



# Green polyurethane from lignin and soybean oil through non-isocyanate reactions



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## ARTICLE INFO

### Article history:

Received 30 September 2014

Received in revised form 17 November 2014

Accepted 19 November 2014

Available online 12 December 2014

### Keywords:

Lignin

Soybean oil

Polyurethane elastomers

Organosilane

Non-isocyanate polyurethane

## ABSTRACT

Here we report the synthesis route to produce non-isocyanate polyurethane elastomer with significantly high biomass contents (85 wt%) prepared from two different biomasses, i.e., lignin and soybean oil, for the first time. Carbonated soybean oil was reacted with coupling agent, 3-aminopropyltriethoxysilane, to form urethane bridges, and then lignin was introduced to produce sustainable polyurethane. All samples were studied by the FT-IR spectra which showed typical linkages of polyurethane. The increase in lignin content resulted in the increase of tensile strength, reaching as high as 1.4 MPa.

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## 1. Introduction

Polyurethanes have been widely used in construction, packaging, insulation, bedding, upholstery, footwear, vehicle parts, panting, etc. They can be in the form of rigid, semi-rigid, flexible foams of a wide range of densities, elastomers, and high viscous liquid [1]. Conventional polyurethanes are usually synthesized through the polycondensation reaction between a diisocyanate and a diol [2–4]. However, isocyanates are notably toxic chemical and synthesized from an even more toxic substance phosgene which causes environmental hazards. Moreover, exposure to isocyanates can cause health effects, such as skin irritation and long-term asthma [5]. Due to the use of isocyanate in conventional polyurethanes, there is a substantial interest to develop alternative, environmentally friendly methods for the preparation of polyurethanes (non-isocyanate routes) and one of the most attractive methods is the reaction of cyclic carbonate with amines [6].

Lignin is a complex chemical compound most commonly derived from wood, plants, and algae, which is one

of the most abundant organic biopolymer available on Earth. It is an amorphous, cross-linked, and three dimensional phenolic polymer consisting of methoxylated phenylpropane structures. Although the exact structure of lignin in nature is still unknown, it is believed that the biosynthesis of lignin involves the polymerization of phenolic units. The composition, molecular weight, and amount of lignin differ from plant to plant; however, it is estimated that lignin contains 30% of the organic carbon available in plant biomass available [7]. Using lignin as one of the raw materials for the polyurethane synthesis has been reported several times before. In 2009, Cateto et al. modified lignin into liquid polyols by oxypropylation process [8]. They prepared polyurethanes with four different types of lignin and the properties of the synthesized polyurethanes were comparable with the polyurethane rigid foams prepared with commercial polyols. Moreover, Saito et al. prepared lignin-based polyurethane thermoplastics by reacting with oligomeric polybutadiene diisocyanate [9]. Robust thermoplastic polyurethanes with high lignin contents (65–70 wt%) was successfully synthesized and discovered that the increase in lignin contents enhances the modulus as well as cross linking degree. In addition, Huo et al. prepared

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polyurethanes by reacting lignin-aminated polyol and glycol with diphenylmethane diisocyanates in the presence of water as blowing agent [10]. The crosslinking kinetics of the formation of lignin-aminated polyol-based polyurethane foam was studied using FTIR–ATR spectroscopy. Despite the inclusion of lignin in polyurethane formulation, all of the polyurethane mentioned above involves using toxic isocyanates. Furthermore, other petroleum derived chemicals such as surfactant or polyols had to be included in order to form polyurethane.

Soybean oil, which can be derived from plant sources, is found abundance in all parts of the world. They are made up of triglyceride molecules; generally, they are composed of three fatty acids that are connected together by a glycerol with each fatty acid containing 14–22 carbons with 0–3 double bonds [11]. In last few decades, they have been utilized to replace petroleum chemicals to produce coatings, inks, plasticizers, lubricants, and agrochemicals [12–18]. Since the soybean oil-based materials are sustainable and biodegradable, the incorporation of soybean oil not only avoids the use of toxic isocyanate, but also contributes to reducing global warming effects. Recently, several researchers accomplished to synthesized polyurethane using soybean oil as material using non-isocyanate reaction route. In 2008, Javni et al. prepared polyurethane by a non-isocyanate route by reacting carbonated soybean oil with diamines [19]. Carbonated soybean oil was reacted with different diamines such as 1,2-ethylenediamine, 1,4-butylenediamine and 1,6-hexylenediamine and cured at 70 °C for 10 h, and then for 3 h at 100 °C and polyurethane was formed. The results indicated that those polyurethane can be prepared with a wide range of mechanical properties which is useful for industrial applications. Furthermore, Suqin Tan et al. prepared rigid polyurethane foam by replacing polypropylene-based polyol with soybean oil-based polyol [20].

Epoxidized soybean oil (ESBO), which is a commercially available product widely used in PVC industry, is used as a starting chemical in this study to produce cyclocarbonate by the chemical fixation of carbon dioxide with the presence of catalyst [21–24]. The benefits of this process includes: solventless system because the vegetable oil itself can act as solvent which dissolves both the catalyst and carbon dioxide; hence it is eco-friendly and also this process utilizes carbon dioxide as a sustainable reactant – it is the cheapest and the most abundant source of carbon available which is also non-flammable and has low toxicity.

In this article, we report the synthesis route for the preparation of polyurethane using 100% sustainable materials. The reaction occurs in 3 steps, and is done in 2 different pot reactions. Briefly, purchased epoxidized soybean oil is carbonated to synthesize carbonated soybean oil. Then carbonated soybean oil was reacted with coupling agent, 3-aminopropyltriethoxysilane (APES) to produce urethane monomers. Finally, prepared urethane monomers were polymerized with lignin to produce sustainable polyurethane. The schematic illustration of the reaction is shown in Fig. 1. In this polymer, aromatic structure of lignin will function as hard (rigid) segment, while polysiloaxane, –Si–O–Si– linkages formed as a result of self-condensation of

APES molecules will function as soft segment. Synthesis of polyurethane involves the solidification of moldable polymer upon cooling, which is a characteristic that thermoplastic polyurethane exhibits. Lignin and soybean oil contents in the polymers were as high as 85 wt%, which is higher than most of the reported work for biomass incorporated polyurethanes, to utilize as much as renewable resources as possible to reduce the use of environmentally hazardous chemicals such as isocyanate and any other petroleum derived chemicals.

## 2. Materials and method

### 2.1. Materials

Epoxidized soybean oil (Spectrum Chemicals, CAS 8013-07-8), Tetra-*n*-butylammonium bromide (TBAB) (VWR, 99+%, CAS 1643-19-2), carbon dioxide (AirGas 50 lb industrial grade, CGA 320), Kraft Lignin (Sigma–Aldrich, CAS 8068-05-1), tetrahydrofuran (Sigma–Aldrich, 109-99-9), 3-aminopropyltriethoxysilane (Sigma–Aldrich, >98%, CAS 919-30-2), lithium chloride (Sigma–Aldrich, anhydrous, >99%, CAS 7447-41-8), and dimethyl sulfoxide (Sigma–Aldrich, 99.96 atom %D CAS 2206-27-1) were used as received.

### 2.2. Methods

#### 2.2.1. Preparation of carbonated soybean oil (CSBO) and characterization

100 g of ESBO was placed in a 500-mL three neck round bottom flask and heated in an oil bath to 140 °C. Then, 6.6 g of TBAB (6.6 weight percent or 5 mol% with respect to the epoxy content) was added and continuous flow of carbon dioxide was introduced at a rate of 0.2 mL/s. The reactor was mechanically stirred at the speed of 500 rpm for 72 h and was operated at the atmospheric pressure.

#### 2.2.2. Preparation of urethane monomer

In a round bottom flask, 3 g of CSBO and 5 mol% of lithium chloride respect to cyclic carbonate group was dissolved in 20 mL of THF. Then, 3-aminopropyltriethoxysilane (molar ratio of CSBO: APES was 1:1) was dropped into the reaction system. The mixture was heated up to and kept at 70 °C for 3 h under stirring. The reaction progress was monitored by FTIR spectroscopy.

#### 2.2.3. Preparation of lignin–soybean oil polyurethane

After 3 h of reaction for the preparation of urethane monomer, the solution of lignin dissolved in tetrahydrofuran/water (60/40 v/v) was added. The reaction mixture was stirred for 12 h, then was poured into mold and air dried for 2 h followed by curing at 60 °C for 7 h. Polyurethanes with various lignin contents were studied.

#### 2.2.4. Characterization

FTIR spectroscopy was performed on Nicolet 6700 FTIR spectrometer with a potassium bromide (KBr) beam splitter. A total of 32 scans were taken with a resolution of 4 cm<sup>-1</sup>. <sup>1</sup>H NMR samples were prepared by dissolving

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