



## Synthesis and properties of soybean oil-based biodegradable polyurethane films

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### ABSTRACT

In this study, a series of biodegradable polyurethane films (PU-Fs) is prepared by step-growth polymerization of hydroxylated soybean oil (SBO-OH) and L-lysine diisocyanate ethyl ester (L-LDI) that are renewable-based di-functional building blocks. The influence of loading ratio by weight (SBO-OH/L-LDI (w/w) = 1:0.5; 1:1 and 1:1.5) on the biodegradable, mechanical and thermal properties of final PU-Fs is systematically investigated. In the first step, epoxy groups of epoxidized soybean oil are converted to corresponding hydroxyl functionalities to react with the diisocyanate groups of L-LDI via film casting method at room temperature. The obtained PU-Fs with higher L-LDI loading exhibit higher thermal and mechanical properties as well as more hydrophobic characteristic compared to others. Moreover, biodegradability of resulting PU-Fs is also studied using hydrolytic and enzymatic degradation experiments. Noteworthy, it is found that around 50 and 60% of PU-Fs are degraded by enzymatic and hydrolytic experiments after 12 weeks.

### 1. Introduction

A great deal of effort has been devoted to the development of bio-based materials particularly due to the requirements of concerning environmental sustainability last three decades [1–3]. The use of renewable resources such as starch [4–6], cellulose [7,8], protein [9,10], vegetable oils [11–13], sugar [14–16] and wood [5] brings several advantages including readily availability, low toxicity and relatively low cost compared to the petrochemical-based raw materials in polymer industry. Among them, the vegetable oils, especially soybean oils, consisting of triglycerides with different chain lengths as well as number of double bonds are suitable for the several polymerization processes such as alkyd resins [17], polyamides [18] and polyurethanes [19,20] via acyclic metathesis polymerization [21], ring-opening metathesis polymerization [22,23], cationic polymerization [24], free radical polymerization [25] and click chemistry [26]. The polymers with high molecular weight cannot be obtained from vegetable oils alone, unless their reactive groups are converted to more reactive hydroxyl, epoxy or carboxyl functionalities.

Polyurethanes resulting from step-growth polymerization of diisocyanate with polyols have unique properties for advancing technology including composites, rubbers, fibers, foams, injection moldings,

coatings and adhesives [27–29]. Recently, more environmentally friendly manufacturing processes have been proposed for the production of polyurethanes using bio-renewable sources. With this purpose in mind, nontoxic biodegradable lysine- and amino acid-based diisocyanates have been utilized in the literature to eliminate the formation of carcinogenic and toxic aromatic diamine by-products coming from diisocyanates [30–35]. The aim of this study was synthesis and characterization of biodegradable polyurethane films starting from both renewable and non-toxic resources, hydroxylated soybean oil and L-Lysine diisocyanate ethyl ester. For this purpose, epoxy groups of soybean oils were converted to hydroxyl functionalities (SBO-OH) by ring opening reaction with hydrochloric acid. Then, step-growth polymerization of L-Lysine diisocyanate ethyl ester and SBO-OH was investigated with different feeding ratios at room temperature. The formation of polyurethane films was monitored by spectroscopic (FT-IR and <sup>1</sup>H-NMR) and thermal analyses (DSC and TGA) by meaning of products and intermediates. Mechanical and biodegradable properties of the resulting PU-Fs were also investigated by tensile test, and hydrolytic and enzymatic degradation experiments, respectively. This strategy enabled to obtain biodegradable polyurethane films from renewable and non-toxic building blocks under mild conditions.

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## 2. Experimental part

### 2.1. Materials

Epoxydized soybean oil ( $M_n = 1000$  g/mol, epoxy content = 7% min.) was purchased from Parchem (ESBO, New York) and used as received. Hydrochloric acid (HCl, 36.5–38%, Sigma-Aldrich, Germany), magnesium sulfate ( $Mg_2SO_4$ , 99.99%, Sigma-Aldrich, Germany), ethyl acetate anhydrous (EtAc, 99.98%, Sigma-Aldrich, Germany), acetone ( $\geq 99.98\%$ , Sigma-Aldrich, Germany), 1,2-dichloroethane anhydrous ( $C_2H_4Cl_2$ , 99.8%, Sigma-Aldrich, Germany), acetic anhydride ( $\geq 98\%$ , Sigma-Aldrich, Germany), potassium hydroxide ( $\geq 85\%$ , Sigma-Aldrich, Germany) and tin(II) 2-ethylhexanoate ( $Sn(Oct)_2$ , 92.5–100%, Sigma-Aldrich, Germany) were used as received. L-Lysine diisocyanate ethyl ester (L-LDI, min 95%, Carbosynth, United Kingdom) was used without any purification. Sodium phosphate monobasic ( $NaH_2PO_4$ , Sigma-Aldrich, Germany), disodium hydrogen phosphate ( $Na_2HPO_4$ , Sigma-Aldrich, Germany), lipase (Sigma-Aldrich, Germany), cobalt(II) chloride ( $CoCl_2$ , Sigma-Aldrich, Germany) and hydrogen peroxide (30%, Sigma-Aldrich, Germany) were used without any purification. All other reagents and solvents were purified by conventional distillation and drying procedures before use.

### 2.2. Instrumentation

$^1H$ -nuclear magnetic resonance ( $^1H$ -NMR) spectroscopic analyses of ESBO and SBO-OH were recorded by a Varian 400 MHz NMR (California, USA) spectrometer in  $CDCl_3$ . Fourier transform infrared (FT-IR) analyses were performed to prove structures of ESBO, SBO-OH and PU-Fs by using Perkin-Elmer (Lambda 25, Waltham, USA) FT-IR Spectrum Two Spectrometer equipped with a diamond ATR device at room temperature scanning range covered  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . Thermogravimetric analysis (TGA) was conducted by Perkin-Elmer (Waltham, USA) Diamond TA/TGA with a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen flow (200 mL/min). Glass transition temperatures ( $T_g$ ) of PU-Fs were determined by using differential scanning calorimeter (Perkin-Elmer, Lambda 25, Waltham, USA) Diamond equipment under nitrogen flow (10 mL/min) with a heating rate of  $10^\circ\text{C}/\text{min}$ . Water contact angle (CA) measurements were done by using KSV Attension Theta optical tensiometer (Vastra Frolunda, Sweden). In addition, Zwick/Roell Z1.0 model universal test machine was used for determination of tensile properties of PU-Fs by using DIN EN ISO 527-1 guideline. For reproducibility, all samples were tested three times under open air atmosphere.

### 2.3. Hydroxylation procedure of ESBO (SBO-OH)

In a 250 mL round bottomed flask, hydrochloric acid (15 mL, 0.15 mol) and acetone (60 mL) were mixed and ESBO (25 g, 0.1 mol) was introduced into the mixture as drop-wise by sight of the agitation. After mixing, the flask was placed in an oil bath and left to stir at about  $40^\circ\text{C}$  for 2 h. At the end of this time, acetone was evaporated and mixture of ethyl acetate-water (3:1) was added to the reaction mixture to yield separated two layers. Organic phase obtained from two layers was washed with large excess of water until neutral pH, dried over anhydrous  $Mg_2SO_4$  and filtered. Then, the solvent was evaporated and yellow viscous compound was obtained. Hydroxyl number of ESBO was determined as 300 mg KOH/g sample by using titrimetric acetic acid acetylation method [36].

### 2.4. Preparation of biodegradable polyurethane films (PU-Fs)

A representative step-growth polymerization procedure for the synthesis of PU-Fs was as follows [37]: SBO-OH (1 g, 0.001 mol), L-LDI (1 g, 0.004 mol) ([NCO]:[OH] = 1:1) (w/w) and 4 mL solution of ten drops  $Sn(Oct)_2$  in 20 mL anhydrous  $C_2H_4Cl_2$  were put in the tightly

closed 50 mL round bottomed flask equipped with a magnetic stir bar under nitrogen atmosphere to degas for 1 min. The reaction mixture was left under continuous stirring for 5 h at room temperature. After given time, viscous transparent yellow PU-Fs were casted in petri dish to remove the solvent for 1 day at room temperature. After evaporation of solvent, the obtained PU-Fs were cut into rectangular shape (1 mm  $\times$  30 mm  $\times$  10 mm) for tensile test. Other two samples ([NCO]:[OH] = 0.5:1 and 1.5:1 (w/w)) were prepared under identical experimental conditions.

### 2.5. Biodegradation experiments

Biodegradations of obtained PU-Fs were investigated in vitro experiments by measured the weight loss of films in different specific degradation solutions. Hydrolytic degradation experiment was carried out in phosphate buffer solution (PBS, 0.01 M, pH = 7.40) with 0.01 M  $CoCl_2$  and  $H_2O_2$  30% solution. On the other hand, enzymatic degradation experiment was carried out in 0.01 M PBS (pH = 7.40) with 1 mg/mL lipase. Each PU-F samples were placed into 8 mL degradation solution and incubated at  $37^\circ\text{C}$  with constant shaking. Then, films were cleaned with deionized water and dried in a vacuum oven at  $50^\circ\text{C}$  for 24 h. The weight loss of films was calculated with following Eq. (1) [38,39]:

$$\text{Weight loss (\%)} = [(W_b - W_a) / W_b] \times 100 \quad (1)$$

Where  $W_a$  and  $W_b$  were the weights of the polyurethane films after and before degradation.

## 3. Results and discussion

Various types of vegetable oils such as olive, canola, corn, soybean, castor and sunflower are renewable feedstocks for the production of polyols that can be readily utilized in the polyurethane synthesis. Approximately all vegetable oils have limited hydroxyl functionalities; however their ester and alkene groups presented in the triglyceride sides enable the introduction of these functionalities on their backbone. To obtain polyurethanes with desired mechanical properties, the vegetable oils should contain at least 2.5 number of C=C bonds per triglyceride unit [40]. Due to its high number of C=C bonds (about 4.6 per triglyceride) and large scale availability, soybean oil (SBO) is the first preferred oil compared to other vegetable oils in the polyurethane synthesis.

In this study, the PU-Fs were synthesized starting from commercially available ESBO by two step reactions. In the first step, epoxy functionalities were converted to hydroxyl groups by oxirane ring-opening reaction in the presence of hydrochloric acid catalyst. At the end of this process, the SBO had sufficient hydroxyl functionalities and its OH number was calculated as 300 mg KOH/g sample by titration method. In the second step, the obtained -OH functionalized soybean oil (SBO-OH) was utilized in the step-growth polymerization with different mass ratio of L-Lysine diisocyanate ethyl ester (L-LDI) in the presence of tin(II) 2-ethylhexanoate catalyst. All reactions were performed at room temperature in dichloroethane for 5 h. Visual appearances of the resulting PU-Fs were also shown in Scheme 1.

### 3.1. Spectral analyses

FT-IR and  $^1H$ -NMR spectroscopies were utilized to verify the chemical structures of PU-Fs and intermediates. In Fig. 1, the absorption bands observed at around 820, 1175, 1725 and  $2915\text{ cm}^{-1}$  were attributed to epoxy group, stretching vibration of ester (C-O-C and C=O) and stretching vibration of non-conjugated unsaturation (C-H) respectively. As can be seen in the spectra of SBO-OH, both absence of epoxy band and presence of hydroxyl stretching band at around  $3440\text{ cm}^{-1}$  arising from ring opening reaction proved that successfully

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