

# Development of high-performance biodegradable rigid polyurethane foams using all bioresource-based polyols: Lignin and soy oil-derived polyols

Xiaogang Luo <sup>a,\*</sup>, Yuqin Xiao <sup>a</sup>, Qiangxian Wu <sup>b,\*\*</sup>, Jian Zeng <sup>c</sup>

<sup>a</sup> School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430073, Hubei, China

<sup>b</sup> Green Polymer Laboratory, College of Chemistry, Central China Normal University, Luoyu Road 152, Wuhan 430079, China

<sup>c</sup> Guangdong Provincial Bioengineering Institute (Guangzhou Sugarcane Industry Research Institute), Guangdong Provincial Key Laboratory of Sugarcane Improvement and Biorefinery, Guangzhou 510316, Guangdong, China

## ARTICLE INFO

### Article history:

Received 13 January 2018

Received in revised form 28 March 2018

Accepted 23 April 2018

Available online 25 April 2018

### Keywords:

Lignin

Soybean phosphate ester polyol

Biodegradable rigid polyurethane foam

## ABSTRACT

Development of biodegradable polyurethane materials is the most promising in the wider context of the “greening” of industrial chemistry. To tackle this challenge, a novel biodegradable polyurethane foam from all bioresource-based polyols (lignin and soy oil-derived polyols) and polymeric methyldiphenyl diisocyanate (pMDI) have been synthesized via a one-pot and self-rising process. All these foam samples have the internal cellular morphology and microstructure. FTIR result exhibits characteristic peaks of polyurethane, and indicates covalent bonds between soy-based polyurethane and lignin, and the lignin powders can react with pMDI via active -H and -CNO. In addition, hydrogen bonding also plays an important role in forming the 3D structures. These interactions and chemical bonds made the prepared foam samples form the 3D macromolecular structure with improved mechanical, thermal, and biodegradable properties. The reaction process is time-saving and cost-effective as it requires no blowing agent and minimum processing steps, while exploring the potential of using the higher content of nature bioresource constituents.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Lack of degradability and the closing of landfill sites as well as growing environment problems have led to concern about polyurethane (PU) foams, which are widely used in all industrial fields and present in many aspects of modern life [1] [2]. The low-density rigid PU foams offer properties of moisture permeability and thermal conductivity along with high-performance because of the ratio of strength to weight, which make PU foams the most common commercial polymeric foams used in the world [3]. Moreover, the shortage of petroleum-based fuel and the problem of the greenhouse gas exhaustion directly drive production of the biopolymer in an environment-friendly manner. Research on the elucidation of the biodegradability of PU from bioresource materials is very urgent [4].

Renewable biomass (such as lignin, plant oil, cellulose, etc.) as raw materials for PU products have unparalleled advantages. Among them,

lignin is a 3D amorphous biopolymer consisting of methoxylated phenyl-propane structure units, and it has numerous and different types of chemical groups, such as alcoholic hydroxyl, carboxyl, phenolic hydroxyl and methoxy groups, etc. [5]. Nowadays, that lignin act as the raw chemical materials in polyurethane industry field has become extremely attractive for its economic and environmental advantages [6–8]. It has been proved it was an alternative route to produce value-added chemicals from lignin [9–11].

Another feasible solution to the above challenge, the production of polyol for PU from vegetable oils has received increasing attention [12,13]. The most important vegetable oils are the highly unsaturated ones [14] with many double bonds, which can be converted into the hydroxyl groups chemically. The soy-based polyol used in this work (SOPEP, Soybean phosphate ester polyol) is synthesized by an acid hydrolyzing method of epoxidized soy-based oil with phosphoric acid. SOPEP could be effectively used for designing rigid PUs with optimal properties based on its physical and chemical properties and the preparation process conditions [15].

So development of the efficient route to design the biodegradable and environment-friendly rigid biobased PU foams from the higher content of nature bioresource materials is one of the most important feasible explorations in industrial fields.

\* Corresponding author.

\*\* Correspondence to: Q. Wu, College of Chemistry, Central China Normal University, Wuhan 430079, China.

E-mail addresses: [xgluo@wit.edu.cn](mailto:xgluo@wit.edu.cn) (X. Luo), [wuqiangxian@mail.ccnu.edu.cn](mailto:wuqiangxian@mail.ccnu.edu.cn) (Q. Wu).

## 2. Materials and methods

### 2.1. Materials

The SOPEP (OH value: 268 KOH mg/g, acid value: 35.6 KOH mg/g) was received from Arkema Inc. (Blooming Prairie, MN, CA), and the chemical structure of SOPEP was shown in our previous work [16]. The lignin powders with 75  $\mu\text{m}$  (Mascoma Corporation, Canada) were extracted from forestry and non-food agricultural materials, such as wood pieces, agricultural residue and switchgrass, and so on, by using bacteria and yeast to produce bioethanol. Several important properties of lignin powders were as follows: TOC, TN, and TS are 57.00%, 0.34% and 0.03%, respectively. And other detailed informations were shown in our published work [17]. The pMDI (RUBINATE®M) samples are from Huntsman Corporation, Woodlands, TX, USA, and the NCO% is 31.20, functionality is 2.70.

### 2.2. Preparation of the foams

The one-pot method for foam preparation from all bioresource-based polyol of SOPEP and lignin powders was adopted [16]. Relating to the total bioresource-based polyol content, the concentrations of other components were as following: The concentrations of the lignin powders used were 0, 5, 10, 15, 20 and 25 w/w% of the total polyols content of the bioresource-based polyols, which are composed of vigorously mixing lignin powders and soy polyol for 3 h to obtain a uniform mixture, the isocyanate index is 1.10 of pMDI. The mixture was homogenized and sonicated for 15 min 3 times to make the lignin powders disperse in the polyol mixture well, and it was degassed for 2 h under vacuum condition, and then pMDI was added with a further 3 min of stirring to prepare the free-rising rigid foam in an open paper cup, the foam was solidified about 30 min. The product foams were removed from the paper cup after sufficient polymerization and crosslinking. Then they were cured for 48 h for testing at room temperature.

### 2.3. Characterization of the foams

The foams were observed and photographed with a digital camera (Canon A630). SEM (Hitachi TM3000, Hitachi Ltd., Japan) was used to measure the morphology and the cell structure of the foam samples.

The samples were cut into 6 mm pieces with a razor blade, and these pieces were Pt-coated to provide the electrically conductive surface before scanning. To avoid excessive charge build-up on the surface of the foams, the accelerating voltage was 15 kV, which might make the BioPU foam samples degrade. The cell structure of the foams parallel to the free-rising direction of the foams was observed.

The FTIR spectrometer of Nicolet iS10 (Thermo Scientific Inc., USA), equipped with a detector of DTGS (deuterated triglycine sulfate) and connected to software of the OMNIC operating system of Version 8.4 was applied to measure FTIR spectra of all the samples. The foam samples were ground into the powders and dried in a vacuum oven at 60 °C for 48 h for the measurement. The sample powders were placed in contact with ATR (attenuated total reflectance) on a multi-bounce plate of ZnSe crystal at 25 °C. The FTIR spectra were collected in the frequency range of 4000–500  $\text{cm}^{-1}$  by co-adding 64 scans and at a resolution of 2  $\text{cm}^{-1}$  with strong apodization. After each scan, a new reference air background spectrum was taken. The plate was carefully cleaned by cleaning with hexane three times, followed by acetone and dried with a soft tissue before loaded with the next sample. The background of the air spectrum of air spectrum was subtracted for all the spectra. The spectra were recorded as absorbance values at each data point in triplicates.

The apparent density of the foam samples was measured according to ASTM standard method D 1622–03. The size of the specimen was 30 mm  $\times$  30 mm  $\times$  30 mm (length  $\times$  width  $\times$  thickness). The apparent densities of average values of five specimens per sample were measured and reported. The compression properties of the foam were obtained with the Universal Testing Machine of Instron 3382 (Instron Corp., USA) at ambient condition. Compression stress at the 10% strain and compression modulus (initial linear slope of the stress-strain curve) in parallel to the direction of the foam rising were measured according to the ASTM standard method D 1621–10. The size of the specimen was 30 mm  $\times$  30 mm  $\times$  30 mm (length  $\times$  width  $\times$  thickness), and the rate of crosshead movement was fixed at 2.5 mm/min for each sample. For each compression data point, an average of five measurements was taken along with the standard deviation.

Thermogravimetric analysis of the samples was performed on a Hi-Res Thermogravimetric Analyzer (TGA) of model Q-500 (TA Instruments, USA) under an atmosphere of nitrogen with a heating rate of 5 °C/min from room temperature to 800 °C.

The soil burial test [18] was carried out by burying the rigid foam samples in a sandy soil containing the left-over food, and the pH of

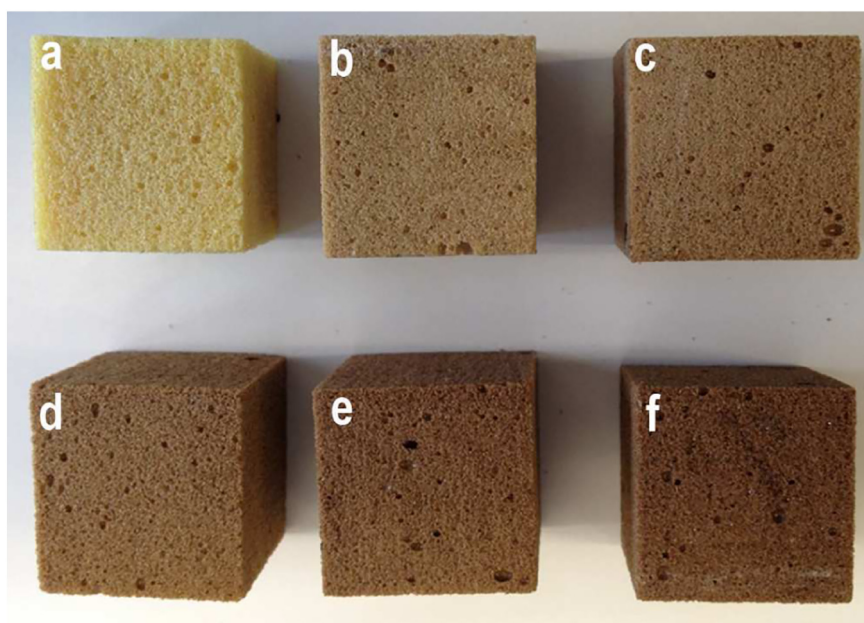


Fig. 1. Photographs of the foams: (a–f) BioPULignin0–BioPULignin25.

Download English Version:

<https://daneshyari.com/en/article/8327413>

Download Persian Version:

<https://daneshyari.com/article/8327413>

[Daneshyari.com](https://daneshyari.com)