurethane foam with liquefied bamboo residues," *Journal of Applied Polymer Science* 116(3), 1694-1699.
- Hu, S. J., Wan, C. X., and Li, Y. B. (2012). "Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw," *Bioresource Technology* 103(1), 227-233.
- Hayden, S., Damm, M., and Kappe, C. O. (2013). "On the importance of accurate internal temperature measurements in the microwave dielectric heating of viscous systems and polymer synthesis," *Macromolecular Chemistry and Physics* 214(4), 423-434.
- Juhaida, M. F., Paridah, M. T., Hilmi, M. M., Sarani, Z., Jalaluddin, H., and Zaki, A. R. M. (2010). "Liquefaction of kenaf (*Hibiscus cannabinus* L.) core for wood laminating adhesive," *Bioresource Technology* 101(4), 1355-1360.
- Krzan, A., and Zagar, E. (2009). "Microwave driven wood liquefaction with glycols," *Bioresource Technology* 12(100), 3143-3146.
- Lee, S. H., Teramoto, Y., and Shiraishi, N. (2002). "Biodegradable polyurethane foam from liquefied waste paper and its thermal stability, biodegradability, and genotoxicity," *Journal of Applied Polymer Science* 83(7), 1482-1489.
- Liu, J. J. (2010). "Liquefaction of bagasse and preparation of polyurethane foams from liquefied products," M.S. Thesis, South China University of Technology, Guangdong, China.
- Li, G. Y., Hse, C. Y., and Qin, T. F. (2012). "Preparation and characterization of novolak phenol formaldehyde resin from liquefied brown-rotted wood," *Journal of Applied Polymer Science* 125(4), 3142-3147.
- Niu, M., Zhao, G. J., and Alma, M. H. (2011). "Thermogravimetric studies on condensed wood residues in polyhydric alcohols liquefaction," *BioResources* 6(1), 615-630.
- Pan, H., Zheng, Z. F., and Hse, C. Y. (2012). "Microwave-assisted liquefaction of wood with polyhydric alcohols and its application in preparation of polyurethane (PU) foams," *European Journal of Wood Products* 70(4), 461-470.
- Qi, J. Q., Xie, J. L., Hse, C. Y., and Shupe, T. F. (2013). "Analysis of *Phyllostachys pubescens* bamboo residues for liquefaction: Chemical components, infrared spectroscopy, and thermogravimetry," *BioResources* 8(4), 5644-5654.
- Xie, T., and Chen, F. G. (2005). "Fast liquefaction of bagasse in ethylene carbonate and preparation of epoxy resin from the liquefied product," *Journal of Applied Polymer Science* 98(5), 1961-1968.

- Xie, J. L., Huang, X. Y., Qi, J. Q., Hse, C. Y., and Shupe, T. F. (2014). "Effect of anatomical characteristics and chemical components on microwave-assisted liquefaction of bamboo wastes," *BioResources* 9(1), 231-240.
- Xu, J. M., Jiang, J. C., Hse, C. Y., and Shupe, T. F. (2012). "Renewable chemical feedstocks from integrated liquefaction processing of lignocellulosic materials using microwave energy," *Green Chemistry* 14(10), 2821-2830.
- Xiao, W. H., Han, L. J., and Zhao, Y. Y. (2011). "Comparative study of conventional and microwave-assisted liquefaction of corn stover in ethylene glycol," *Industrial Crops and Products* 34(3), 1602-1606.
- Zhang, H. R., Pang, H., Zhang, L., Chen, X. D., and Liao, B. (2013). "Biodegradability of polyurethane foam from liquefied wood based polyols," *Journal of Polymers and the Environment* 21(2), 329-334.
- Zhao, Y., Yan, N., and Feng, M. (2012). "Polyurethane foams derived from liquefied mountain pine beetle-infested barks," *Journal of Applied Polymer Science* 123(5), 2849-2858.

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