

Synthesis of Bio-Based Polyurethanes from Epoxidized Soybean Oil and Isopropanolamine

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ABSTRACT: Epoxidized soybean oil (ESO) and isopropanolamine were used to synthesize a new polyol mixture for preparation of bio-based polyurethanes. The chemical synthetic route for reaction of ESO with isopropanolamine was analyzed by ¹H-NMR. The results suggested that both ester groups and epoxy groups in ESO had reacted with amino group of isopropanolamine through simultaneous ring-opening and amidation reactions. Epoxy groups in various situations exhibited different reactivity, and the unreacted epoxy groups were further opened by hydrochloric acid. The synthesized polyol mixture had high hydroxyl number of 317.0 mg KOH/g. A series of polyurethanes were prepared by curing the synthesized polyol mixture with 1,6-diisocyanatohexane along with different amount of 1,3-propanediol (PDO) as chain extender. Tensile tests showed that yield strengths of the polyurethanes ranged from 2.74 to 27.76 MPa depending on the content of PDO. Differential scanning calorimetry analysis displayed one glass transition temperature in the range of 24.4–28.7°C for all of the polyurethane samples, and one melt peak at high content of PDO. Thermogravimetric analysis showed that thermal degradations of the polyurethanes started at 240–255°C. In consideration of simple preparation process and renewable property of ESO, the bio-based polyurethane would have wide range of applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

In view of shortage of fossil fuel resources and serious environmental pollutions, lipids are receiving more and more attention as important renewable natural resources for production of bio-based plastics and composites in recent years.^{1–3} Varieties of lipid-based polymers such as polyolefin, polyester, and polyurethane have been synthesized and tested, and lipid-based polyurethanes are particularly concerned attributing to relative simple synthetic routes and widely potential applications. Preparation of lipid-based polyurethanes is generally fulfilled by converting the plant oils into polyols, followed by curing with diisocyanate reagents.^{4–6}

It has been demonstrated that the properties of polyurethane greatly depend on the hydroxyl value and structure of polyols. Therefore, different chemical routes have been proposed for converting lipids into polyols with desired hydroxyl values. Ester bonds and unsaturated double bonds in lipids are the mostly

applied reactive sites to derivate hydroxyls for producing lipid-based polyols. Ester bonds of palm oil were alcoholized with glycerol to form monoglyceride which had two hydroxyls.⁷ Ester bonds of linseed oil were amidated with diethanolamine to produce *N,N'*-bis(2-hydroxyethyl) linseed amide polyol.⁸ Unsaturated double bonds of different plant oils were oxidized by ozone and then were turned into hydroxyls by hydrogenation.^{9,10} Hydroxybromination of new sunflower oil (high oleic acid content) was achieved through reaction of unsaturated double bonds with *N*-bromosuccinimide, though the yield of the product was only 40%.¹¹

Another widely used approach to synthesize lipid-based polyols is by converting lipids into epoxidized lipids, followed by reacting with different ring-opening reagents to generate hydroxyls. Hydrolysis of epoxidized lipids in the presence of acid catalysts, such as acetic acid and phosphoric acid, had been investigated to produce lipid-based polyols.^{12,13} Halogenated and

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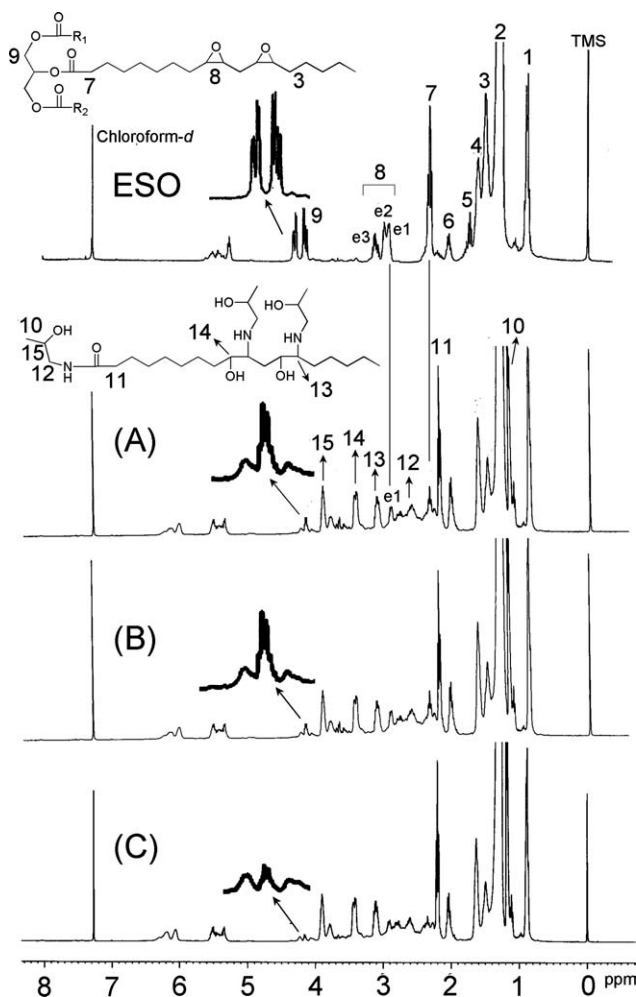


Figure 1. Reaction of epoxidized soybean oil (ESO) with isopropanolamine after 6 h as the molar ratio of amino group to epoxy group was 1.5 : 1 (A), 2 : 1 (B), and 2.5 : 1 (C), respectively.

nonhalogenated soybean oil-based polyols were prepared via the reaction of epoxidized soybean oil (ESO) with hydrochloric acid, hydrobromic acid, methanol, or hydrogen.¹⁴ Preparations of polyols by reaction of epoxidized lipids with diols or lactic acid were also reported recently.^{15,16}

However, the hydroxyl values of the polyols obtained by above reaction routes are usually lower than 300 mg KOH/g,^{9,10,12,14,16} which led to low mechanical properties of the produced polyurethanes. The low hydroxyl values also limit the use of polyols as feedstock for rigid polyurethane foams, which usually require the hydroxyl value in the range of 300–650 mg KOH/g.¹⁷ Recently, polyols with hydroxyl values higher than 300 mg KOH/g were obtained by modification of soybean oil and castor oil, but the reactions involved high temperature (150°C) and use of strong base catalyst.¹⁷

In the present study, a novel lipid-based polyol with high hydroxyl value was synthesized from ESO and isopropanolamine with mild reaction conditions. The chemical reaction mechanism was analyzed extensively with NMR spectroscopy. The

synthesized polyol was subsequently applied for preparing bio-based polyurethanes by curing with 1,6-diisocyanatohexane, and the basic properties of the obtained polyurethanes were characterized with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile tests. In view of the simple and mild preparation process, the authors expect that this synthetic route provide a green approach for synthesis of lipid-based polyurethanes.

EXPERIMENTAL

Materials and Instrumental Analysis

Chloroform-*d* (containing 0.03 % tetramethylsilane, TMS), isopropanolamine, hydrochloric acid (HCl), acetone, chloroform, and 1,3-propanediol (PDO) were all purchased from Sigma-Aldrich (Saint, MO, USA). 1,6-diisocyanatohexane (98%) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Water was purified with a Millipore Mill-Q system (Billerica, USA). ESO was chemo-enzymatically synthesized following a procedure described in our previous study.¹⁵ All other reagents were of analytical grade.

¹H nuclear magnetic resonance (¹H-NMR) analysis was performed on a Bruker Avance II⁺ spectrometer. Chloroform-*d* was used as sample solvents. Chemical shifts were recorded relative to TMS.

IR characterization was conducted with a Fourier transform infrared spectrometer (FTIR, Magna-IR 750, Nicolet) equipped with a horizontal germanium attenuated total reflectance accessory. The spectra were recorded with a resolution of 4 cm⁻¹ in absorbance model.

The hydroxyl number of the synthesized polyol was determined according to the ASTM E-1899-07 standard test method with a titration apparatus (902 Titrando, Metrohm). The acid number of the polyol was determined according to the ASTM D974-02 standard test method.

The viscosity of the polyol was measured with a viscometer (DV-1, Yueping, Shanghai, China). The temperature was

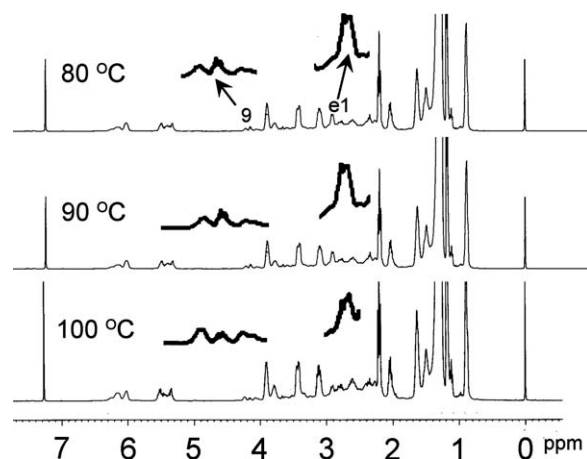


Figure 2. Reaction of epoxidized soybean oil (ESO) with isopropanolamine after 6 h at 80°C, 90°C, and 100°C, respectively.

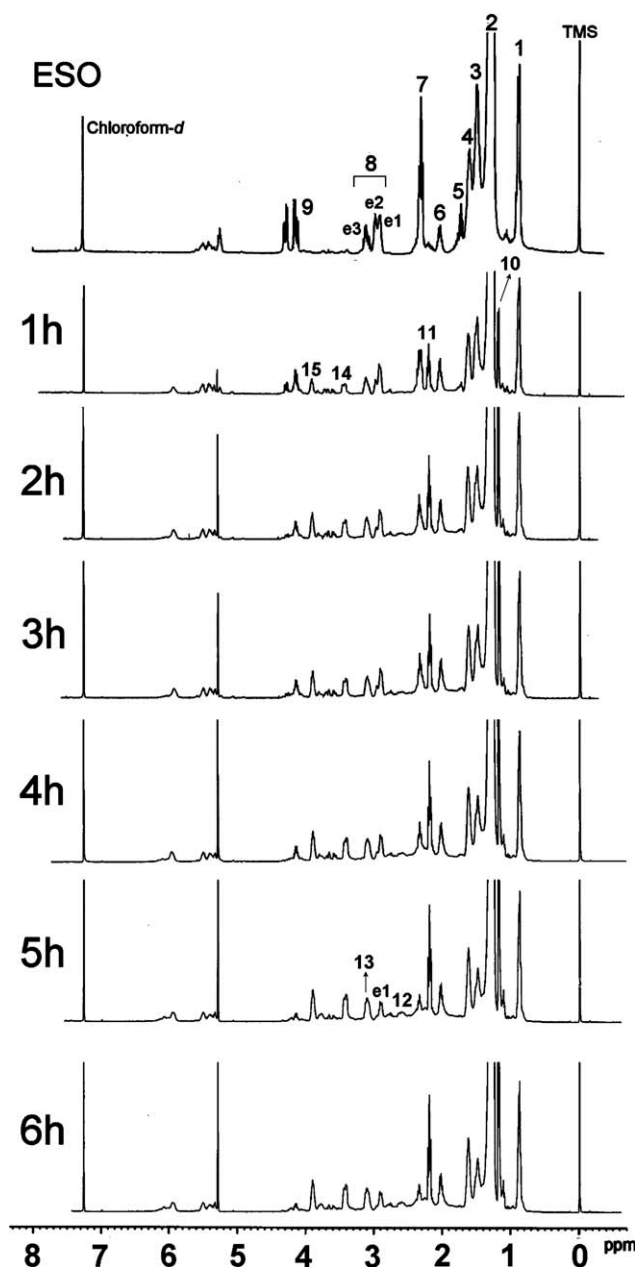


Figure 3. $^1\text{H-NMR}$ spectra of the product from reaction of epoxidized soybean oil (ESO) with isopropanolamine after different reaction time.

maintained at $50 \pm 2^\circ\text{C}$ using a thermostatically controlled tank during the measurements.

The thermal properties of the synthesized polyol and polyurethanes were measured by DSC experiments which were conducted on a TA Instruments Q1000 Differential Scanning Calorimeter at a programmed ramp rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere with a gas flow of $50 \text{ mL}/\text{min}$. The samples were subjected to two heating and cooling cycles between -100 and 150°C . The second heating and cooling cycle was recorded and the DSC curve was used to determine the melting point (T_m) and glass transitions temperature (T_g) by a linear extrapolation method and the midpoint inflection method, respectively.

TGA was performed on a Perkin–Elmer Pyris-7 thermogravimeter in nitrogen with a gas flow rate of $20 \text{ mL}/\text{min}$. The samples were heated from 50 to 650°C at a heating rate of $10^\circ\text{C}/\text{min}$.

The tensile tests were conducted according to ASTM-D638-99 using an Instron universal testing machine (Model-3365) at a cross-head speed of $50 \text{ mm}/\text{min}$. The test specimens were prepared in dumbbell-shape (type IV specimen in ASTM D638-99) with a length of 33 mm for narrow section, a width of 6 mm , and a thickness of 3 mm . For each polymer, at least five identical specimens were prepared and tested. The yield strength, ultimate strength, and elongation at break of the polymers were obtained from the tensile tests and reported as average values.

Reaction of Epoxidized Soybean Oil with Isopropanolamine

ESO 20 g and preset amount of isopropanolamine were charged in a 250-mL flask. The molar ratio of amino group to epoxy group was set as $1.5 : 1$, $2 : 1$, $2.5 : 1$, respectively. The flasks were put into a heating jacket with temperature adjustable in the range of $80\text{--}100^\circ\text{C}$. The reaction was allowed for 6 h under 600 rpm magnetic stirring. Then the reaction mixture was mixed with 100 mL chloroform. To remove the unreacted isopropanolamine, the mixture was wash with 100 mL water for four times. The product dissolved in chloroform was recovered by rotary evaporation. Typically, about 22.4 g waxy product was obtained.

To monitor the reaction process, $30 \mu\text{L}$ reactant mixtures were withdraw at time internal and then mixed with 1 mL chloroform. After washing with 1 mL water for four times, the chloroform was dried-off by rotary evaporation and the product was recovered for NMR characterization. $^1\text{H-NMR}$ [$\text{CDCl}_3/\text{tetramethylsilane (TMS)}$, δ , ppm]: $3.80\text{--}3.9 \text{ (m, } -\text{CH(OH)-, isopropanolamine residue)}$, $3.43 \text{ (m, } -\text{CH(OH)-)}$, 3.11

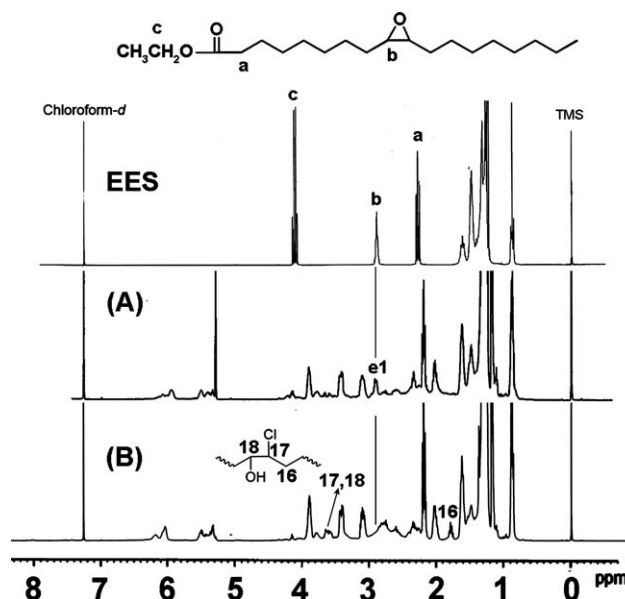


Figure 4. $^1\text{H-NMR}$ spectra of epoxidized ethyl stearate (EES), the polyols before (A) and after (B) treatment with hydrochloric acid.

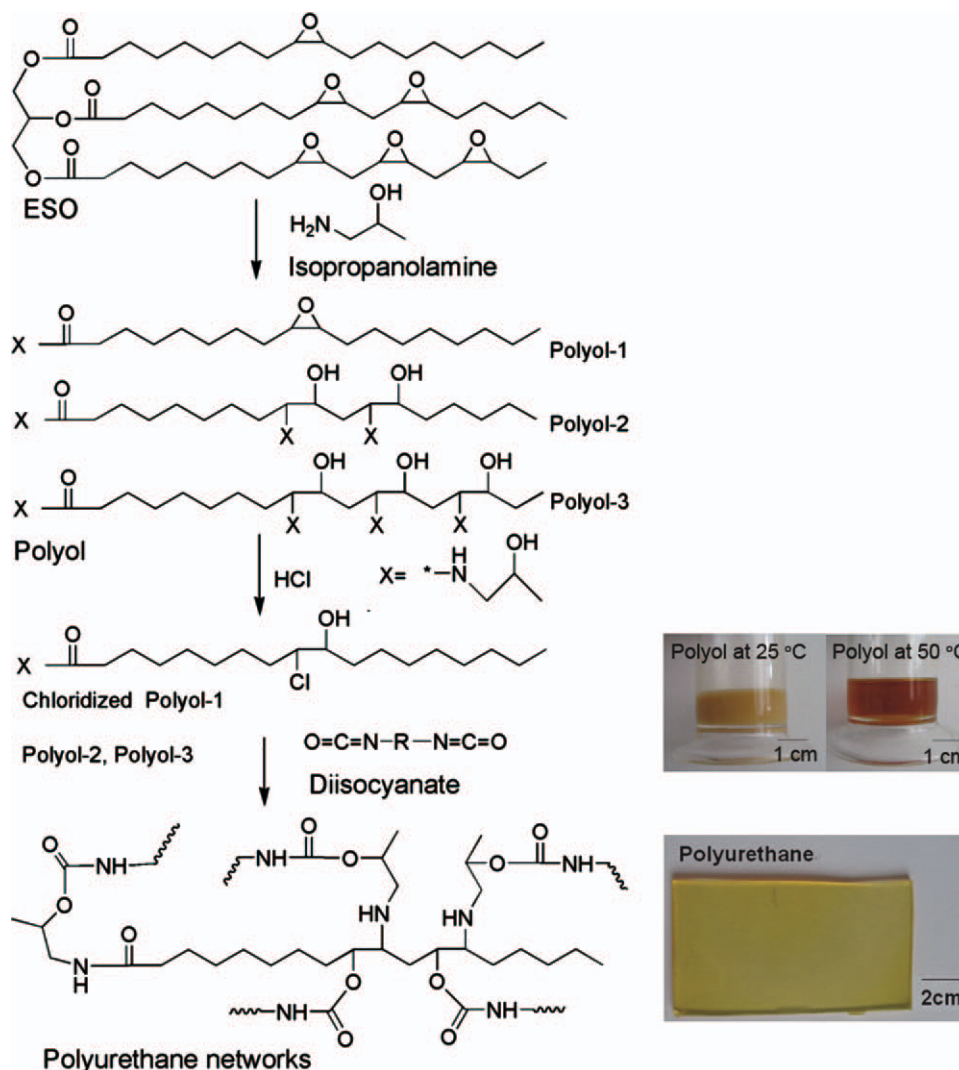


Figure 5. Schematic illustration of the reaction route for preparation of polyurethane networks from epoxidized soybean oil (ESO) and isopropanolamine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(m, $-\text{CH}(\text{NH})-$), 2.20 (t, $-\text{CH}_2\text{COO}-$), 1.20–1.70 (m, $-\text{CH}_2-$ aliphatic backbone), 1.10–1.20 (m, $-\text{CH}_3$, isopropanolamine residue), 0.88 (t, $-\text{CH}_3$).

Opening of Unreacted Epoxide Ring with HCl

Ten gram product from reaction of ESO with isopropanolamine was charged in a 100-mL flask. After adding 30 mL acetone, the flask was put into a 40°C heating jacket with a magnetic stirring of 600 rpm. When the mixture was clear, 60 mL 1 mol/L hydrochloric acid was added. The reaction was allowed for 1 h. Then 10% (w/v) sodium hydroxide solution was dropped to neutralize the reactant mixture to pH value about 7.0. The mixture was then mixed with 100 mL chloroform, followed by washing with 100 mL water for four times. After drying off the chloroform with a rotary evaporator, roughly 7.7 g waxy fatty acid based polyol was obtained. $^1\text{H-NMR}$ [$\text{CDCl}_3/\text{tetramethylsilane (TMS)}$, δ , ppm]: 3.80–3.91 (m, $-\text{CH}(\text{OH})-$, isopropanolamine part), 3.50–3.70 (m, $-\text{CH}(\text{Cl})-$, $-\text{CH}(\text{OH})-$), 3.43 (m, $-\text{CH}(\text{OH})-$), 3.11 (m, $-\text{CH}(\text{NH})-$), 2.20

(t, $-\text{CH}_2\text{COO}-$), 1.81 (m, $-\text{CH}_2-\text{CH}(\text{Cl})-$), 1.20–1.70 (m, $-\text{CH}_2-$ aliphatic backbone), 1.10–1.20 (m, $-\text{CH}_3$, isopropanolamine part), 0.88 (t, $-\text{CH}_3$).

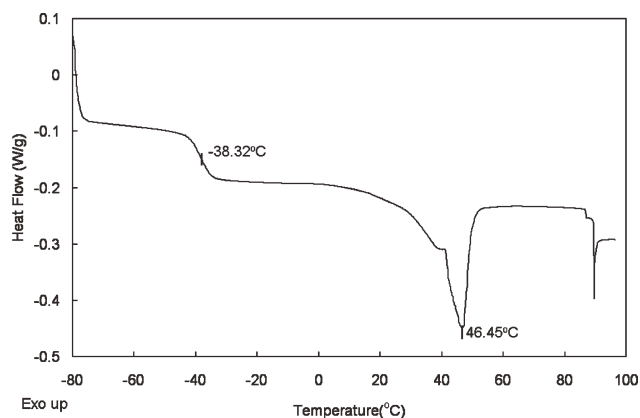


Figure 6. DSC curve of the synthesized polyol.

Table I. Properties of the Synthesized Lipid-Based Polyol

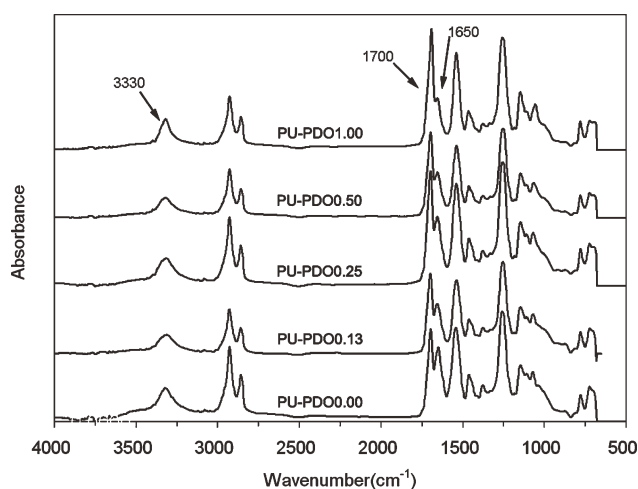
Sample	Properties	Values
Polyol	Hydroxyl number (mg KOH/g)	317.0 ± 0.8^a
	Acid number (mg KOH/g)	1.91 ± 0.02^a
	Melt point ($^{\circ}\text{C}$)	46.45
	Viscosity at 50°C (mPa s)	1222 ± 9^a
	Color	Amber at 25°C

^aAll measurements were conducted at least in triplicate, and the results were expressed as mean \pm SD ($n = 3$).

Preparation of Bio-Based Polyurethanes

A series of lipid-based polyurethanes were prepared by curing the polyol mixture with 1,6-diisocyanatohexane along with different amount of PDO as chain extender. The molar ratio of isocyanate group to hydroxyl group was set as 1.02 : 1 in all the samples, and the molar composition of the samples (mol OH of polyol : mol OH of PDO : mol isocyanate of 1,6-diisocyanatohexane) was set as 1.00 : 0.00 : 1.02, 1.00 : 0.13 : 1.15, 1.00 : 0.25 : 1.28, 1.00 : 0.50 : 1.53, and 1.00 : 1.00 : 2.04, respectively. Accordingly, the sample was coded as PU-PDO0.00, PU-PDO0.13, PU-PDO0.25, PU-PDO0.50, and PU-PDO1.00, respectively.

To avoid the presence of bubbles in polyurethane, 1,6-diisocyanatohexane was added in two portions. Typically, 10 g polyol was put in a 50-mL beaker and then heated to 80°C . Thereafter, 1 g 1,6-diisocyanatohexane was added. After being mixed homogeneously with a glass stick, the polyol, and diisocyanate mixture was kept at 80°C for 3 h before the left portion of 1,6-diisocyanatohexane and definite amount of PDO were added. The mixture was mixed homogeneously again, and was poured into a mold, which was then degassed at minus one atmosphere for 3 min to remove bubbles. Finally, the mold was put into an 80°C oven, and the polymerization reaction was lasted for 48 h. The prepared polyurethane was left for 24 h at room temperature, and was ready for IR, DSC, TGA, and tensile test characterization.

**Figure 7.** IR characterizations of the synthesized bio-based polyurethanes.

RESULTS AND DISCUSSION

Reaction of Epoxidized Soybean Oil with Isopropanolamine

According to our previous study,¹⁵ the enzymatically prepared ESO has average molecular weight of 930 Da and 3.2 epoxy groups per molecule. Figure 1 shows the $^1\text{H-NMR}$ spectra of ESO and the polyol obtained by reacting ESO with isopropanolamine. The molar ratio of amino group to epoxy groups was 1.5 : 1 (A), 2 : 1 (B), and 2.5 : 1 (C), respectively. By comparing the NMR spectrum of ESO with that of polyol, the significant decrease of signal 8 (attributing to H atom in the epoxide rings) and the appearance of signals 13 and 14 confirmed the ring-opening reaction of ESO by the amino group of isopropanolamine. Decrease of signal 7, corresponding to $-\text{CH}_2-$ next to ester group, and the concurrently appearance of signal 11, corresponding to amide group, suggested the cleaving of ester bonds and the formation of amide linkage. As the ratio of amino group to epoxy group increased from 1.5 : 1 to 2.5 : 1, the signals 9 and 7 decreased remarkably, indicating that higher conversion was achieved with higher ratio of amino group to epoxy group.

Figure 2 presents the effect of temperature on the reaction of ESO with isopropanolamine. Both signal 9 and peak e1 (in signal 8) decreased as the temperature increased, indicating that higher conversion was achieved at higher temperature. However, the reaction mixture became darker at higher temperature. Therefore, the reaction was run at 80°C afterward in view of the almost disappearance of signal 9 at this temperature.

The dynamic process of the reaction of ESO with isopropanolamine was monitored with $^1\text{H-NMR}$ (Figure 3). The reaction was carried out at 80°C and the ratio of amino group to epoxy group was 2.5 : 1. Both signals 8 and 9 decreased gradually during the reaction, which confirmed the simultaneously occurrence of ring-opening and amidation reactions between ESO and isopropanolamine. Another indication was that the reactions proceeded very fast in the first 2 h. Roughly 60% of epoxy groups were reacted in 1 h. After 2 and 6 h, the conversion of epoxy groups reached to about 80% and 86%, respectively,

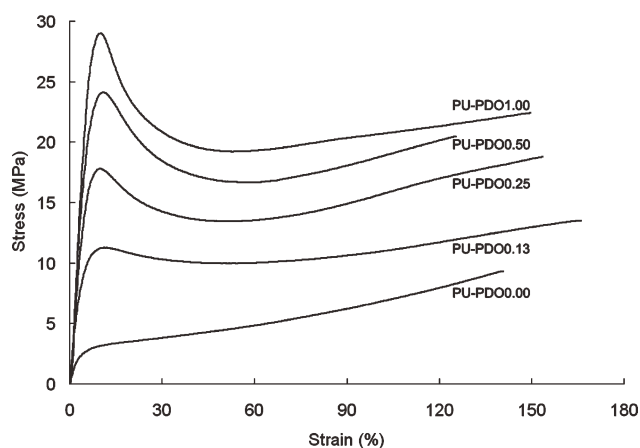
**Figure 8.** Typical stress-strain curves of the synthesized bio-based polyurethanes.

Table II. Properties of the Synthesized Bio-Based Polyurethanes

Sample code	PU-PDO0.00	PU-PDO0.13	PU-PDO0.25	PU-PDO0.50	PU-PDO1.00
Glass transition temperature (T_g , °C)	28.69	24.5	28.10	25.82	24.36
Stress at yield point (MPa) ^a	2.74 ± 0.25	11.96 ± 1.01	18.75 ± 1.34	24.23 ± 0.17	27.76 ± 1.77
Elongation at yield point (%) ^a	5.55 ± 0.28	11.39 ± 0.79	10.42 ± 0.59	11.11 ± 0.39	9.86 ± 0.20
Tensile strength at break (Mpa) ^a	9.3 ± 0.15	12.81 ± 0.97	19.80 ± 1.45	20.44 ± 1.22	22.89 ± 0.70
Elongation at break (%) ^a	140.83 ± 3.9	161.14 ± 7.76	168.61 ± 12.08	116.97 ± 10.31	154.50 ± 9.23
Temperature of 5% weight loss in TGA analysis (°C)	240	253	251	254	255
Color	Yellow	Yellow	Yellow	Yellow	Yellow (blurry)

^aFive specimens were tested and the results were expressed as mean ± SD ($n = 5$).

deduced from peak areas under signal 8. The depletion of ester groups showed a similar pattern, and nearly 93% of ester groups were reacted within 6 h, which implied that ester groups were more reactive than epoxy groups under the reaction conditions. It had to be pointed out that signal 13 and signal 8 (peak e3) were overlapped at 3.1 ppm. During the reaction, decrease of signal 8 (peak e3) was accompanied with increase of signal 13, therefore, the peak area at 3.1 ppm did not change apparently during the process. But the shape of the peak at 3.1 ppm changed apparently in NMR spectra as shown in both Figures 1 and 3, indicating the replacement of peak e3 by signal 13.

Opening of Unreacted Epoxide Ring with HCl

As discussed above, small part of epoxy groups remained unreacted after 6 h. Both Figures 1 and 3 showed that there were three peaks, e1 (2.91 ppm), e2 (2.98 ppm), and e3 (3.10 ppm) in signal 8, attributing to the complex situation of epoxy groups in ESO. After reaction, peaks e2 and e3 almost disappeared while peak e1 was mostly left. NMR spectrum of the polyol obtained after 6 h reaction [Figure 4(A)] was compared with that of ethyl epoxy stearate (EES), indicating that the chemical shift of peak e1 was exactly the same as that of epoxy group in EES (signal b). So, the peak e1 was corresponding to the epoxy group, which was located in the fatty acid chain having only one derivative epoxy group. Peaks e2 and e3 in Figures 1 and 3 were corresponding to a situation that the fatty acid chains had more than one epoxy groups.¹⁸

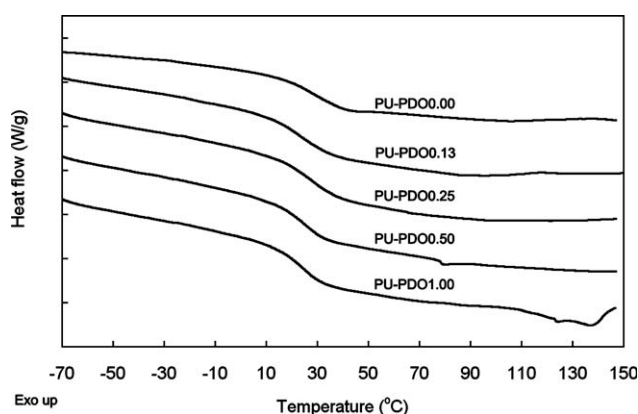


Figure 9. DSC curves of the synthesized bio-based polyurethanes.

To generate more hydroxyls, hydrochloric acid was used to open the left epoxy groups. As shown in Figure 4(B), peak e1 disappeared after hydrochloric acid treatment, indicating that epoxy rings were opened by hydrolytic acid. Appearance of signal 16, corresponding to $-\text{CH}_2-$ next to $-\text{CHCl}-$, further confirmed this ring-opening reaction. Based on the above results, it could be concluded that epoxy groups in ESO showed different reactivity toward isopropanolamine. To open the left epoxy groups, which exhibited lower reactivity, more rigorous ring-opening reagent such as hydrochloric acid was needed. The whole synthetic route for preparation of the polyol was schematically illustrated in Figure 5.

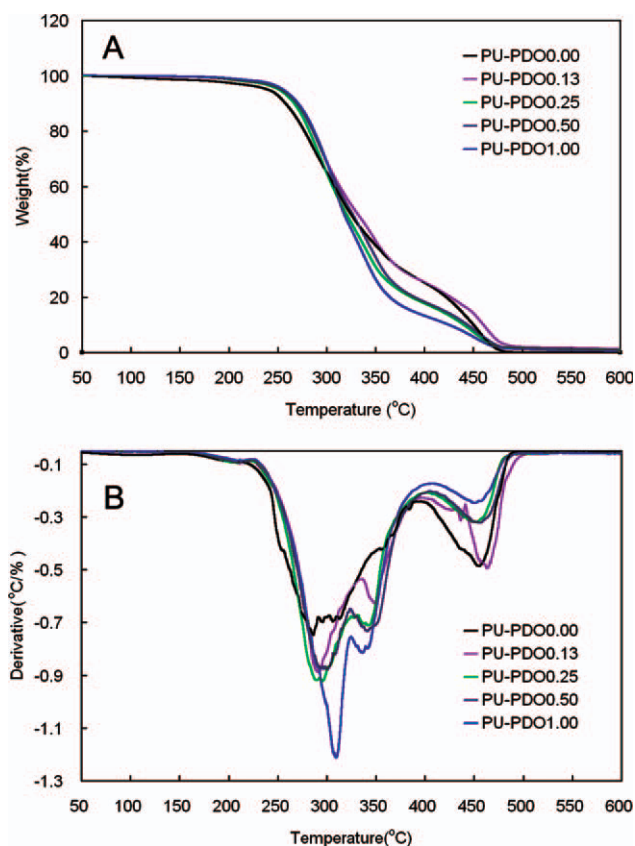


Figure 10. TGA plots (A) and the derivative curves (B) of the synthesized bio-based polyurethanes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The synthesized polyol mixture was waxy at room temperature and the DSC curve showed that the polyol mixture had a melting point at 46.45°C and a glass transition temperature at 38.32°C (Figure 6). Other properties of the polyol mixture including hydroxyl number, acid number, and viscosity were summarized in Table I. It can be seen that the synthesized polyol had quite high hydroxyl number of 317.0 mg KOH/g. In general, the commercial petroleum-based polyols suitable for producing rigid polyurethanes have a hydroxyl number in the range of 300–650 mg KOH/g.¹⁷ Therefore, the synthesized polyol has the potential to produce rigid lipid-based polyurethanes. The acidity of the polyol was 1.91 mg KOH/g, which might be attributed to the formation of carboxylic acids during the preparation process.¹⁰ Usually, an acid number below 10 mg KOH/g was considered low enough for commercial grade polyols.¹⁹

Preparation of Bio-Based Polyurethanes

The polyol mixture was then applied to prepare polyurethanes by curing with 1,6-diisocyanatohexane along with different amount of PDO as chain extender. Figure 7 presents the IR spectra of the bio-based polyurethanes. The peak at 3,330 cm⁻¹ was corresponding to stretching vibration of N—H in —NH—COO—, which indicated the formation of polyurethane.²⁰ The peak at 1,700 cm⁻¹ was corresponding to stretching vibration of C=O in —NH—COO—, which further confirmed the formation of polyurethane. The peak at 1,650 cm⁻¹ was corresponding to stretching vibration of C=O in —CO—NH—, which indicated the presence of amide group formed in the reaction of ESO with isopropanolamine. When PDO content increased in the sample, the peak at 1,650 cm⁻¹ decreased and the peak at 1,700 cm⁻¹ increased because the concentration of amide group decreased in the sample, while the concentration of urethane group increased.

Figure 8 shows the typical stress–strain curves of the bio-based polyurethanes, and the mechanical properties of the polyurethanes were summarized in Table II. With the addition of PDO, well-defined yield points on stress–strain curves of the polyurethanes were observed, and the yield strength increased with increasing PDO content. The yield strength of sample PU-PDO0.50 was 24.2 MPa that was eight times higher than that of sample PU-PDO0.00. Sample PU-PDO1.00 showed yield strength of 27.8 MPa, but this sample was blurry due to phase separation resulted from the high PDO content. The tensile strength was also increased with the increase of PDO content, and sample PU-PDO0.50 showed a tensile strength of 20.4 MPa which was two times higher than that of PU-PDO0.00. So, the polyurethane mechanical properties could be easily improved by addition of PDO.

Figure 9 shows the DSC curves of the prepared polyurethanes. The glass transition temperature, T_g , was in the range of 24.36–28.69°C, not apparently affected by the addition of PDO. Only one T_g was observed for the samples PU-PDO0.00, 0.13, 0.25, which indicated that the components were compatible and the polyurethanes were amorphous. For sample PU-PDO0.50, a weak melt point was observed at 80.16°C, which implied the existence of phase separation in the sample though the sample was still transparent. For sample PU-PDO1.00, a melt point was

clearly observed around 140°C, and the sample was opaque due to the phase separation.

The thermal stability of the bio-based polyurethanes was determined by TGA analysis and the results were shown in Figure 10. Polyurethane without addition of PDO (sample PU-PDO0.00) started to decompose at 240°C (temperature of 5% weight loss) due to the weak urethane bonds. The temperature of 5% weight loss for other samples was higher than 250°C, which might be attributed to the addition of PDO. The first fast decomposition of the samples happened in the range of 280–360°C. The second fast decomposition occurred at around 460°C, due to gasification of any remaining components. The samples were completely decomposed at 500°C (the yield was only 0.1~1.2%). The low yield was mostly due to usage of 1,6-diisocyanatohexane which did not contain benzene ring structure. Low yield was also observed when L-lysine diisocyanate was used as coupling agent,²¹ while higher yield was observed when 4,4'-methylenediphenyl isocyanate was applied.²² Other basic properties of the synthesized polyurethanes were all summarized in Table II. Lipid-based polyurethanes have been investigated to be used as thermal insulation materials¹⁷ and candidate biomaterials.²¹ In view of the bio-based property of ESO and qualified application of 1,6-diisocyanatohexane in synthesis of bioelastomers,²³ the obtained polyurethanes in this study would have a wide range of potential applications.

CONCLUSIONS

ESO and isopropanolamine are desired feedstock for production of bio-based polyurethanes. Both ester groups and epoxy groups in ESO were reacted with amino group to generate hydroxyls, and the hydroxyl value of the polyol was about 317 mg KOH/g. The polyol mixture was reacted efficiently with 1,6-diisocyanatohexane to form bio-based polyurethanes. The yield strengths of the polyurethanes were adjustable in the range of 2.74–27.76 MPa by adding different amount of PDO. One glass transition temperature at 24.4–28.7°C was detected for the polyurethanes, and phase separation was observed only when the content of PDO was high. The polyurethanes were stable at 240°C in a nitrogen atmosphere. Because of the high performance and mild preparation process, the lipid-based polyurethanes prepared in this work may have wide range of applications.

ACKNOWLEDGMENTS

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