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Preparation of Polyurethane Foams Using Fractionated Products in Liquefied Wood

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ABSTRACT: Liquefaction of sawdust was studied using glycerol and methanol as mix solvents. A new bio-polyol product consisting of high purity multi-hydroxy compounds was obtained by precipitation of the hydrophobic organics from the liquefied product in an aqueous solution. As identified by GC-MS, the dominate components in bio-polyol were glycerol, glycerol derivatives, and multiple types of sugar derivatives. By using the mass ratio of m (sawdust) : m (glycerol) = 1 : 1, the total content of multi-hydroxy compounds reached 90.84%. The hydroxyl number of the bio-polyol was 1287 mgKOH/g with a rotational viscosity of 1270 cP. Preparation of polyurethane foams using bio-polyol and isocyanate was also studied. Water was used as an environmental friendly blowing agent. The factors that influence the cell structure of foams (i.e., catalyst, dosage of blowing agent, and mass ratio of bio-polyol to PEG-400 were studied. The compressive strength of the synthesized foam was 150 Kpa, which met the requirement of Chinese specification for rigid foams. The synthesized foams were characterized by FTIR, SEM, and TG. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40096.

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INTRODUCTION

Polyurethanes (PUs) are versatile engineering materials with a wide range of utilization because their properties can be readily tailored using different combinations of components.[1] PU foam is usually synthesized by the reaction of diisocyanate with polyol. In general, a blowing agent, catalyst and surfactant are also employed to regulate the properties and morphology of the cell structures. In recent years, effective utilization of biomass resources has paid great attention to seek substitutes for fossil resources.[2] This is not only out of concern of future shortage in petroleum supplies but also due to a greater desire for more environmental friendly products. As an important conversion method, liquefaction techniques can convert solid lignocellulosic biomass into liquid products which contain sufficient -OH groups to offer potential value replacing polyester or polyols in PU foams.[3] Products derived from lignocellulosic biomass are also friendly to the environment.[4]

The conversion of lignocellulosic biomass to liquid biopolyols can be achieved by a liquefaction process assisted by petrochemical polyhydric alcohols with appropriate molecular weights. A large variety of biomass such as wood,[5] wheat straw,[6] bagasse,[7] cornstalks,[8] cellulose,[9] and starch[10] has been studied for the production of biopolyols. Generally, the biopolyols are promising properties for the production of PU foams, with comparable properties to their petroleum analogs.[5–7,10] However, all these liquefaction processes require high volumes of petroleum-derived solvents to be used as liquefaction agents. That means the superior properties of the biopolyols are mainly due to the high amount of petroleum-derived solvents in the biopolyol products. The large usage of petroleum-based solvents considerably increases the production cost of biopolyols and consequently hinders future commercialization protentials. One reason for the high usage of solvents in the liquefaction process is that considerable lignin derivatives are obtained during the liquefaction. These undesired products (phenolics), usually lack hydroxyl functionalities which lead to low activity and negatively affect bubble stability during the reaction with diisocyanate. However, there are few reports on how to separate the phenolics from the biopolyols to avoid the negative effect on the polyurethane foams. This is because additional operation processing tends to be quite costly and gives a lower yield of the final biopolyol products.

Thus, this article proposed a study on the preparation of polyurethane foams using bio-polyols from liquefied woody biomass

excluding negative components. It is a different feedstock and an improved method to convert lignocellulosic materials to a high grade polyol. On the basis of our previous research,[11] a new kind of polyol product with multiple sugar derivatives were developed. The newly synthesized bio-polyols, consisting of at least 2–5 reactive hydroxyl groups, are proposed to have plenty reactive functionalities during polyurethane foam production. It was well known that the highly cross-linked structure of the rigid polyurethane foam will show good mechanical properties by using these polyols. Therefore, in this article, the polyuthane foams were prepared using the bio-polyols generated from different amounts of liquefying agent. The chemical compositions of the bio-polyols were analyzed. The physical properties of the bio-polyols were tested. The relationship between the chemical components in bio-polyol and cell structure of synthesized foams was discussed. Several factors on the foamability and properties of foams including mass ratio of bio-polyol to PEG, amount of blowing agent and catalyst dosage are discussed.

EXPERIMENTAL

Chemicals

The sawdust for this study was obtained from a local sawmill in Pineville, LA (USA) and pulverized to pass through an 60 mesh sieve followed by drying at 105°C overnight. This ground material was kept in sealed bags until needed, at which time, a small sample of the material was further dried in an oven at 105°C overnight. The elemental analysis for the sawdust: C (46.61%), H (6.63%), and O (46.76%). The weight percentage of ethanol-toluene soluble matter in the raw material was 8.12% and was defined in accordance with a ASTM D1107-96.[12] The weight percentage of lignin in the extracted raw materials was 29.25% according to ASTM D 1106-96.[13] Surfactant 193 is obtained from Dow Corning company(Midland, MI) with main components consisting of dimethyl methyl(polyethyleneoxide siloxane, polyethylene oxidemonoallylether and polyethylene glycol). High functionality polymeric diphenylmethane diisocyanate (MDI) was purchased from Huntsman (West Deptford, NJ) with the product name Rubinate 1850 (Isocyanate Equivalent Weight: 135, NCO content: 31.0%, Viscosity: 700 cps, Gravity: 1.25, Functionality: 2.90). All the other reagents used in this work were of analytical grade.

Liquefaction of Sawdust in Glycerol-Methanol Solution Under Microwave Energy

In a typical operation, liquefaction of biomass was carried out in a Milestone microwave laboratory system (Shelton, CT) equipped with 100 mL sealed teflon reaction vessels and with an internal temperature sensor. Samples were irradiated in 5 min under 500 W as the starting microwave power. The sample temperature was controlled at 180°C. The reaction mixture consisted of 2.0 g sawdust powder, 2.0 g glycerol, 12.0 g methanol, and 0.10 g catalyst (sulfuric acid) and was mixed with magnetic stirring during liquefaction. After liquefaction for 15 min, the vessels were allowed to cool at room temperature before opening.

The gaseous products were vented because the yield of gaseous products was negligible. Then, the liquid and solid products were filtered. The filtrate was then evaporated at 70°C under vacuum to remove the methanol from the liquid product. After that, by adding 10 mL of water into the liquid product, the hydrophobic compounds (phenolic compounds) were precipitated from the aqueous solution. The bio-polyol products were obtained by removal of the water from the aqueous solution using a rotation evaporator. The molecular structures of different fractions were characterized by gas chromatography-mass spectrometry (GC-MS) and Fourier-transform infrared (FTIR) spectrometry.

Preparation of Polyurethane Foams Using Fractionated Liquefied Product

The foams were prepared by a one step method. The foaming systems used in this work consisted of two components, A and B. Component A is a group of substances containing polyols, catalyst (dibutyltin dilaurate), blowing agent (distilled water) and surfactant (Dow corning 193). Component B is an isocyanate (MDI).

Component A was obtained by accurately mixing of polyols (2.5 g), PEG-400 (2.5 g), catalyst (dibutyltin dilaurate, 0.05–0.1 g), blowing agents (water, 0.2–0.3 g)), and surfactant (Dow corning 193, 0.1 g) in a beaker for 15 s using a mechanical stirrer (3000 rpm). Component B is an isocyanate (MDI, 7–9 g). The two components were mixed together using a mechanical stirrer at room temperature. Immediately, the resultant mixture was poured into an open cylindrical mold and allowed it to freely rise at room conditions. The obtained foams were allowed to cure at room temperature for 1 h. The properties of the foams were measured after curing at room conditions for 2 days.

Analysis Methods

The general profile for the bio-polyols was obtained using an Electron Ionization Mass Spectrometer (EI-MS). Analysis of the products was conducted on a mass spectrometer (Agilent 5975C VL MSD) and the products were separated into their components using an gas chromatograph (Agilent 7890A) equipped with a fused capillary column (HP-5, L = 30 m, i.d 0.32 mm, film thickness 0.25 μm) 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°C for 2 min and then heated to 250°C at the rate of 10°C/min. while the injector temperature was 250°C. The identification of the components of the products was confirmed using total ion chromatograms as well as fragmentation pattern.

Fourier transform infrared (FTIR) spectroscopic analysis was performed on a Thermo Nicolet (NEXUS 670) FTIR Spectrometer to determine the functional groups in the bio-polyol products and synthesized polyurethane foams. FTIR spectra (resolution: 4 cm^{-1}, scan: 64, range, 4000–600 cm^{-1}) were taken after spreading a thin film of sample on the detector at a controlled ambient temperature (25°C). A background spectrum was also collected under identical conditions.

A NeoScope JCM-5000 scanning electron microscope (SEM) (5–10 kV accelerated voltage) was used to examine the morphology of the synthesized foams in order to evaluate different factors on the cell structure of foams. Specimens for SEM inspection were gold-plated prior to analysis.

TG/DTG analysis of the foams was conducted on a thermal analyzer, Netzsch409PC, to simultaneously obtain thermogravimetric data. About 1–2 mg of foam was used in the analysis of TG/DTG. Pyrolysis was started at 50°C and ended at 600°C with a heating rate of 10°C/min under a flow of 100 mL/min of nitrogen gas.

Acid number was measured according to Chinese specifications (HG 2708-1995).[14] Viscosity was measured using a Cole Parmer (Vernon Hills, IL) 98936 series viscosity centipoises according to ASTM D4402 standard.[15]

RESULTS AND DISCUSSION

Effect of Different Amounts of Glycerol on the Chemical Composition of Bio-Polyols

Figure 1 shows the distribution of the components in gas chromatography using different amounts of glycerol in liquefaction processing. The yield of the lignin derivatives precipitated from the liquid product is 24.3% (accounting to weight of sawdust). The yield of polyols excluding glycerol is ~65%. Other reaction parameters regarding the liquefaction such as reaction time, reaction temperature, and catalyst type will be available in another manuscript.[11] In this article, the changes of components using different dosages of glycerol, and the influence of these molecules on the cell structure of polyurethane foams were studied. As shown in Figure 1, many multi-hydroxy molecules such as glycerol derivatives and methyl sugar derivatives were identified in the bio-polyol. Most of them have hydroxyl groups with the number of 2–5, which indicate crosslink potential when react with isocyanate. Only trace amounts of the aromatics and phenolics could be identified, including 4-hydroxy-3-methoxy benzoic acid methyl ester and 2-[4-isopropoxy-3-methoxy phenyl] propan-2-one. This result indicates that the low activity organics, especially phenolics (from decomposition of lignin), have been successfully removed from liquefied products. The proportion changes of different bio-polyols are summarized in Table I. It can be seen that with the increasing amount of glycerol in the liquefaction reaction, the total content of the galactopyranoside derivatives decreased from 36.85 to 16.952% while the unreacted glycerol increased from 34.832 to 54.395%. Therefore, bio-polyol-1 can provide a large amount of sugar structures (high functionality component) in polyurethane foams, which has a similar micro structure as the commercial polyol products derived from sucrose. Although 10–20% of glycerol derivatives such as 3-methoxy-1,2-propanediol were identified in bio-polyols, they do not have a negative effect on the properties of the polyol products because they can also provide sufficient hydroxyl groups during the reaction with diisocyanate to form polyurethane foams.

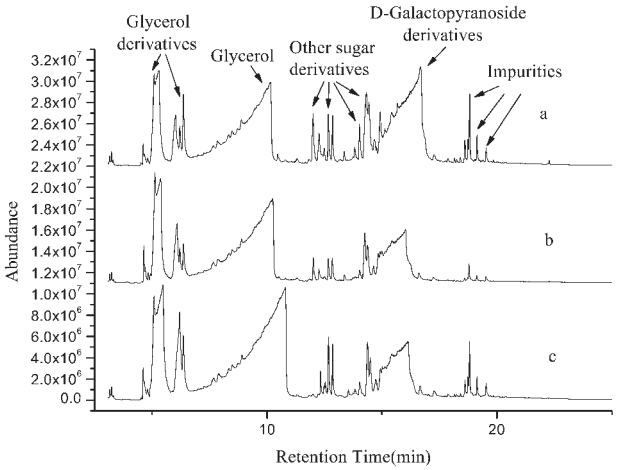

Figure 1. Bio-polyols obtained from liquefied products using different amount of glycerol (a. 1 g; b. 2 g; c. 3 g).

Table I. The Proportion Changes of Multihydroxy Compounds in Liquefied Products Using Different Amount of Glycerol

	Proportion of the components in liquefied products using different amount of glycerol		
Components	Bio-polyol-1[a]	Bio-polyol-2[b]	Bio-polyol-3[c]
Glycerol derivstives(including 1,3-dimethoxy-2-propanol and 3-methoxy-1,2-propanediol)	11.273	18.815	18.298
Levulinic acid, methyl ester (Pentanoic acid, 4-oxo-, methyl ester)	1.379	0.867	0.464
Glycerol	34.832	50.138	54.395
Other sugar derivatives	1.894	0.903	0.296
D-Galactopyranoside derivatives (including α-D-Galactopyranoside methyl ester and β-D-Galactopyranoside methyl ester	36.850	21.887	16.952
Aromatics and phenolics	1.036	0.270	0.434
Unknown	12.736	7.12	9.161

[a] Bio-polyol-1: polyol product using 1 g glycerol as liquefying agent.
[b] Bio-polyol-2: polyol product using 2 g glycerol as liquefying agent.
[c] Bio-polyol-3: polyol product using 3 g glycerol as liquefying agent.

Table II. Physical Properties of the Synthesized Polyols

Properties	Bio-polyol-1[a]	Bio-polyol-2[b]	Bio-polyol-3[c]
Hydroxyl number (mgKOH/g)	1093	1287	1323
Density (g/cm^3)	1.243	1.238	1.231
Acid number (mgKOH/g)	7.7	7.3	8.0
Viscosity(c.p.)	1530	1270	1080

[a] Bio-polyol-1: polyol product using 1 g glycerol as liquefying agent.
[b] Bio-polyol-2: polyol product using 2 g glycerol as liquefying agent.
[c] Bio-polyol-3: polyol product using 3 g glycerol as liquefying agent.

Physical Properties and Chemical Analysis of the Bio-Polyols

Table II shows the physical properties of the synthesized polyols. The products appeared as a viscous liquid at room temperature, with a viscosity of 1080–1530 cP at 25°C. The hydroxyl and the acid value of the polyols were determined as 1093–1323 mg KOH/g and 7.3–8.0 mg KOH/g, respectively. The physical and chemical properties suggest that the synthesized polyols have great potential for further reaction with isocyanate to produce foam applications. It is important to note that the molecules in biopolyols have plenty of primary hygroxyl groups which indicate these products should have good reactivity with isocyanate. Furthermore, the hydroxyl number of the synthesized polyols is much higher than any other polyol products reported in the literature.[16,17] Thus, they can be used together with other low reactive polyols as platform chemicals to decrease the production cost of PU foams.

Figure 2 shows the FTIR curve of bio-polyol product using 2 g of glycerol as a liquefying agent. The glycerol derivatives and sugar derivatives have multiple hydroxyl groups. The band of stretching vibration at 3400–3600 cm^{-1} is associated with –OH groups in molecular structures of these components. The stretching vibration at 2972–2953 cm^{-1} and deformation vibrations at 1370–1450 cm^{-1} are related to CH_2 and CH chain formation, which is reflection of the carbon skeleton of sugar derivatives. Besides, glycosidic bond in sugar derivatives gave intensities of transmission bands at 1100–1200 cm^{-1}, which is related to C—O groups in methyl glucoside.

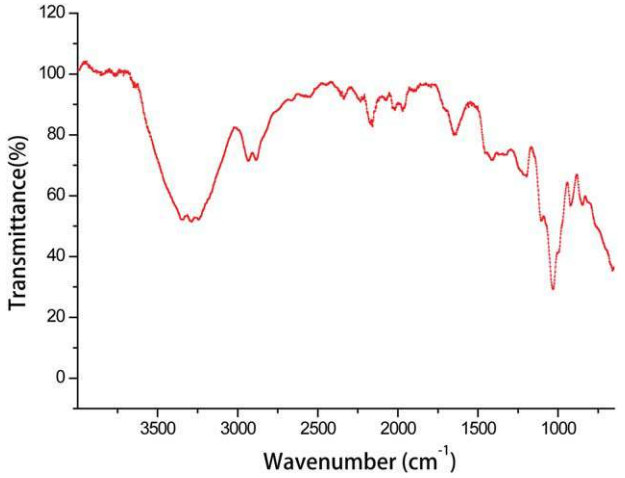

Figure 2. FTIR analysis of bio-polyol generated from liquefied product using 2 g of glycerol as solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Micro Structure and Chemical Properties of the Synthesized Foams

The bio-polyols obtained in liquefaction processing were directly used to prepare the polyurethane foams by blending with a certain amount of PEG-400. Table III shows the basic foam formulation for eight experiments regarding the influence of the reaction conditions on the cell structure, such as the dosage of blowing agent, the mass ratio of the bio-polyol to PEG-400, and the amount of catalyst in foaming processing.

Morphologies of PU Foams. SEM images of polyurethane foam samples are shown in Figure 3 in sequence according to Table III. It can be seen that all the bio-polyols generated from different amounts of liquefying agent gave acceptable quality for preparation of polyurethane foams (Sample A, B, C). As shown

Table III. Foam Formulations for the Bio-Polyols From Liquefied Product

No.	Corresponding samples in Figure 3	Component A					Component B
		Weight of bio-polyol/g	Weight of PEG-400/g	Catalyst/g	Surfactant/g	Blowing agent/g	Mass of MDI/g
1[a]	Sample A	2.5	2.5	0.05	0.1	0.2	7.5
2[b]	Sample B	2.5	2.5	0.1	0.1	0.3	7.1
3[c]	Sample C	2.5	2.5	0.1	0.1	0.3	7.2
4[b]	Sample D	5.0	0	0.1	0.1	0.3	6.9
5[b]	Sample E	3.5	1.5	0.1	0.1	0.3	8.3
6[b]	Sample F	2.5	2.5	0.1	0.1	0.2	7.1
7[b]	Sample G	2.5	2.5	0.1	0.1	0.4	7.7
8[b]	Sample H	2.5	2.5	0.05	0.1	0.2	7.0

[a] Bio-polyol-1: polyol product using 1 g glycerol as liquefying agent.
[b] Bio-polyol-2: polyol product using 2 g glycerol as liquefying agent.
[c] Bio-polyol-3: polyol product using 3 g glycerol as liquefying agent.

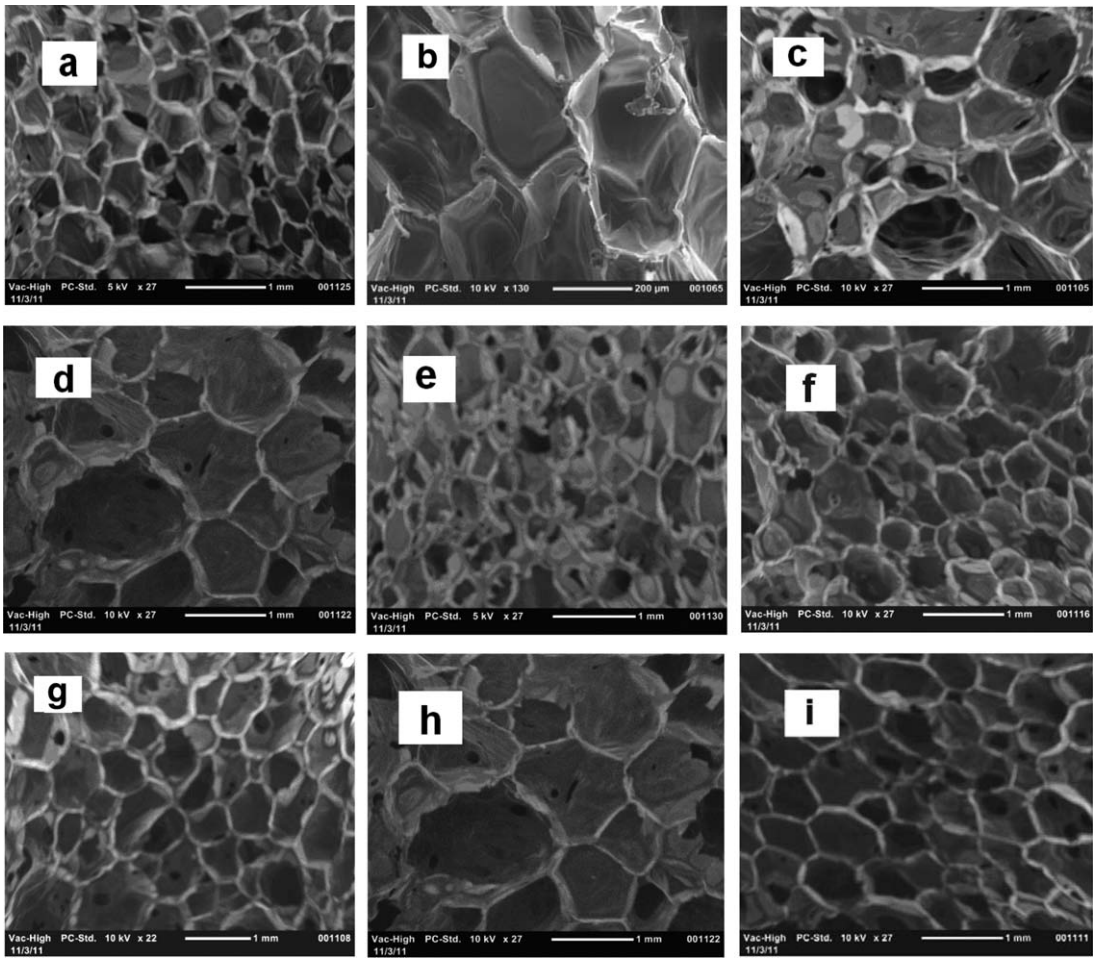

Figure 3. SEM morphologies of rigid foams under different foam formulations. (a,b: Sample A; c: Sample B; d: Sample C; e: Sample D; f: Sample E; g: Sample F; h: Sample G; i: Sample H).

in Figure 3 (Sample A), the particles have a honeycomb structure, with a size distribution of 200–400 μm in diameter, and a uniform and smooth surface texture. It is well known that the cell size of the rigid foam has an important effect on mechanical properties.[18] The excellent honeycomb structure obtained during foam formation made it possible for a considerable amount of still air to be trapped, thus, leading to an increased passive insulation. In addition, it was found that the cells under the surface maintain a high percentage of close area (Sample A), which is an important factor related to thermal conductivity. However, with the increasing amount of glycerol derivatives in bio-polyol (Table I), the cell size appeared irregular and the percentage of close area decreased (Sample B, C). This indicates that the low molecular weight chemicals with 2–3 OH functionalities (glycerol derivatives) could not provide a stable foam structure during the foaming reaction. Moreover, the size distribution of the foams is about 0.5–1.2 mm, which is not satisfactory to be used as rigid foams.

Table IV. Physical Properties of Polyurethane Foams

Properties		Synthesized foam	China specification[b]
Thermal conductivity W/(m·K)		0.029	0.024
Density (kg/m^3)		38.8	30–50
Compressive strength (vertical to foam rise direction) kPa		150	150–300
Dimensional stability (70°C)[a]	L	0.72 %	1%
	W	0.55 %	1%
	H	0.86 %	1%

[a] W, L, and T indicate the width, length, and thickness of the foam, respectively.
[b] China specification (JC/T 998-2006): Spray polyurethane foam for thermal insulation.

By considering the above issues, the amount of reactants in the foam formula were modified in order to find a better solution to obtain uniform microstructure of the synthesized foams. First, the ratio of the bio-polyol to PEG-400 was investigated. It was found that with a decreasing usage of PEG, the cell structure of the foams not only became irregular but also had negative effect on the mechanical property of the foams (Sample D, E). It was visually observed that these foams are quite brittle and

very easy to reduce into powder. In other words, fossil solvents such as polyethylene glycol can likely improve flexibility in the synthesized foams. Accordingly, a suitable method to improve the properties of the bio-polyols is to carry out a reaction using bio-polyols and ethylene oxide. This results in bio-polyol products with long molecular chains similar to PEG structure, which has a positive effect on the mechanical properties of the foams.

During the experiment, it was found that the high viscosity bio-polyols (bio-polyol only) are very difficult to mix well in the course of foaming, which caused less foaming efficiency and more undesired bubble size. It is better to reduce the viscosity by blending with other fluidizable polyols during the foaming processing. On the other hand, the effect of catalyst amount and blowing agent dosage were also tested. When the amount of blowing agent increased to 0.4 g in the formula, the cell size was amplified to around 500–1500 um (Figure 3, Sample G). As shown in Figure 3 (Sample F, H), the microstructure of the foams generated from lignocellulosic materials is comparable to those reported in literatures for the foams using the catalyst from 0.05 to 0.1 g.[1] These results indicate the optimum amount of blowing agent is 0.2–0.3 g, and catalyst dosage is 0.05–0.1 g.

Under this condition, the compressive strength of the synthesized foam was 150 Kpa, which met the requirement of Chinese specification for rigid foams(JC/T 998-2006). Other properties of the synthesized foams were listed in Table IV.

FTIR Spectra of Synthesized Foams. FTIR spectra of the synthesized foams are presented in Figure 4. The results show that these synthesized foams have similar transmittance bands in FTIR spectra. This indicates that all of the bio-polyol products have the same chemical groups such as hydroxyl, C—H, and C—O groups. These groups originated from sugar derivatives, glycerol derivatives, and PEG-400. The spectrum of synthesized foam presents all of the distinctive bands of the polyurethane polymer. The band of OH stretching vibration at 3400–3600 cm^{-1} is associated with the free H_2O, -OH groups of non-bonded polyol or OH groups within the polymer structure. The intensities of transmission bands at 2972–2953 cm^{-1} are related to CH_2 and CH chain formation. The intensities of transmission bands at 1500–1230 cm^{-1} are related to C—N and C—N—H chain formation. The intensities of transmission bands at 1100–1200 cm^{-1} are related to C—O groups.

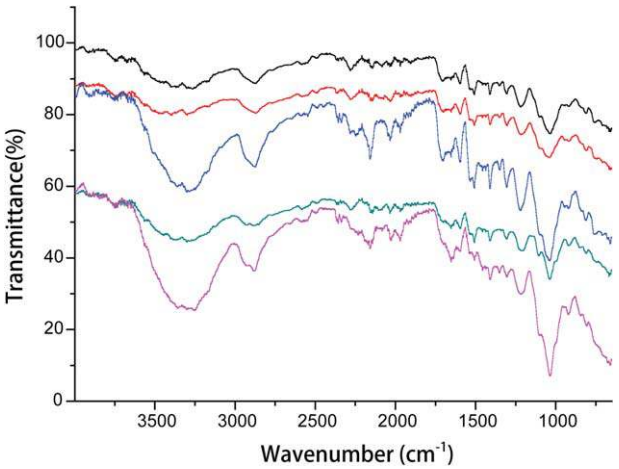

Figure 4. FTIR spectra of synthesized foams (a: Table III, formula 1; b: Table III, formula 2; c: Table III, formula 3; d: Table III, formula 4; e: Table III, formula 5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Thermal Properties of Polyurethane Foams. Figure 5 shows the curves of thermogravimetry (TG) of selected samples in Table III. The bimodal weight loss in the DTG curve with maxima at 330 and 420°C is observed in most of samples. No apparent weight loss for the foam sample was found below 200°C. When the temperature was increased to 300–350°C, the decomposition peak of the foam was shown at around 330°C in the DTG data. After that, the decomposition temperature was recorded from 400 to 420°C. The decomposition could be related to the depolymerization of the isocyanurate groups during these temperatures.[19] With the increasing amount of bio-polyols used in PU foams [Figure 5(b,d,e)], a peak of weight loss was observed at the temperature of 200°C. This result could be attributed to the large proportion of the bio-based polyols in PU foams. Those bio-polyols contain low molecular weight organics such as levulinic acid derivatives,1,3-dimethoxy-2-propanol, and 3-methoxy-1,2-propanediol, which leads to high

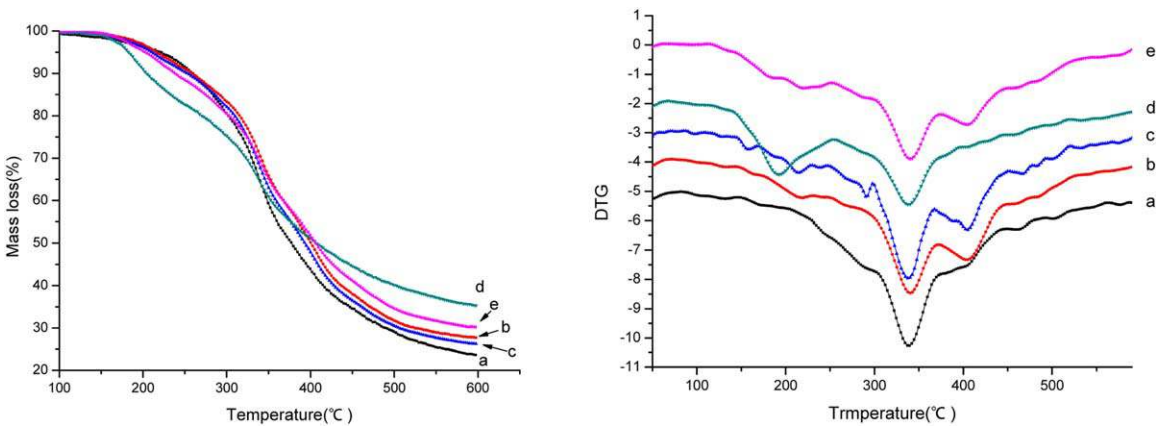

Figure 5. Thermogravimetry curves and DTG curves of synthesized foams (a: Table III, formula 1; b: Table III, formula 2; c: Table III, formula 3; d: Table III, formula 4; e: Table III, formula 5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

volatility at around 200°C [Figure 5(d)]. This problem can be solved by adding 30% of high molecular petroleum based polyols [Figure 5(e)]. After the formation of three dimensional crosslinked polyurethane groups, the thermal stability of the product can be significantly improved.

CONCLUSIONS

Preparation of PU foams using the bio-polyols generated from liquefaction reaction using different amount liquefying agent was studied. The chemical components of the bio-polyols were identified by GC-MS. The results showed that the polyol product contained multiple hydroxyl compounds such as glycerol derivatives and sugar derivatives. Further studies should address modification of the bio-polyol molecular structure by reacting the bio-polyols with ethylene oxide or propylene oxide. This method might be a good choice to not only improve the mechanical properties but also enhance the reactivity because of the prime hydroxyl groups can be increased in polyols.

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REFERENCES

1. Hakim, A. A. A.; Nassar, M.; Emam, A.; Sultan, M. *Mater. Chem. Phys.* **2011**, *129*, 301.
2. Gandini, A. *Macromolecules* **2008**, *41*, 9491.
3. Bhunia, H. P.; Nando, G. B.; Chaki, T. K.; Basak, A.; LenKa, S.; Nayak, P. L. *Eur. Polym. J.* **1999**, *35*, 1381.
4. Breslin, V. T. *J. Environ. Polym. Degrad.* **1993**, *2*, 127.
5. Zhang, H. R.; Pang, H.; Zhang, L.; Chen, X.; Liao, B. *J. Polym. Environ.* **2013**, *21*, 329.
6. Chen, F. G.; Lu, Z. M. *J. Appl. Polym. Sci.* **2009**, *111*, 508.
7. Zou, X.; Qin, T.; Wang, Y.; Huang, L.; Han, Y.; Li, Y. *Bioresour. Technol.* **2012**, *114*, 654.
8. Yan, Y. B.; Pang, H.; Yang, X. X.; Zhang, R. L.; Liao, B. *J. Appl. Polym. Sci.* **2008**, *110*, 1099.
9. Kunaver, M., Jasiukaitytė, E., Čuk, N. *Bioresour. Technol.* **2012**, *103*, 360.
10. Yoshioka, M.; Nishio, Y.; Saito, D.; Ohashi, H. *J. Appl. Polym. Sci.* **2013**, *130*, 622.
11. Xu, J. M.; Jiang, J. C.; Hse, C. Y.; Shupe, T. F. *Green Chem.* **2012**, *14*, 2821.
12. The standard test method for ethanol-toluene solubility of wood. ASTM **2007** D 1107–96.
13. The standard test method for acid-insoluble lignin in wood. ASTM **2007** D 1106–96.
14. Test method of acid value for polyester polyols. HG 2708–1995.
15. Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer. ASTM D4402.
16. Hu, S. J.; Wan, C. X.; Li, Y. B. *Bioresour. Technol.* **2012**, *103*, 227.
17. Jin, Y. Q.; Ruan, X. M.; Cheng, X. S.; Lü, Q. F. *Bioresour. Technol.* **2011**, *102*, 3581.
18. Li, X. B.; Cao, H. B.; Zhang, Y. *J. Wuhan Univ Technol.–Mater. Sci.* **2008**, *23*, 125.
19. Lee, C. S.; Ooi, T. L.; Chuah, C. H.; Ahmad, S. *J. Am. Oil Chem. Soc.* **2007**, *84*, 1161.