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

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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

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