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Synthesis and properties of polyurethane foams prepared from heavy oil modified by polyols with 4,4′-methylene-diphenylene isocyanate (MDI)

Xianwu Zou *, Tefu Qin *, Yong Wang, Luohua Huang, Yanming Han, Yan Li

Research Institute of Wood Industry, Chinese Academy of Forestry, 100091 Beijing, PR China

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ABSTRACT

The aim of the present study was to determine whether polyurethane (PU) foams can be prepared from heavy oil derived from biomass liquefaction. Since the hydroxyl number of the heavy oil was only 212 mg KOH/g, it was modified by polyols, and a hydroxyl number of 564.5 mg KOH/g was obtained. However, secondary hydroxyls rather than primary hydroxyls were introduced. As a result, when 10 wt.% activated heavy oil was added to bio-polyols, compressive strength of foams increased by 32% over that without the addition of heavy oil. When activated heavy oil wholly replaced polyethylene glycol 400, the high content of secondary hydroxyls depressed the foam reaction and resulted in partial dissociation of the heavy oil from the network structure and weakening of the thermal stability of the PU foams. Therefore, increasing the content of primary-hydroxyls by directional modification is necessary to make the process commercially feasible.

1. Introduction

Diminishing petroleum reserves and growing concerns about global climate change make it imperative to develop new processes for the production of fuel and chemicals based on renewable biomass resources (Edward et al., 2008; Tushar et al., 2010; Yuriy et al., 2007). Although biomass can be effectively converted into bio-oils by liquefaction, including hydrothermal upgrading (Yuan et al., 2009), pyrolysis (Balat et al., 2009; Goyal et al., 2008; Mohan et al., 2006), and solvolysis (Krzan and Zagar, 2009; Yuan et al., 2007; Zhang et al., 2007), bio-oils, especially heavy oils, cannot be used as transportation fuels due to poor volatility, high viscosity, coking, corrosiveness, and cold flow problems (Huber et al., 2006). Furthermore, upgrading of heavy oils is difficult and uneconomical (Czernik and Bridgwater, 2004). In order to improve the economics of liquefaction processes, it will be necessary to develop uses for heavy oil. Studies have shown that products from biomass liquefaction can be used as components of polymer composites (Doherty et al., 2011; Satyanarayana et al., 2009). Biomass liquefaction with polyols has attracted considerable attention because the liquefaction products can be used in the synthesis of polyurethane (PU) (Hassan and Shukry, 2008; Jin et al., 2011). Wang et al. (2008) liquefied corn stover in acidified ethylene carbonate (EC) at 170 °C for 90 min, and studied the mechanical properties of PU foams prepared from liquefied corn stover with polymethylene polyphenylene isocyanate (PAPI). The authors found that by changing the [NCO]/[OH] ratio, PU foam properties could be adjusted for various end uses. Kurimoto et al. (2001a) prepared PU films by solution-casting after co-polymerization of liquefied woods and polymeric methylene diphenylene diisocyanate (PMDI) at a [NCO]/[OH] ratio of 1.0, and found that increasing the amounts of liquefied woody components in the PU films was beneficial to crosslinking densities and glass transition temperatures (T_g) of the films. Kurimoto et al. (2001b) assessed wood species effects on characteristics of liquefied wood and properties of PU films prepared from the liquefied wood, and found that varying the viscosity was a way to control the mechanical properties of PU films at a constant [NCO]/[OH] ratio.

Although the products from biomass liquefaction with polyols have shown obvious reactive activity in the synthesis of PU, it is still unclear whether heavy oil derived from biomass liquefaction can be used to manufacture PU foams. In order to assess the effect of heavy oil on the properties of PU foams, it is necessary to analyze the structure of heavy oil and investigate the reactive mechanisms of heavy oil in the synthesis of PU foams. In the present study, heavy oil was prepared by biomass alcoholysis with acidified 1-octanol. The functional groups and hydroxyl numbers of the heavy oil before and after modification, were analyzed by Fourier transform infrared spectroscopy (FT-IR) and alkalimetric titration, respectively. Furthermore, PU foams were prepared by copolymerization of the modified heavy oil with 4,4′-methylene-diphenylene isocyanate (MDI), and the properties of the PU foams were characterized with a universal mechanical testing machine and differential scanning calorimetry (DSC) in order to probe the reactive mechanisms of heavy oil in the synthesis of PU foams

* Corresponding authors. Tel./fax: +86 10 62889467.
E-mail addresses: xwzou@home.ipe.ac.cn (X. Zou), qintefu@caf.ac.cn (T. Qin).

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and study the feasibility of increasing the content of heavy oil in PU foams.

2. Methods

2.1. Preparation of heavy oil

Poplar wood from the suburb of Beijing, PR China was ground and sieved. Only the particle size fraction between 0.18 and 0.90 mm sieve was used for liquefaction experiments. After being dried at 105 °C for 12 h, the biomass powder was liquefied with acidified 1-octanol at 130 °C for 1 h (Zou et al., 2009). The liquefaction products were cooled to room temperature, and the heavy oil was separated from the liquefaction products as described by Zou et al. (2009).

2.2. Modification of heavy oil

The heavy oil (150 g), polyethylene glycol (PEG) 400 mixed with glycerin at the mass ratio of 3:1 (450 g), and 75% sulfuric acid (6 g) were placed in a three-neck flask (1000 ml) equipped with a reflux condenser, a thermometer, and a motor-driven stirrer, and the mixture was refluxed at 150 °C for 50 min with continuous stirring. The flask was immersed in cold water to quench the reaction and the modified heavy oil including all the components in the three-neck flask were neutralized with 10% KOH, and dehydrated by vacuum evaporation. For comparison, the heavy oil, modification solvents and sulfuric acid were mixed at room temperature for 50 min, neutralized and dehydrated.

2.3. Characterization of heavy oil

2.3.1. Measurement of hydroxyl number of heavy oil before and after modification

The hydroxyl numbers of heavy oil before and after modification were determined according to the Chinese National Standard (GB12008.3-89) by alkalimetric titration. Firstly, the heavy oil (1 g) was esterified with phthalate (25 ml) at 115 ± 2 °C for 1 h, then the esterified heavy oil was titrated with a 1 M sodium hydroxide solution to the equivalence point. The blank solution was also titrated under the same conditions. Finally, the hydroxyl numbers of samples were calculated by the equation detailed by Wang et al. (2008). In addition, the hydroxyl numbers of the raw heavy oil, PEG 400 and the modification solvents were surveyed under the same conditions.

2.3.2. FT-IR analysis of heavy oil before and after modification

The functional groups of heavy oil modified at 150 °C were analyzed with a FT-IR spectrometer (Bruker Tensor 27, Germany), operated with 16 scans at a resolution of 4 cm^{-1} and a wave number range from 4000 to 400 cm^{-1}. For comparison, FT-IR analysis of heavy oil modified at room temperature was performed under the same conditions.

2.4. Synthesis of PU foams with activated heavy oil

Activated heavy oil was mixed with PEG 400 to prepare bio-polyols, in which the content of activated heavy oil varied from 0 to 100 wt.%. Then, 100 g bio-polyols, 16 g blowing agent (1,1-dichloro-1-fluoroethane, HCFC-141b), 2 g surfactant (silicone), and 25 g catalyst solvent (triethylenediamine: ethylene glycol = 1:3w/w) were mixed in a 500 ml paper cup at 1000–1200 rpm for 1 min followed by the addition of 74.6–147.8 g 4,4′-diphenylmethane diisocyanate (MDI) to achieve a [NCO]/[OH] ratio of 1.05 and agitated at 1400–1600 rpm until a creamy consistency was obtained (about 6–12 s) at room temperature for copolymerization. The polymerized mixture was spread into a seal mold to form uniformly sized PU foams. The foams were cured for 24 h at room temperature. Three replicate samples were prepared for each foam. The [NCO]/[OH] ratio is given as follows:

$$[\mathrm{NCO}]/[\mathrm{OH}]\mathrm{ratio} = \frac{M_{\mathrm{MDI}} \times W_{\mathrm{MDI}}}{M_{\mathrm{PEG\ 400}} \times W_{\mathrm{PEG\ 400}} + M_{\mathrm{activated\ heavy\ oil}} \times W_{\mathrm{activated\ heavy\ oil}}} \quad (1)$$

where M_{MDI} is the content of the isocyanate group in MDI (23.81 mmol/g), $M_{\mathrm{PEG\ 400}}$ is the content of the hydroxyl group in PEG 400 (285/56.1 mmol/g), $M_{\mathrm{activated\ heavy\ oil}}$ is the content of the hydroxyl group in activated heavy oil (564.5/56.1 mmol/g), W_{MDI}, $W_{\mathrm{PEG\ 400}}$ and $W_{\mathrm{activated\ heavy\ oil}}$ are the weights (g) of MDI, PEG 400 and activated heavy oil, respectively.

MDI, HCFC-141b and silicone were obtained from Yantai Wanhua Polyurethane Co., Ltd. (Shandong, China). Besides these three reagents, all other reagents were of analytical grade and obtained from Sino-pharm chemical reagent Co., Ltd. (Beijing, China).

2.5. Characterization of PU foams

2.5.1. Mechanical properties of PU foams

The compressive strength of PU foams was measured with a universal mechanical testing machine (Shimadzu AG-2000A, Japan) at 25 °C. Sample size was 50 (length) × 50 (width) × 50 (thickness) mm. Applied stress was varied in order to control the compressive speed at 5 mm/min. Compression strength (σ, Pa) was calculated according to the ISO 844-2004 Standard. All samples were measured five times and averages were calculated.

2.5.2. Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) and pyrolysis temperature (T_p) of each PU foams were measured using a differential scanning calorimeter (Netzsch STA449, Germany). A 20 ± 2 mg sample was scanned from room temperature to 600 °C in order to illuminate the energy consumption property during the pyrolysis process of PU foams. All scans were done under a dry nitrogen flow of 50 ml/min at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Hydroxyl number analysis of heavy oil before and after modification

Table 1 shows the hydroxyl numbers of heavy oil, PEG 400, modification solvents and the mixture of heavy oil with modification solvents before and after modification. The hydroxyl number of raw heavy oil was only 212 mg KOH/g, which is lower than the hydroxyl number requirement (300–600 mg KOH/g) for PU foaming preparation (Liu et al., 2009). Therefore, the PU foams cannot be directly prepared with heavy oil.

Table 1
Hydroxyl number of heavy oil before and after modification.

Components	Hydroxyl number (mg KOH/g)
Heavy oil	212.0
PEG 400	285.0
Modification solvents	588.7
The mixture of heavy oil and modification solvents before modification reaction	494.5
The mixture of heavy oil and modification solvents after modification reaction	564.5