Preparation of Semirigid Polyurethane Foam with Liquefied Bamboo Residues

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ABSTRACT: Bamboo residues were liquefied by using a solvent mixture consisting of polyethylene glycol 400 and crude glycerol (4/1, w/w) with 98% sulfuric acid as catalyst at 160°C for 120 min. The liquefied bamboo had hydroxyl values from 178 to 200 mg KOH/g and viscosities from 507 to 2201 mPa S. The obtained bamboo-based polyols were reacted with various amounts of polyaryl polymethylene isocyanate (PAPI), using distilled water as blowing agent, silicone as surfactant, and triethylenediamine and dibutyltine dilaurate as cocatalyst to produce semirigid polyurethane (PU) foams. The [NCO]/[OH] ratio was found to be an important factor to control the mechanical properties of PU foams. At a fixed [NCO]/[OH] ratio, both density and compressive strength of PU foams decreased with the increase of bamboo content. The microstructure of PU foams indicates that [NCO]/[OH] ratios are important for cell formation and chemical reactions. The uniformity and cell structure of the foams are comparable to their corresponding compressive strengths. Moreover, the thermogravimetry analysis showed that all the semirigid PU foams had approximately the same degradation temperature of about 250 to 440°C. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1694–1699, 2010

Key words: bamboo residue; liquefaction; polyol; polyurethane foam

INTRODUCTION

Bamboo (*Phyllostachys pubescens*) is one of the most important forest resources around the world.[1] Over 1200 species of bamboo are known to exist worldwide, with an estimated 22 million hectares distributed throughout the forests of Asia, Africa, and South and Central America.[2] Bamboo can be harvested in 3 to 7 year cycles, and it is recognized as a rapidly renewable resource with environmental advantages over finite raw materials and long-cycle renewable resource extraction. Bamboo is being used for flooring, paneling, furniture, fencing, engineered lumber, and even structural elements. However, over 60% of the bamboo becomes process waste nowadays in bamboo plantations and associated processing industries. Bamboo residues have been disposed of in land-fill sites or incinerated, resulting in resource waste and environmental pollution. There is an urgent need for alternative utilizations of the bamboo residues.

Conversion of biomass to bio-based products is one of the promising ways to benefit agriculture, processing industries, and the environment. Lignocellulosic biomass could be liquefied to produce polyol products which contain multiple hydroxyl groups. Some environmentally friendly polyester and polyurethane (PU) foams have been prepared from the liquefied polyol products.[3–14] Yao et al.[12] prepared rigid PU foams from a combined liquefaction mixture of wood and starch at a isocyanate/hydroxyl group ([NCO]/[OH]) ratio of 1.05. Kurimoto et al.[6] liquefied wood using glycerol-polyethylene glycol cosolvent and prepared polyurethane forms with polymeric methylene diphenylene diisocyanate (MDI) at a [NCO]/[OH] ratio of 1.0 by a solution-casting technique. Wang et al.[15] prepared PU foams using liquefied corn stover and polymethylene polyphenylisocyanate (PAPI) using a one-shot method, with water as blowing agent, silicone as surfactant, and triethylamine and dibutyltine dilaurate as cocatalyst. Although bamboo liquefaction has been previously reported,[16] the data on the semirigid PU foams made from liquefied bamboo

and using crude glycerol from byproducts of the biodiesel industry as a liquefying reagent has not been reported.

The objective of this research was to liquefy bamboo at mild conditions, estimate the characteristics of liquefied bamboo with various bamboo wood content, and evaluate the effect of different [NCO]/[OH] ratios on the physical properties of liquefied bamboo-polyurethane (LB-PU) foams. The physical properties of PU foams include density and compressive strength. Structural and microstructure properties of PU foams were measured using FTIR and scanning electron microscopy. Thermal stabilities of PU foams were determined using thermo gravimetric analysis.

MATERIALS AND METHODS

Materials

The bamboo (*Phyllostachys pubescens)* residues were obtained from a bamboo forest in the suburb of Nanchang, China. The bamboo residues were ground and air dried, and only the fractions with a particle size of 0.18–0.85 mm were used for liquefaction experiments. The chemical compositions of the sample were analyzed by the Van Soest measurement method,[17] using an Ankom Fiber Analyzer (ANKOM220, ANKOM Techno. Corp., NY). The bamboo residues was about 10.14% ± 0.70% of moisture content, 47.50% ± 0.51% of cellulose, 18.80% ± 0.43% of hemicelluloses, 23.72% ± 0.67% of lignin, 9.51% ± 0.05% of extracts from benzene and alcohol (2 : 1, v/v), and 1.61% ± 0.05% of ash content.

Sulfuric acid (98%) was used as a catalyst. Polyethylene glycol (PEG 400, 99.9%) and crude glycerol (75% glycerol with small amounts of esters, alcohol and other impurities) were used as solvents in the liquefaction process. Crude glycerol was obtained from byproducts of the biodiesel industry. Polyaryl polymethylene isocyanate (PAPI, PM-200) was obtained from Yantai Wanhua Polyurethane Co. (Shandong, China), and the NCO group content was 30.03%. Distilled water and silicone were used as the blowing agent and surfactant, respectively. Triethylamine and dibutyltine dilaurate were used as the cocatalysts to prepare PU forms. All chemicals used (except PAPI and crude glycerol) were reagent grade and obtained from Shanghai Chemical Reagent Co., China.

Bamboo liquefaction

Liquefying chemicals (80 g PEG 400, 20 g crude glycerol, and 3 g sulfuric acid) and bamboo residues (20–50 g) were added into a three-necked flask (1000 mL) equipped with a reflux condenser, a thermometer, and a motor-driven stirrer. The bamboo liquefaction was conducted at 160°C for 120 min with continuous stirring and in the air at atmospheric pressure. After liquefaction reaction, the flask was immersed in cold water to quench the reaction, and the liquefied products (bamboo polyols) were collected in sealed polypropylene containers and stored in a 10°C refrigerator for later use and analysis. The liquefied products were totally utilized for preparation of PU foams without purification and washing.

Acid values of the bamboo polyols

Acid values of the bamboo polyols were determined and used for hydroxyl value calculation.[18] A mixture of 1 g polyol sample and 20 mL dioxane-water solution (4/1, v/v) was titrated with a 1 mol/L NaOH to pH 8.3 by using a pH-meter to indicate the end-point. Acid value was calculated using the following equation:

$$\text{Acid value (mg KOH/g)} = (C - D) \times N \times 56.1/W$$

where C, volume of NaOH standard solution consumed in sample titration (mL); D, volume of NaOH standard solution consumed in blank titration (mL); W, sample weight (g); and N, equivalent concentration of NaOH standard solution (mol/L).

Hydroxyl value of bamboo polyol

Ten milliliters of phthalic anhydride solution (dissolving 150 g phathalic anhydride in 900 mL of dioxane and 100 mL pyridine) and 1 g of polyol sample were added into a 150 mL beaker. The beaker was covered with aluminum foil and put into a boiling water bath for 20 min. After cooling down, 20 mL of dioxane-water solution (4/1, v/v) and 5 mL of water were added to the beaker, and then titrated with 1 mol/L NaOH to pH 8.3 by using a pH-meter to indicate the end-point. Blank titration was conducted using the same procedure. The hydroxyl value was calculated using the following equation:

$$\text{Hydroxyl value (mg KOH/g)}$$
$$= (B - S) \times N \times 56.1/W + \text{Acid value}$$

where B, volume of NaOH standard solution consumed in blank titration (mL); S, volume of NaOH standard solution consumed in sample titration (mL); W, sample weight (g); and N, equivalent concentration of NaOH standard solution (mol/L).

Hydroxyl value for the crude glycerol was 991 mgKOH/g; and 268 mgKOH/g for the PEG 400.

TABLE I
Wood Content and Characteristics of Liquefied Bamboo (LB)

Sample names	Bamboo/solvent (w/w)	Acid number (mgKOH/g)	Hydroxyl number (mgKOH/g)	Viscosity (mPa s at 25°C)	Moisture content (%)	Weight before liquefied (g)	Weight after liquefied (g)
LB-1	0.20	16.21	200.51	507	3.42	120	114.63
LB-2	0.25	16.32	196.32	651	3.56	125	118.01
LB-3	0.30	17.23	182.36	899	4.01	130	122.36
LB-4	0.35	17.12	180.21	1432	3.98	135	126.03
LB-5	0.40	18.25	178.36	2201	3.54	140	129.87

Viscosity of bamboo polyol

The viscosities of bamboo polyols were measured by using a viscometer (NDJ-8S, Shanghai Precision Instrument Co., Shanghai, China) at 25°C.

Moisture content of bamboo polyol

The moisture content of bamboo polyol was determined by the Karl Fischer method (ASTM E203-96) using a moisture meter (KF-1, Shanghai Nuoding Company, Shanghai, China).

Preparation of polyurethane foam from bamboo polyol

Twenty grams of bamboo polyol, 0.4 g water, 0.4 g silicone, and 0.4 g cocatalysts (triethylenediamine/ibutyltine dilaurate = 1/1, w/w) were mixed well in a paper cup for about 30 s. A prescribed amount of PAPI 15.9–30.2 g ([NCO]/[OH] ratio, 0.4–1.4) was added into the mixture, which was then stirred with a high-speed stirrer (3000 rpm) for about 6–12 s. After stirring, the foam was allowed to rise at the ambient condition. After that the foam was cured at room temperature for at least 2 days before testing and analysis. Three duplicate experiments were conducted for each sample. The [NCO]/[OH] ratio is given as follows:

$$[NCO]/[OH] ratios = \frac{M_{PAPI} \times W_{PAPI}}{M_{poly} \times W_{poly} + (W_{water} \times 1000/9)}$$

where M_{PAPI} is the content of the isocyanate group in PAPI (7.15 mmol/g), M_{poly} the content of the hydroxyl group in LB (hydroxyl number/56.1, the unit is mmol/g), and W_{PAPI}, W_{poly}, and W_{water} are the weights (g) of PAPI, polyol, and water, respectively.

Characterization and property measurements of PU foam

The chemical structures of the obtained PU foams were characterized using an FTIR spectrophotometer (Nicolet5700, NICOLET, Madison, WI). A scanning electron microscope (Hitachi S-3500 N) was used to examine the morphology of the foam. The accelerated voltage was 20 kV. Thermogravimetric analysis (TGA) of the foams was performed using a Thermogravimetric Analyzer (TG/DTA PYRIS DIAMOND Instruments, Waltham, MA) by heating 5.6 mg of the form at 10°C/min from 33 to 600°C under a nitrogen flow of 200 mL/min. Duplicated tests were conducted.

For density measurements, the PU foams were cut into specimens and the foam densities were measured according to GB/T6343-1995. The density for each foam was ascertained using the average value from six specimens.

The compressive strength was determined using a universal tensile test machine (Instron 3369, USA). The test was carried out according to GB/T8813-1988. The two surfaces of the samples were carefully cut to be strictly parallel. Tests were performed at room temperature with a constant crosshead speed of 2.5 mm per minute, and the load was applied until the foam was compressed to ∼ 10% of its original thickness. The compressive strength for each foam was ascertained using the average value from six specimens.

RESULTS AND DISCUSSION

Characterization of bamboo polyol

The characteristics of bamboo polyol are listed in Table I. The weights before and after liquefaction were provided in Table I. The weight loss was due to the loss of moisture and evaporation of solvent during liquefaction. The weight loss due to solvent evaporation would be eliminated in a large scale production system with efficient solvent recycling. The obtained bamboo-based polyol was a viscous liquid. The viscosity of polyols increased from 500 to 2200 mPa s with the increase of bamboo/solvent ratios. The moisture content of polyols was from 3.5 to 4%. This polyol had a hydroxyl value from 178 to 200 mg KOH/g, which is suitable for semirigid PU foam preparation.[19]
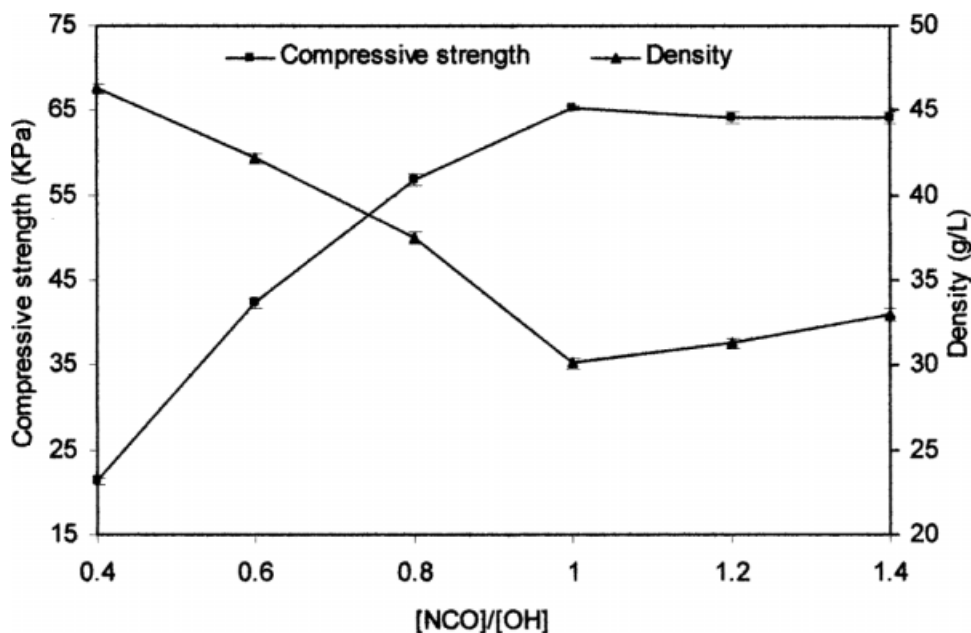
Figure 1 The effect of [NCO]/[OH] ratios on the compressive strength and density of PU foams (using polyol sample of LB-3).

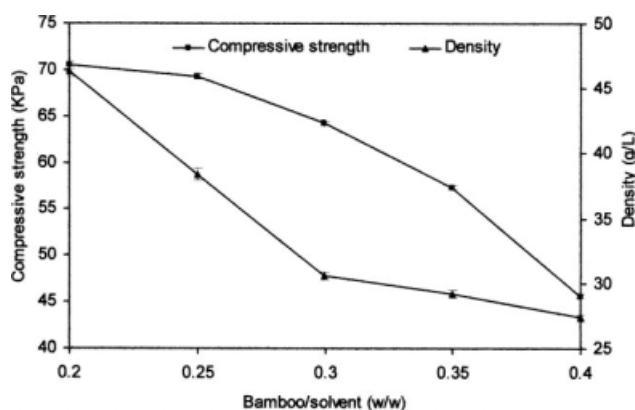### Physical properties of PU foam

Effects of different [NCO]/[OH] ratios

The compressive strength is one of the important properties of polyurethane foams when they are used as load bearing materials. Compressive strength was utilized to evaluate the foam morphology and network structure since it is sensitive to both.[20] The effects of different [NCO]/[OH] ratios on the density and compressive strength of PU foams are shown in Figure 1. It was found that with the increase of [NCO]/[OH] ratios from 0.4 to 1.4, compressive strength increased and reached its maximum strength (65.35 kPa) at the [NCO]/[OH] ratio of 1.0 and then slightly decreased with the further increase of [NCO]/[OH] ratios. Similar results were found from the literature that the mechanical properties increase with an increase in the [NCO]/[OH] ratio up to 1.0, whereas the PU foams tend to be brittle when the [NCO]/[OH] ratio goes to beyond 1.0 and at the very high ratios.[21] The density decreased with the increase of the [NCO]/[OH] ratio and slightly increased after its minimum value at the [NCO]/[OH] ratio of 1.0. It is generally known that the mechanical properties of a cellular material mainly depend on its density.[22] However, in this study, when the [NCO]/[OH] ratio is increased, the increase of the compressive strength is accompanied by a decrease of foam density. This can be explained by the formation of hard segments. With the increase of [NCO]/[OH] ratio, the hard segment formed through the reaction between isocyanate and polyol increased. The concentration of the hard seg-

ment affects the mechanical property of PU foams, and higher concentrations can increase the hardness of PU foams but decrease its flexibility. As seen with polyols from other sources,[20,21] when the [NCO]/[OH] ratio of formulations using these bamboo polyols is varied, the physical properties are altered.

Effects of different bamboo contents

The effect of bamboo content on the density and compressive strength of PU foams at the [NCO]/[OH] ratio of 1.0 is presented in Figure 2. It can be seen that with the increase of the bamboo content, both compressive strength and density were decreased. With a fixed ratio of [NCO]/[OH], the

Figure 2 The effect of bamboo wood content on the compressive strength and density of PU foams at the [NCO]/[OH] ratio of 1.0.
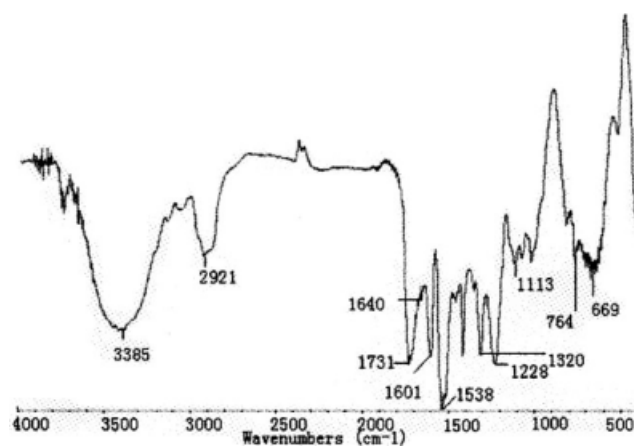
Figure 3 FTIR spectrum of PU foams prepared from the polyol sample of LB-3.

mechanical properties of the cellular material may depend on its density. The decrease of the compressive strength may be due to the decrease of the foam density. Hydroxyl value decreased with the increase of bamboo content (Table I). At a fixed ratio of [NCO]/[OH] and with the increase of bamboo content, unreacted components during liquefaction could not form effective chemical bonds and structure, therefore, decreasing the compressive strength of the foams. The higher bamboo content, the lower economic costs for PU foams, but the mechanical properties were poor. Therefore, large amount of bamboo participating in the reaction would not be preferred.

Chemical structure of PU foam

A typical FTIR spectrum of the PU foams prepared from bamboo polyol is shown in Figure 3. The peak at the wavenumber of 3385 cm^{-1} can be attributed to the stretching vibration of NH. A characteristic peak at 2921 cm^{-1} may be caused by the stretching vibration of CH$_2$. A characteristic peak of allophanates at 1640 cm^{-1} was observed in the spectrum, but it overlapped with other peaks. Characteristic peaks of carbamic acid ester groups at about 1731 cm^{-1} and 1601 cm^{-1} and a strong C—O—C stretching vibration peak at 1113 cm^{-1} indicate that both

polyether and diisocyanate participated in the reaction. The two bonds at 1538 cm^{-1} and 1228 cm^{-1} can be attributed to δ(N—H) + υ(C—H) and δ(N—H) + υ(C—N) urethane linkages, respectively. No characteristic peak was observed at 2270 cm^{-1}, which indicates unreacted NCO groups. This suggests that the isocyanate group in the PU foam was completely consumed by the production of urethane or urea linkages.

Morphology of PU foam

The cross-sectional surfaces of PU foam with different [NCO]/[OH] ratios observed with scanning electron microscopy (SEM) are shown in Figure 4. It was found that the foams had a higher number of cells as the [NCO]/[OH] ratios increased. This indicates that more carbon dioxide gas was generated at the higher level of [NCO]/[OH] ratios and the number of closed cells was increased. At a [NCO]/[OH] ratio of 0.4, the uniformity of the cells was poor with contracted bubbles due to the insufficient amount of PAPI, resulting in incomplete reaction and inefficient cell formation and uneven cell size. As [NCO]/[OH] ratios increased to 0.6–0.8, the cell number increased, and the cell wall was thicker, but the structure of the cells was still irregular, which might be attributed to inadequate amounts of PAPI with insufficient carbon dioxide generation.[23] As the [NCO]/[OH] ratio increased to 1.0, it was found that the shapes of the cells were spherical. The spherical-shaped cells are found to be closed cells. SEM micrographs indicate that the variation of [NCO]/[OH] ratios plays an important role in the microstructure of PU foams. The cell structure and size of PU foams have important effects on thermal conductivity and mechanical properties.[24,25] As seen in Figure 1, the integrity of the microstructure of the foams is comparable to their corresponding compressive strengths.

Thermal degradation of PU foams

Thermal decomposition behaviors of PU foams are presented in Figure 5. The PU foams showed a complex degradation mechanism. The TG curve

[NCO]/[OH]0.4   [NCO]/[OH]0.6   [NCO]/[OH]0.8   [NCO]/[OH]1.0
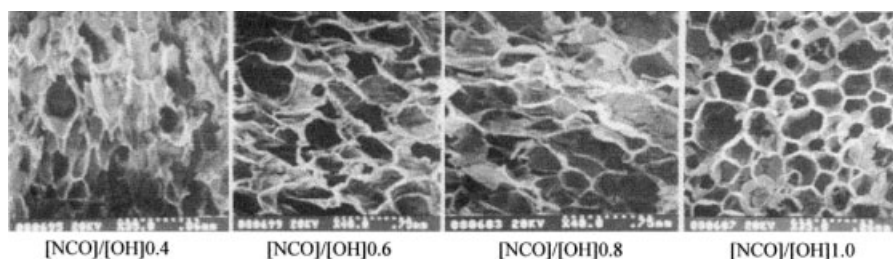
Figure 4 SEM micrographs of PU foams prepared from the polyol sample of LB-3 with different [NCO]/[OH] ratios.
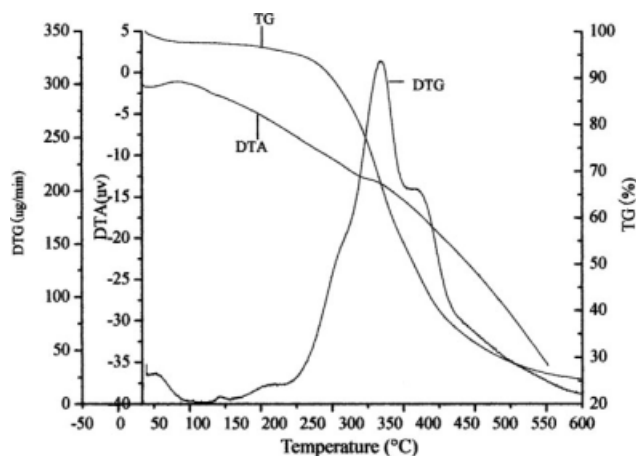
Figure 5 The TG/DTG and DTA thermogram of PU foam prepared with LB-3.

indicates that the PU foam lost its 1% weight at 42°C, and its 50% weight at 381°C. The maximum weight loss occurred at about 342°C. The DTG curve shows the stages of degradation occurred during heating. The decomposition stages for PU foams occurred at 250–440°C with a peak at 342°C, which was influenced by the hard and soft segments and chain extender[26] and might correspond to a urethane bond break. There is another peak at 381°C, which may be attributed to polyol decomposition. The similar results were reported by Chuayjuljit et al.[22] for polyol decomposition at 377°C. The DTA curve of the PU foam was smooth with a weak endothermic peak at about 341°C, which corresponded with the decomposition peak of the PU foam. All the PU foams have approximately the same degradation temperatures.

CONCLUSIONS

Bamboo residues were liquefied by using a solvent mixture consisting of polyethylene glycol 400 and crude glycerol (4/1,w/w) with 98% sulfuric acid as catalyst at 160°C for 120 min. The bamboo-based polyol could be used as one of the raw materials for preparing semirigid polyurethane foams. The prepared polyol was reacted with various amounts of polyaryl polymethylene isocyanate (PAPI), distilled water as blowing agent, silicone as surfactant, and triethylenediamine and dibutyltine dilaurate as cocatalyst. The increase of bamboo content reduced the hydroxyl value of polyols. The [NCO]/[OH] ratio was found to be an important factor to control the mechanical properties of PU foams. At a fixed [NCO]/[OH] ratio, both density and compressive strength of PU foams decreased with the increase of

bamboo content. The results of the morphology observed using SEM revealed that the cells of these foams were closed cells. The microstructure of PU foams indicates that [NCO]/[OH] ratios are important for cell formation and chemical reactions. The uniformity and cell structure of the foams are comparable to their corresponding compressive strengths. The thermogravimetry analysis showed that all the semirigid PU foams had approximately the same degradation temperatures of about 250 to 440°C.

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