A Novel Vegetable Oil–Lactate Hybrid Monomer for Synthesis of High-T_g Polyurethanes

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INTRODUCTION Plant oils are attractive renewable alternatives to petroleum for production of both materials and fuels.[1–7] In recent years, a variety of polymeric materials have been developed and tested with plant oils as feedstocks. Among other products, plant oil-based polyurethanes (PUs) are the most extensively studied attributing to their simple preparation yet greatly promising applications.[8–10] However, the plant oil-based PUs reported hitherto possess glass transition temperature (T_g) generally below 40 °C.[8,10] That will limit the stiffness of the materials under warm conditions. Ideally, PUs with tunable T_g in a much broader temperature range can significantly enhance the potential of such materials for general-purpose applications.

Plant oil-based PUs have been generally prepared by first converting the plant oils into polyols, followed by curing with diisocyanate reagents.[8–10] The preparation of polyols from plant oils can be realized through several approaches. It was reported that plant oils including trilinolein (or triolein), low-saturation canola oil, and soybean oil could be ozonolyzed in methylene chloride or methanol and were then hydrogenated sequentially to form polyols.[8] Similarly, canola oil was ozonolyzed in water to produce ozonide that was then reduced to polyol in tetrahydrofuran.[9] The functionality, in terms of the number of hydroxyl groups contained in each polyol monomer molecule, was often less than 3.0 for polyols prepared through this approach. Alternatively, plant oils have been alcoholyzed with glycerol to produce monoglycerides, with each of which contains two hydroxyl groups at the glycerol end.[2,11] Such polyols would generate PUs with the long fatty acid moiety as the pendant group. Another widely adopted approach is to oxidize the fatty acid chains to form epoxide rings and produce polyols with various ring-opening reagents. For example, halogenated and nonhalogenated soybean oil-based polyols have been reported by treating epoxidized soybean oil (ESO) with hydrochloric acid, hydrobromic acid, methanol, or hydrogen.[10,12,13] Epoxide rings in epoxidized plant oils could also be partially opened by water in the presence of glacial acetic acid by heating to ~75 °C.[14,15] Such polyols prepared by ring-opening reaction possess hydroxyl groups mostly located in the middle of the fatty acid chains, and partial fatty acid chains, the portion of fatty acids between hydroxyl group and the chain end, form the pendant groups.[10]

Plant oil-based PUs were always amorphous because of random crosslinking structure and displayed low glass transition temperatures.[8,10] The T_gs reported so far were generally <40 °C, attributing mainly to both the low functionality of the polyols and the presence of pendant groups. Generally, higher functionality would lead to higher T_g because of the formation of more crosslinked structures. For example, polyols with functionalities in the range of 3.0–5.2, prepared via ring opening of several epoxidized plant oils, were used to generate PUs by polymerization with 4,4′-methylenebis(phenyl isocyanate) (MDI).[10] It was shown that the T_g increased with increasing of the functionality of the polyols, with the linseed oil-based polyols possessing the highest functionality 5.2 giving a T_g as high as 77 °C.[10] However, general plant oil-based PUs only showed low T_gs around 30 °C, such as soybean oil-based PU showing a T_g of 31 °C.[10] It was suspected that the pendant groups in the PUs acted as plasticizer, leading to the low T_g of the final material. Ozonolysis method could reduce the content of pendant fatty acid chains and produce polyols mainly with terminal primary hydroxyl groups.[8] However, the functionality of the polyols was not more than 3.0, and soybean oil-based PU prepared by this method gave a low T_g of only 22 °C.[8] The

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low T_gs make plant oil-based PUs mostly in a leathery state (transient from glassy to rubbery) at room temperature and ideal for use as soft materials, resulting, however, in somewhat low strength and moduli,[10] which limit their use as general stiff plastic materials.

We have developed a new class of oleic acid-based PUs through an epoxy ring-opening reaction by carboxylic group, generating PUs that have short pendant fatty acid groups.[16] This work seeks to broaden the physical properties of plant oil-based PUs by introducing a biorenewable hybrid monomer, thus increasing the functionality of the monomer. In particular, we investigated the conjugation of ESO, which was prepared by epoxidation of soybean oil using lipase as catalyst, with lactic acid (LA) via ring-opening reaction. We expect that through such a synthetic strategy, a new class of partially biorenewable PUs with controllable T_g in a broad temperature range can be produced.

EXPERIMENTAL

Materials and Instrumental Analysis

Soybean oil, oleic acid, ESO, ethanol, Chloroform-*d* (containing 0.03% TMS), 4,4′-methylenebis(phenyl isocyanate), and lipase from *Candida Antarctica* immobilized on an acrylic resin (Novozym 435) were purchased from Sigma–Aldrich (MO). Hydrogen peroxide (H_2O_2, 35% w/w in water solution) was obtained from Fluka (MO). Lactic acid (LA) with purity >98% was purchased from MP Biomedicals (OH). Water was purified with a Mill-Q system from Millipore (Billerica). All other reagents were of analytical grade.

^1H Nuclear Magnetic Resonance (^1H NMR) analysis was performed on a VAC 300 spectrometer, an upgraded IBM instrument with a VXR-300 of Unity (Varian, CA, USA) with chloroform-*d* containing 0.03% tetramethylsilane (TMS) as the solvent. Electrospray ionization mass spectrometry (ESI-MS) was performed in positive-ion model on a LTQ XL Linear Ion Trap Mass Spectrometer (Thermo Fisher Scientific, MA). A Fourier transform infrared (FTIR) spectrometer (Nicolet Series II Magna-IR System 750, Nicolet Instrument, WI) equipped with a horizontal germanium attenuated total reflectance accessory was used to monitor preparation of PU materials starting from soybean oil and LA. Differential scanning calorimetry (DSC) experiments were conducted on a TA Instruments Q1000 Differential Scanning Calorimeter (DE, USA) at a programmed ramp rate of 10 °C/min and with a temperature range from −100 to 200 °C. Thermogravimetric Analysis (TGA) spectra were recorded on a Perkin-Elmer Pyris Diamond Thermal Analyzer (MA, USA). The change in weight loss of the samples was measured by heating in nitrogen atmosphere (20 mL/min) at a programmed ramp rate 10 °C/min from 50 to 580 °C.

Preparation of ESO

Epoxidation of soybean oil was conducted following a modified procedure as previously reported.[17–19] Typically, 1000 mg of soybean oil, 100 μg of oleic acid, 100 mg of Novozym 435, and 5 mL of toluene were mixed in a 20-mL capped glass vial that was then placed in a shaker with a rotating speed of 300 rpm and maintained at 40 °C. Epoxidation reaction was initiated by adding 700 μL of H_2O_2 (35 wt %, out of bottle) to the above mixture and was allowed to continue for 48 h. Lipase was then removed from the reaction solution by filtration, and the clear filtrate was rinsed with water for at least three times to remove any residual H_2O_2. The ESO product was recovered by drying, and generally 1050 mg was obtained. According to NMR results, there were 4.3 double bonds per soybean oil molecule and 3.2 epoxy groups per ESO molecule, respectively. Thus, the conversion rate of double bonds was 74.4%.

^1H NMR [$CDCl_3$/tetramethylsilane (TMS), δ, ppm] of ESO: 5.25 (m, —*CH*(OH)—), 4.29 (q, —CH_2—, glycerol), 4.16 (q, —CH_2—, glycerol), 2.80–3.20 (m, —CH_2OCH_2—), 2.30 (t, —CH_2COO—), 1.20–1.80 (m, —CH_2— aliphatic backbone), 0.90 (t, —CH_3).

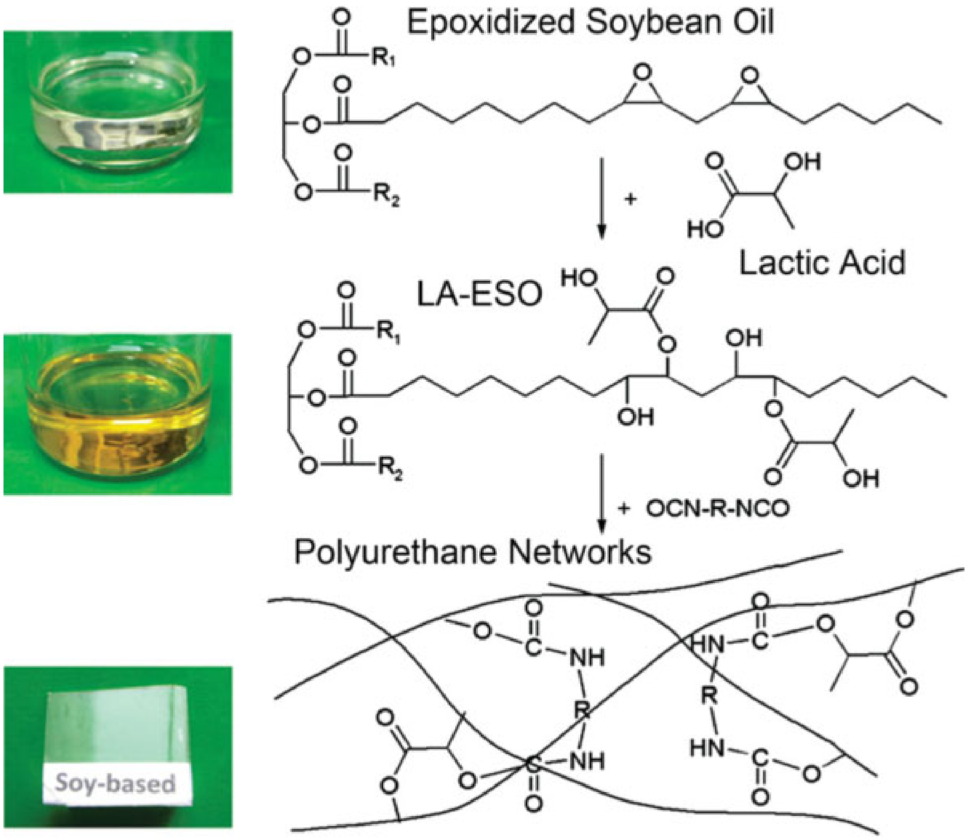
Preparation of Polyol LA-ESO from ESO and LA

Typically, 1000 mg of ESO and 600 mg of LA were charged in a reactor that contained a stirrer bar. The reactor was purged with nitrogen for roughly 15 min to remove the air and then was sealed. Put the reactor on a 90 °C hot plate with a magnetic stirring at 300 rpm. The reaction was allowed to continue for 6 h. The final reaction mixture was washed with water to remove unreacted chemicals till the pH value of the washing solution turns to 7.0, and the desired product lactic acid-epoxidized soybean oil (LA-ESO) was recovered by evaporating the water off under reduced pressure. Generally, 1190 mg of product was obtained. Around 2.1 epoxy groups per ESO molecule were opened by LA, and the conversion rate of epoxy group was ~70%.

^1H NMR [$CDCl_3$/tetramethylsilane (TMS), δ, ppm] of LA-ESO: 5.25 (m, —CH(OH)—, in glycerol), 4.90 (m, —COO—*CH*(—CH_2—)—), 4.30 (m, CH_3—*CH*(OH)—COO—), 4.29 (q, —CH_2—, in glycerol), 4.16 (q, —CH_2—, in glycerol), 3.60 (m, —*CH*(OH)—, in aliphatic backbone), 3.10–3.85 (m, polyether backbone), 2.30 (t, —CH_2COO—), 1.20–1.80 (m, —CH_2— aliphatic backbone), 0.90 (t, —CH_3).

Preparation of Ethyl Epoxy Stearate

Ethyl epoxy stearate (EES) was synthesized from oleic acid through sequential epoxidation and esterification reactions. The epoxidation reaction of oleic acid was first conducted with hydrogen peroxide with lipase as the catalyst following a modified procedure as reported previously,[20] and the esterification reaction between the oleic acid epoxide and ethanol was subsequently performed. Typically, 1500 mg of oleic acid and 10 mL of toluene were mixed in a 20-mL capped glass vial under stirring at 40 °C for 10 min before the addition of 150 mg lipase (Novozym 435). The mixture was stirred for additional 10 min, and the epoxidation reaction was initiated by the addition of 600 μL of H_2O_2 (35 wt %, out of bottle) to the reaction mixture. The reaction was allowed to continue for 10 h. The epoxy stearic acid product was recovered from the reaction solution by the same procedure as that applied for ESO. Generally, 1550 mg of product was obtained. Nearly, all the double bonds of oleic acid were converted into epoxy groups according to NMR result.



SCHEME 1 Reaction route for preparation of polyurethane materials from soybean oil and lactic acid.

^{1}H NMR [$CDCl_3$/tetramethylsilane (TMS), δ, ppm] of epoxy stearic acid: 2.94 (m, $-CH_2OCH_2-$), 2.36 (t, $-CH_2COO-$), 1.20–1.80 (m, $-CH_2-$ aliphatic backbone), 0.90 (t, $-CH_3$).

EES was then produced by esterification of epoxy stearic acid with ethanol. One gram of epoxy stearic acid was mixed with 10 mL of ethanol in a 20-mL capped glass vial that was placed in a shaker with a rotating speed of 300 rpm at 40 °C. Esterification was initiated by adding 100 mg of Novozym 435 to the mixture, and the reaction was continued for 24 h. Clear EES was recovered by removing the enzyme through filtration, followed by evaporation to remove unreacted ethanol. Generally, 1070 mg of product was obtained. Nearly, all the epoxy stearic acid was converted into EES according to NMR result.

^{1}H NMR [$CDCl_3$/tetramethylsilane (TMS), δ, ppm] of ethyl epoxy stearate: 4.12 (q, $-COOCH_2-$), 2.91 (m, $-CH_2OCH_2-$), 2.30 (t, $-CH_2COO-$), 1.20–1.80 (m, $-CH_2-$ aliphatic backbone), 0.90 (t, $-CH_3$).

Ring-Opening Reaction between EES and LA

Typically, 200 mg of EES and 68 mg of LA were applied, following the same procedure as described for the reaction between ESO and LA, except that the reaction only continue for 3 h.

^{1}H NMR [$CDCl_3$/tetramethylsilane (TMS), δ, ppm] of the product: 4.90 (m, $-COO-\mathit{CH}(-CH_2-)-$), 4.30 (m, $CH_3-\mathit{CH}(OH)-COO-$), 4.12 (q, $-COOCH_2-$), 3.60 (m, $-\mathit{CH}(OH)-$), 3.10–3.85 (m, polyether backbone), 2.30 (t, $-CH_2COO-$), 1.20–1.80 (m, $-CH_2-$ aliphatic backbone), 0.90 (t, $-CH_3$).

Preparation of PU Materials

The PU materials were prepared by mixing LA-ESO with 4,4′-methylenebis(phenyl isocyanate) (MDI) at 70 °C. Typically, 100 mg of LA-ESO was mixed with MDI with an amount ranged from 10 to 90 mg, and the mixture was then applied on clean glass plates that were maintained at 70 °C. The glass plates were then moved into an 80 °C oven for a 20 h curing process. The synthesized PU materials were peeled off from the glass plates for characterization tests.

RESULTS AND DISCUSSION

Preparation of LA-ESO Polyol

As shown in Scheme 1, we expect that the addition of lactate to the fatty acid chains of lipids will not only increase the amount of hydroxyl group of each lipid monomer (functionality) but also allow the hydroxyl groups being more flexible and reactive by stemming out from the main chain of lipids through the pendant lactate. Increasing the functionality and reactivity will afford higher degree of crosslinking in the final PU products and, thus, increase their T_g. Accordingly, we first epoxidized lipids via a lipase-catalyzed oxidation reaction, and the epoxidized lipids were then reacted with LA to generate a polyol monomer, LA-ESO that was

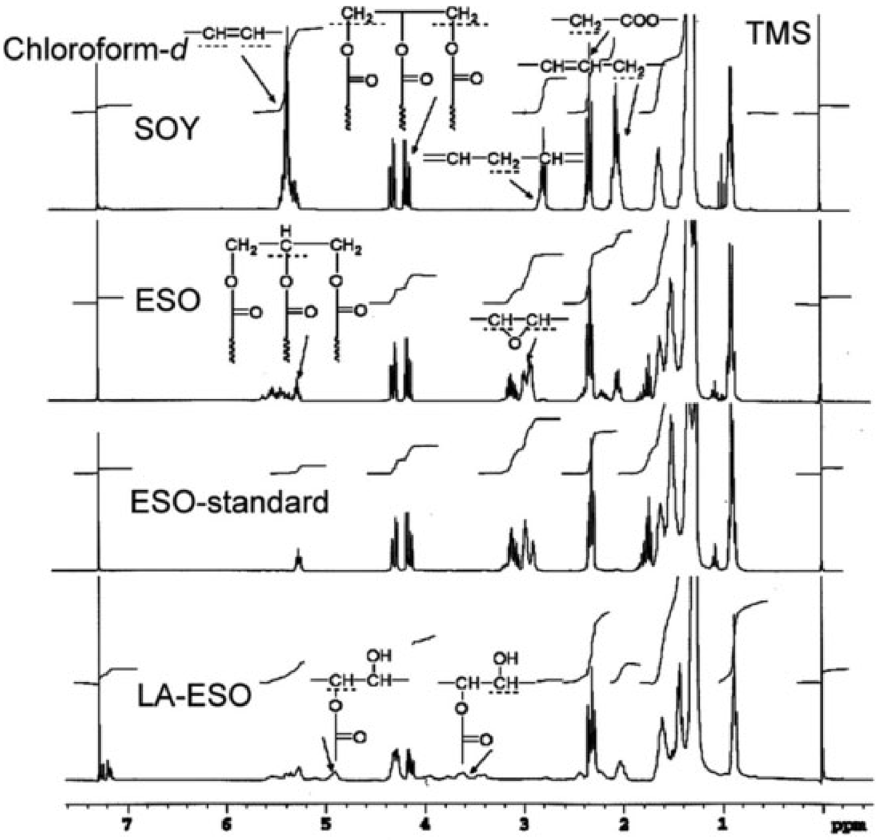


FIGURE 1 ^{1}H NMR spectra of soybean oil (SOY), epoxidized soybean oil (ESO), commercially available ESO (ESO-Standard), and LA-ESO polyol.

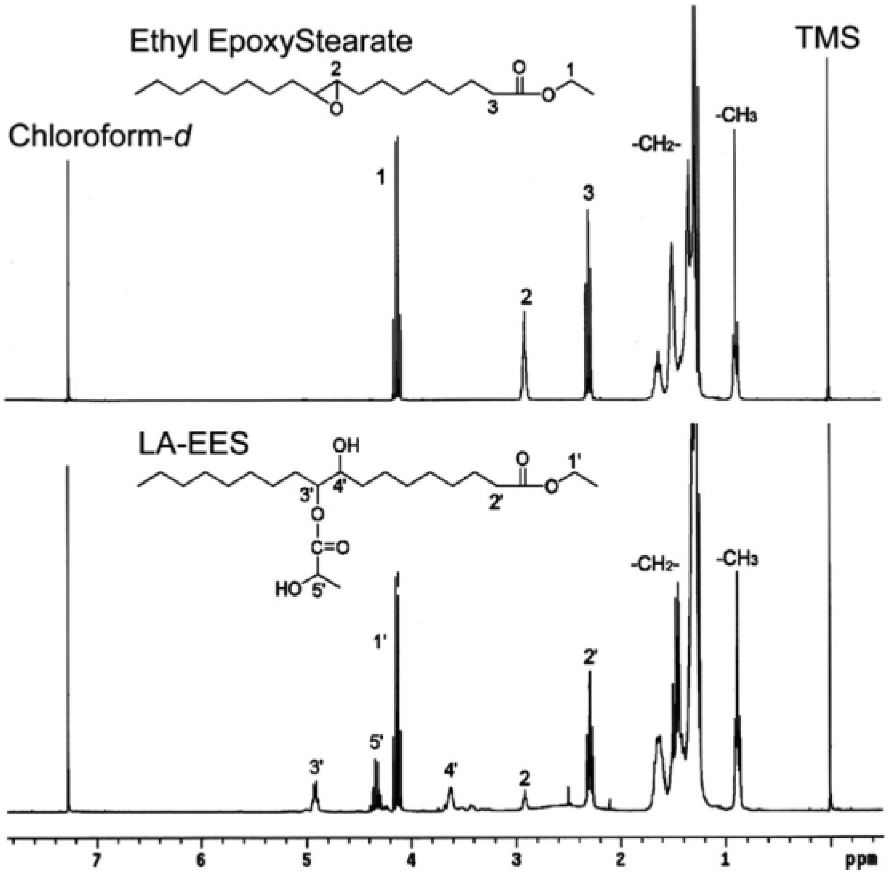


FIGURE 2 ^{1}H NMR spectra of ethyl epoxy stearate, and its ester product after reacting with lactic acid (LA-EES)

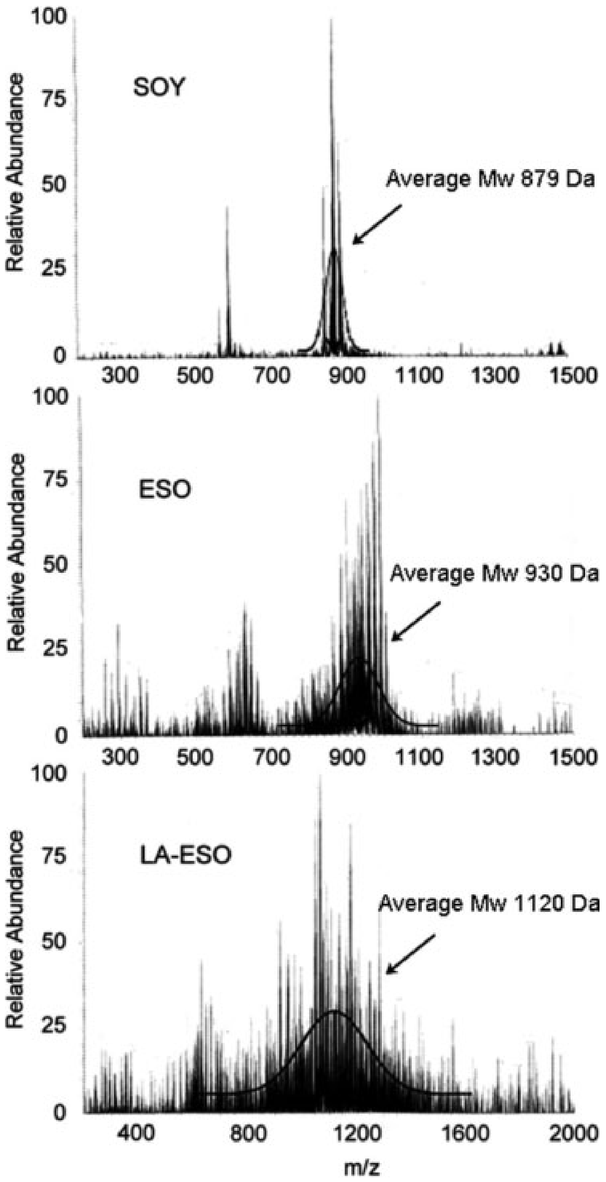


FIGURE 3 ESI-MS analysis of soybean oil (SOY), epoxidized soybean oil (ESO), and and LA-ESO polyol.

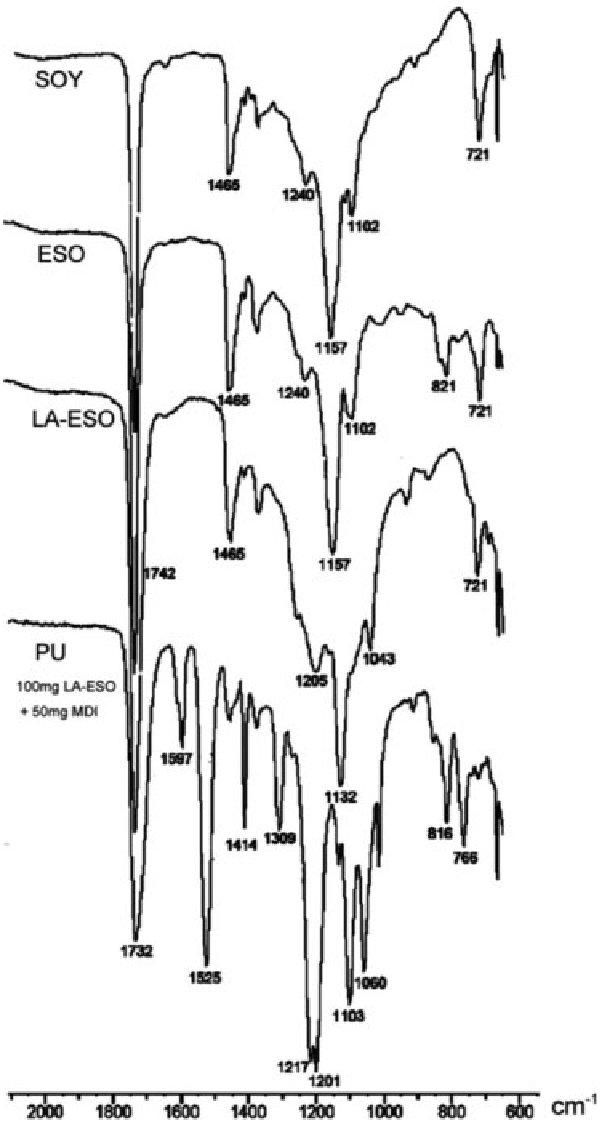


FIGURE 4 IR spectra of reaction intermediates and products (SOY: soybean oil; ESO: epoxidized soybean oil; PU: polyurethane networks)

subsequently reacted with 4,4′-methylenebis(phenyl isocyanate) (MDI) to form PUs (Scheme 1).

Figure 1 shows the ^{1}H NMR spectra of the chemicals involved in the preparation procedure. The formation of epoxide rings on the fatty acid chains of soybean oil was evident from the peaks shown at 2.8–3.2 ppm in the ^{1}H NMR spectrum of the epoxidized soybean oil (ESO in Fig. 1) when compared with that of its parent soybean oil (SOY). The NMR spectrum of our ESO product is the same as that observed for a commercially available ESO standard. For the same consideration, the disappearance of those peaks in the LA-ESO spectrum should be a confirmation of the ring-opening reaction between ESO and LA. Furthermore, the occurrence of the peaks at 4.9 and 3.6 ppm in the LA-ESO spectrum also indicated that formation of new ester and

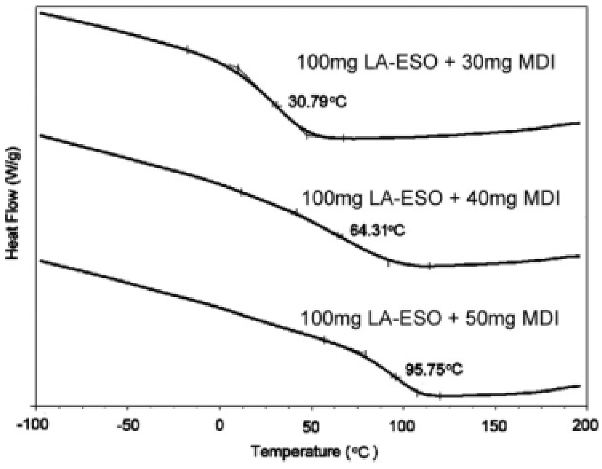
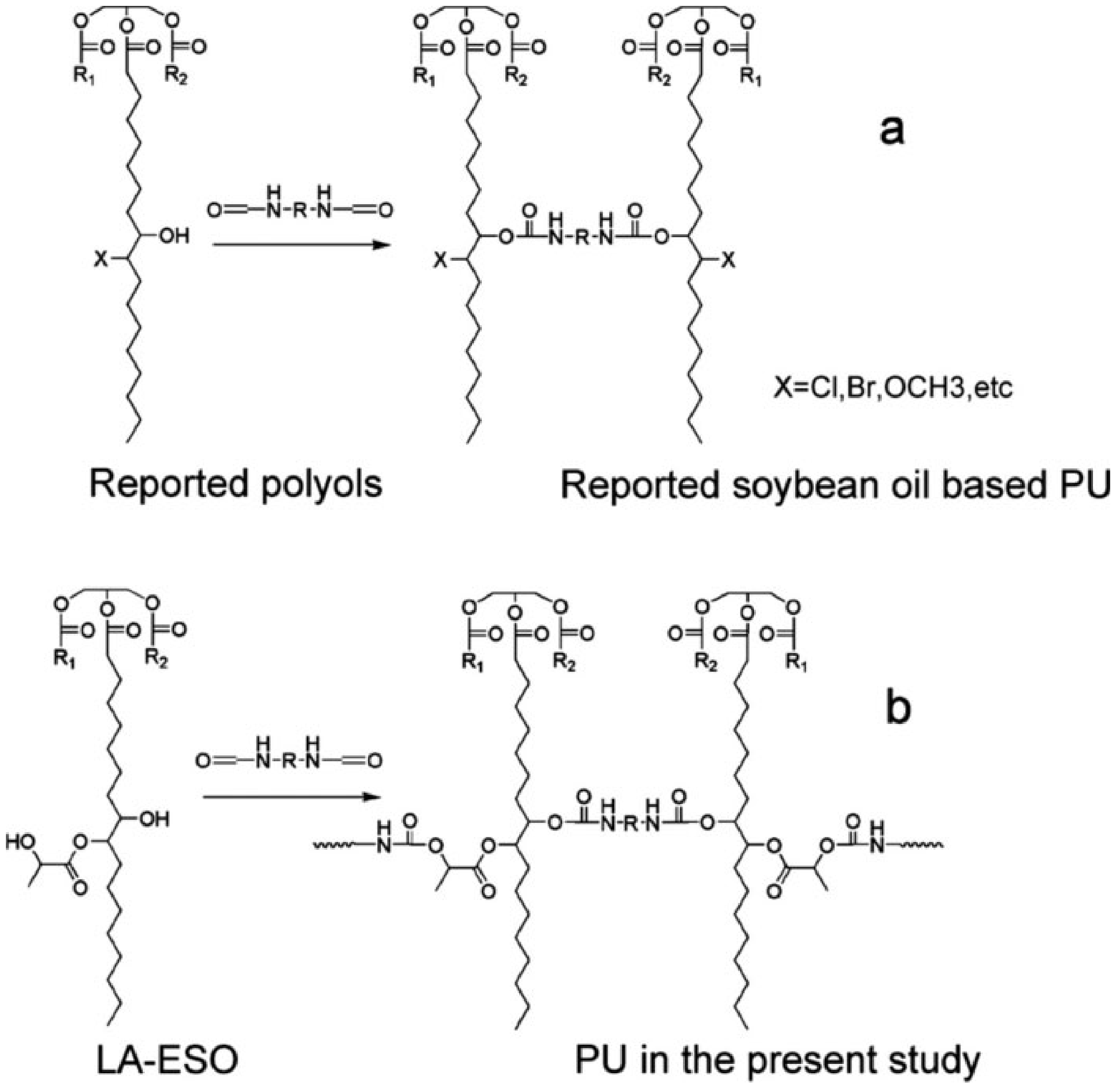


FIGURE 5 DSC analysis of LA-ESO polyurethane.



SCHEME 2 Crosslinking structures of plant oil based polyurethane networks. (a) Noncontinuous crosslinking in previously reported work and (b) Continuous crosslinking achieved through the introduction of lactic acid in this work.

hydroxyl groups as a result of the LA enabled ring-opening reaction.

We further demonstrated that such a synthetic approach was generally applicable to any unsaturated lipids. Following the same procedure, EES was prepared and applied for ring-opening reaction with LA. Figure 2 shows the ^{1}H NMR spectra of EES, and its ester product after reacting with LA. The peak at 3.2 ppm of EES (H of epoxide ring, Peak 2 in Fig. 2) almost disappeared after the ring opening reaction. Similar observations were reported previously for ring-opening reaction of epoxides by carboxylic groups in an oligomerization reaction of epoxy stearic acid.[16] Similar to the reaction with ESO, the occurrence of the peaks at 4.9 and 3.6 ppm further confirmed that, as expected, LA had opened the epoxy ring efficiently to form ester bonds and hydroxyl groups.

The molecular weights of the products generated from ESO and LA were determined by ESI-MS, and the results are presented in Figure 3. The spectrum of soybean oil applied in this work showed one major group of peaks around 879 *m/z* and one minor group at 600 *m/z*, indicating the presence of small amount of diglycerides in the soybean oil.[12] Corresponding to the major peaks of triglycerides, ESO showed a major group of peaks with average M_w of 930, indicating the addition of 3.2 oxygen atoms on average to each triglyceride molecule. That is a moderate yield of epoxidation reaction considering each triglyceride molecule of soybean oil contains 4 to 5 C=C double bonds. As can be seen in Figure 1, the peak at 2.0 ppm corresponding to unsaturated double bonds still presented in the spectrum of LA-ESO polyol product, supporting the retention of C=C double bonds in the product. The LA-ESO product showed an average M_w at 1120, indicating the addition of 2.1 LA groups on average to each epoxidized triglyceride molecule, in other words, a yield of nearly 70% of the ring-opening by LA. That may be a result of other side reactions such as epoxy homopolymerization that the epoxy rings may undergo.[12,16] Accordingly, the LA-ESO hydroxyl content was 4.2 hydroxyl groups per triglyceride molecule, a functionality of 4.2, as the addition of each LA molecule would lead to the formation of 2 hydroxyl groups on the fatty acid chain (Scheme 1).

Preparation of PU Materials Based on LA-ESO

PU materials were then prepared by reacting the LA-ESO polyol with MDI. Typically, 100 mg of LA-ESO was mixed well with 10–90 mg of MDI and the molar ratio of isocyanate group to hydroxyl group (NCO/OH) was controlled in the range of 0.21:1–1.89:1. When MDI was less than 30 mg (NCO/OH $<$ 0.63:1), LA-ESO was not efficiently crosslinked and remained in a liquid state. When NCO/OH $>$ 1:1, the PU product became rigid and adhered to the glass plates. The synthesis process was monitored by using IR (Fig. 4). The appearance of peak at 821 cm^{-1} in the IR spectrum of ESO confirmed the epoxidation of soybean oil, additional evidence to the NMR analysis in Figure 1; the disappearance of this peak in LA-ESO product indicated the complete consumption of epoxy groups, also agreeing with the NMR analysis in Figure 1. The appearance of peaks at 1309 and 1525 cm^{-1} in the PU product confirmed the formation of urethane bonds (the two peaks were due to the asymmetric stretching vibrations and *N*—H deformation of the —OCONH— bond, respectively).[21] The IR spectrum of PU also showed several interesting characteristics different from other types of PUs. First, there were two peaks presented at 1217 and 1201 cm^{-1} accounting for C—N stretching vibrations, whereas one peak was reported for other types of PU materials.[21,22] Second, the peak of C—O stretching vibrations also accordingly resulted in two peaks (1103 and 1060 cm^{-1}). Such observations were speculated to be the results of the presence of two types of hydroxyl groups available in the LA-ESO polyols, that is, the hydroxyl groups generated on the fatty acid chains by ring-opening reaction and the pendant hydroxyl groups on the LA moiety.

The T_g of the PU products showed an interesting dependence on the content of LA-ESO (Fig. 5). As the NCO/OH ratio changed from 0.63, 0.84 to 1.05:1, the T_g of PU increased from 31, 64 to 96 °C correspondingly. As mentioned earlier, PU from soybean oil reported previously exhibited much lower T_gs in the range of 31–22 °C.[8,10] The unique structure of the polymer prepared in this work may be accounted for such a difference. First, polyol LA-ESO has a higher functionality (4.2) than the previously reported soybean oil-based polyols (3.5 or 2.5), attributing to the additional hydroxyl groups introduced through LA molecules. Polyols with high functionalities afford PU materials of higher T_g as has been demonstrated previoiusly.[10] Second, the PU prepared in this study may possess a unique urethane bond crosslinking structure different from previously reported materials (Scheme 2). Previously reported synthetic routes generally produced one hydroxyl group to the fatty acid chain through each epoxide group [Scheme 2(a)],[8,10,12] leading to discontinuous urethane bond connection as each fatty acid chain mostly has only one hydroxyl group (as the functionality of the triglyceride was mostly 2.5–3.5). Polymerization in this case can only be realized through the hydroxyl group on a second fatty acid chain of a triglyceride molecule. In the contrast, LA-initiated ring-opening reaction of epoxide group lead to the introduction of two hydroxyl groups to each epoxide group, thus making it possible to have continuous linkage through one single fatty acid moiety of the triglycerides [Scheme 2 (b)]. In addition, the carboxyl group introduced by the addition of LA also increases the possibility of formation of hydrogen bond, further enhancing the rigidity of the materials.

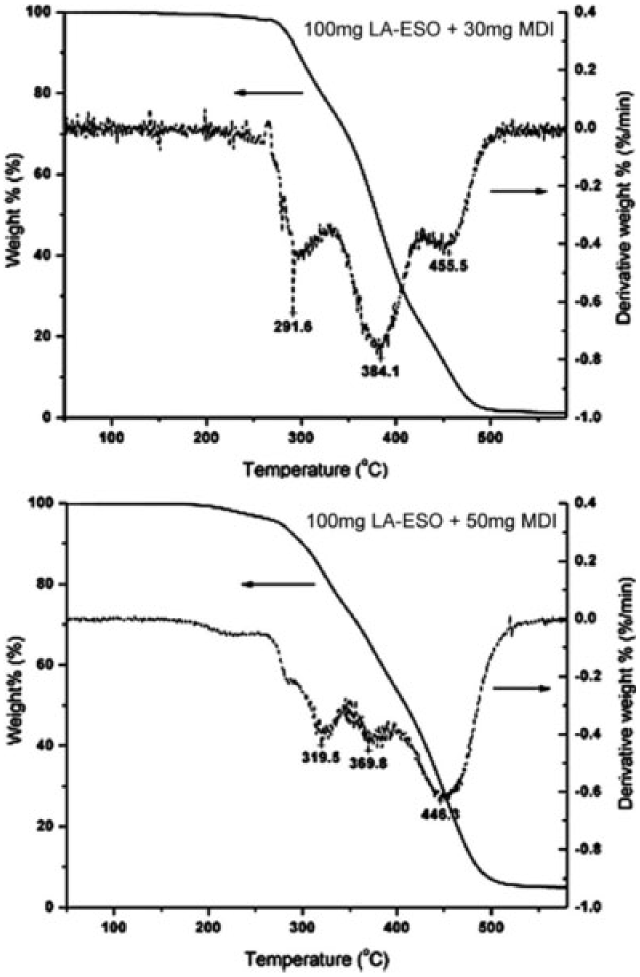


FIGURE 6 TGA chromatograms of LA-ESO-based polyurethanes.

Thermal stability of LA-ESO PU materials was evaluated via TGA analysis as shown in Figure 6. A three-step thermal degradation, evident from the appearance of three peaks on the derivative weight loss curves, was observed in all the tested samples. The first decomposition peak ($T_{\max}$ peak) occurred in the range of 292–320 °C, corresponding to the decomposition of weak urethane bonds. The second $T_{\max}$ peak took place at 370–385 °C, mostly due to decomposition and char formation of crosslinked polymer networks. The third $T_{\max}$ peak was observed at 446–456 °C, which could be related to the gasification of any remaining components. TGA spectra of PUs generally have two decomposition temperature ranges,[23] and the third weight loss peak observed in this work might be related to the second breakdown temperature range of urethane bonds. Similar to T_g, the thermostability of the PU materials also increased as the NCO/OH ratio increased.

CONCLUSIONS

Soybean oil and LA are highly desired renewable feedstocks for preparation of a broad range of polymeric materials including PUs. The LA-ESO polyols prepared through this work introduced two hydroxyl groups per epoxy group, leading to a unique crosslinking structure different from previously reported vegetable oil-based PU. The T_g of the LA-ESO-based PU can be controlled in a broad temperature range, up to 96 °C, in contrast to T_gs $<$ 40 °C as have been reported previously for plant oil-based PUs. The LA-ESO-based PU materials contain both ester and urethane bonds in the backbone chain of the polymer, resulting in a three-step thermal decomposition property.

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