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Effects of CS/EC ratio on structure and properties of polyurethane foams prepared from untreated liquefied corn stover with PAPI

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ABSTRACT

Corn stover (CS) was liquefied by using ethylene carbonate (EC) as liquefying solvent and sulfuric acid as a catalyst at 170 °C for 90 min. Polyurethane (PU) foams were prepared from liquefied corn stover (LCS) and polymethylene polyphenylisocyanate (PAPI) by one-shot method at a [NCO]/[OH] ratio of 0.6 in the presence of blowing agent, surfactant and co-catalyst. The effects of CS/EC ratio (w/w) on the structural, mechanical and thermal properties were studied by means of Fourier Transform Infrared Spectroscopy (FT-IR), thermal analysis (TGA/DSC) and universal tensile machine. FT-IR analysis indicated that urethane linkages were formed; free isocyanate groups existed in samples. All samples had a low thermal stability and decomposition occurred in four successive stages. With the increase in CS/EC ratio, tensile strength and Young's modulus first increased and then decreased, and elongation rate at break decreased. Properties of LCS-PU foams can be changed by varying the CS/EC ratio.

1. Introduction

Biomass resource such as agricultural residues are renewable natural polymers and easily obtainable. Only the amount of the world's corn stover (CS) is estimated to be about 1.27 billion tons in 2004 (China Agriculture Yearbook, 2005). However, large quantities of agricultural residues are discarded, which not only increase the burden of environment but also cause that the valuable energy contained in agricultural residues are not involved in the energy cycle. In recent years, effective utilization of biomass resources has paid growing attention right from the starting to seeking a substitute for petroleum and environmental protection.

Liquefaction techniques can convert the solid lignocellulosic biomass into liquid products which contain some –OH groups and have potential values of substituting the polyester or polyether polyol to prepare PU foams (Bhunia et al., 1999), which can be friendly to the environment (Breslin, 1993). Some researches utilizing liquefied polyol products to prepare polyurethane have been reported (Montane et al., 1998; Yu et al., 2006; Kurimoto et al., 1992, 2000, 2001a,b; Lee et al., 2002; Yao et al., 1995, 1996; Wang et al., in press). Other studies utilizing the natural materials such as starch, soybean oil and cellulose to prepare or modify the properties and degradability of polyurethane have been carried out (Rivera-Armenta et al., 2004; Ciobanu et al., 2004; Huang and Zhang, 2002; Araujo et al., 2005; Lu et al., 2005; Ha and Broecker, 2002; Pechar et

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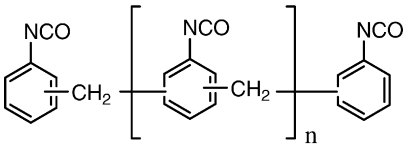
al., 2006; Kwon et al., 2007). In fact, the characters of liquefied products from different liquefaction formulations are different (Liang, 2005) and the properties of PU foams depend on the structures of the polyols and isocyanate (Hepburn, 1982). However, in previous studies, the liquefied products from only one liquefaction formulation are used and investigated. The effects of liquefaction formulations on the properties of polyurethane have been reported very little (Kurimoto et al., 2000).

The costs as well as mechanical properties are the main constraints that limit the biodegradable materials to be widely used (Lu et al., 2005). The increase in CS charge can be contributed to the decrease in the prices. This study was aimed at estimating the effects of CS/EC ratio (w/w) on structural, mechanical and thermal properties of LCS-PU foams at a [NCO]/[OH] ratio of 0.6. The effects of factors such as liquefaction time and the charge of catalyst will be further investigated. In this study, LCS-PU foam was prepared by one-shot method through co-polymerization of non pretreated LCS and PAPI in the presence of blowing agent, co-catalyst and surfactant. Structural, mechanical and thermal properties of LCS-PU foams were measured with FT-IR, universal tensile machine, thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

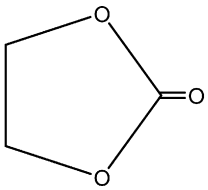
2. Experiment

2.1. Materials and methods

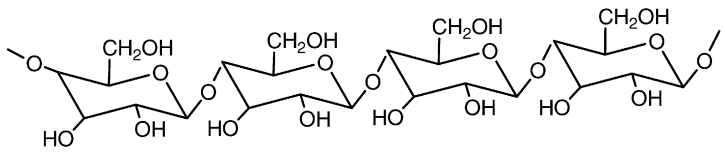
Corn stover with moisture content of 8–10% from a local farm in Beijing suburb of China was milled and only the fractions with particle size of 20–80 meshes were used for the liquefaction experiments. The components of corn stover were analyzed by ANKOM220 cellulose analysis (ANKOM company, USA). The results were soluble materials, 33.16%; cellulose, 34.15%; hemicellulose, 23.86%; lignin, 6.61%; acid insoluble materials, 1.86%. Sulfuric acid (97%, v/v) was used as the catalyst. Ethylene carbonate (99.90%) was used as the solvent in the liquefaction process. PM-200 as the PAPI was obtained from Yantai Wanhua Polyurethane Co., Ltd. (Shandong, China) and the NCO group content was 30.03%. Water and silicone were used as the blowing agent and surfactant, respectively. Triethylamine and dibutyltine dilaurate were used as the co-catalysts. All chemicals used were of reagent grade and were obtained from commercial sources. The chemical structures of cellulose, PAPI and ethylene carbonate were as follows:



PAPI



ethylene carbonate



cellulose

2.2. Preparation of LCS

Oven-dried corn stover flour 40–80 g, ethylene carbonate 200 g and sulfuric acid 7.4 g were placed in a three-neck flask (1000 ml) equipped with a reflux condenser, a thermometer, and a motor-driven stirrer and refluxed at 170°C for 90 min with continuous stirring. Then, the flask was immersed into cold water to quench the reaction and the LCS as the biopolyols was collected for later analysis and use.

The acid number of LCS was gained by titratation method with a 0.5 M sodium hydroxide solution, and the hydroxyl number was measured by referring to Kurimoto et al. (2000). The moisture contents of LCS were determined by the Karl Fischer method using a CBS-1A model moisture content meter, Beijing Chaosheng company (Beijing, China).

Insoluble residues (unliquefied corn stover) ratio (IRR) of LCS was measured by the following method. A mixture of 2 g LCS was diluted using 50 ml dioxane–water (4:1, v/v) and the insoluble residues were filtered using a Buckner funnel and filter paper (the weight was marked). The residue rinsed thoroughly with the dioxane and 10 blank filter papers were heated for 24 h at 105 °C. The average water content in blank filter paper was calculated. The insoluble residues ratio is given as follows:

$$\mathrm{IRR} = \frac{w_2 - w_3}{w_1} \quad (1)$$

where w_2 and w_3 are the dry weight of the filter paper with the insoluble residues and the filter paper, respectively; w_1 is the weight of the LCS, 2 g.

The characteristics of LCS are listed in Table 1.

2.3. Preparation of LCS-PU foams

The foams were prepared by the one-shot method. A mixture of 15 g LCS, 0.5 g water, 0.15 g silicone, and 0.3 g co-catalysts (triethylamine:dibutyltine dilaurate = 1:1, w/w) was mixed in a 150 ml polypropylene cup at 1000–1200 rpm for 1 min followed by the addition of 9.60–11.36 g PAPI ([NCO]/[OH] ratio, 0.6) and agitated at 1400–1600 rpm until cream time (about 6–12 s) at room temperature for co-polymerization. The polymerized mixture was poured and daubed onto smooth glass to uniform thin layer of PU foam. The obtained foams were cured for 7 d at room temperature, and then were conditioned for 16 h at 23 °C, 50% RH (relative humidity) according to ISO 1184-1983 Standard. Every experiment was replicated three times. The [NCO]/[OH] ratio is given as follows: