

A novel polyurethanes from epoxidized soybean oil synthesized by ring opening with bifunctional compounds

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Received: 3 August 2016 / Revised: 7 November 2016 / Accepted: 24 November 2016 /
Published online: 1 December 2016
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Abstract The present work reports the first synthesis of biobased polyurethanes utilizing soy-based polyols that are synthesized by epoxy ring opening of epoxidized soybean oil with chemicals bearing two different functionalities. Apart from polyols, the syntheses of which are described in our previous report where thio-glycolic acid (TGA) and methyl ester of TGA (MTGA) were utilized for ring opening, a new polyol that was prepared by epoxy ring opening with glycolic acid (GA) was used for the synthesis of the polyurethanes. GA, which has both hydroxyl and carboxyl functionality, was used to open epoxy ring for the first time. The soybean oil-based polyurethanes (PUs) were formed by the reaction of 4,4'-methylenebis(phenyl isocyanate) (MDI) with the polyols that were synthesized using TGA (polyol-1), GA (polyol-2) and MTGA (polyol-3) to open epoxy rings, in bulk. The PUs were characterized using DSC, FTIR, XRD, SEM and thermogravimetric analysis. New polyurethanes demonstrated a wide range of tensile properties ranging from very flexible to rigid (from 3.44 to 39.7 MPa) as the molar ratio of OH to NCO was changed from 1.85/1 to 2.12/1. With the same polyol/MDI ratio, the best tensile properties were obtained with polyol 1 which has the highest OH functionality.

Keywords Rigid-flexible biobased polyurethane · Ring opening · Bifunctional compounds · Glycolic-thioglycolic acid · Biobased polyol

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Introduction

Since petrochemicals that are used worldwide in the chemical industry are limited resources and there is a growing demand for environmentally friendly and renewable feedstocks, considerable efforts are made on the synthesis of polymers from renewable raw materials, such as plant oils and cellulose [1]. Vegetable oil-based polymers have many advantages over polymers prepared from petroleum-based monomers. They are biodegradable and in many cases comparable in cost with petroleum-based polymers. Exploration of biobased polymers from renewable resources is one of the challenges in polymer chemistry [2–4].

Vegetable based polyurethanes produced from modified vegetable oils and diisocyanates can be comparable in many ways with polyurethanes derived from petrochemical based polyols and their preparation has been the subject of many studies [5–14].

Vegetable oils are one of the most abundant and cheapest biological resources, and their use as a base stock has many advantages, such as low toxicity and good biodegradability. They are considered to be one of the most important renewable raw materials for the production of biobased thermosetting polyurethanes [15].

Vegetable oils are chemically modified prior to polyurethane synthesis. One useful reaction for the modification of vegetable oils is the epoxidation of double bonds. For this purpose, soybean oil was epoxidized using peroxyacetic acid generated in situ by the reaction of glacial acetic acid with hydrogen peroxide in the presence of amberlite as the catalyst [16–18]. Epoxidized soybean oil (ESBO) is provided commercially at reasonable cost and can be used as a starting material for chemical modifications due to its reactive epoxy groups. Ring opening reaction is used to introduce one or more hydroxyl group into fatty acid chain of vegetable oils [19, 20]. In this way, polyols with one or more hydroxyl group are synthesized; and these polyols are used as raw materials for the synthesis of polyurethanes where double or multiple hydroxyl group (functionality) is usually required [8, 21]. Ring opening reaction is carried out with amines, alcohols, carboxylic acids, acid anhydrides and thioethers, all of which bear one type of functional group. Examples are acrylic acid, ethanol, *n*-hexyl amine, ethylene diamine, acetic anhydride and 1,2 propanediol [22–26].

In this study, glycolic acid (GA) bearing two different functional groups, hydroxyl and carboxylic acid, was used for ring opening of epoxidized soybean oil and a new polyol was synthesized and defined as polyol 2. Ring opening was confirmed using FTIR and NMR spectroscopy. Differential scanning calorimetry (DSC) and thermogravimetric analysis were performed for the investigation of thermal behavior. Gel permeation chromatography (GPC) was used for the determination of molecular weights. The synthesis of the other two polyols, namely polyol 1 and polyol 3, were reported in our previous study [27].

Polyol 1, polyol 2, polyol 3 and 4,4'-methylenebis(phenyl isocyanate) (MDI) were used for polyurethane synthesis. A hard film, 3 mm in thickness was obtained with polyurethanes prepared by hand mix method using glass mold. The polyurethanes were characterized using FTIR, DSC and thermogravimetric analysis

were used. Tensile properties, i.e., elastic modulus, tensile strength, elongation at break were also measured using a Shimadzu AG-IC 20KN/50KN tensile machine.

Experimental

Materials

Soybean oil and 4,4'-methylenebis(phenyl isocyanate) were purchased from Sigma-Aldrich. Thioglycolic acid (98%), glycolic acid (98%), methyl thioglycolate (95%), perchloric acid (30%), glacial acetic acid (99.85%), hydrogen peroxide (30% w/w in H₂O), toluene, methylene chloride, sodium sulfate anhydride and sodium bicarbonate were purchased from Merck KGaA, Germany. All these chemicals were used as received.

Characterization

FTIR spectra were recorded on a Shimadzu IR prestige-21 spectrophotometer, which is equipped with ATR device having a diamond crystal, in a scanning range of 650–4000 cm⁻¹ for 25 scans at a spectral resolution of 4 cm⁻¹. Data were collected and processed using IR solution software. ¹H and ¹³C NMR spectra were recorded using SHIMADZU Prestige-21 (200VCE) spectrophotometer operating at 300 and 75 MHz, respectively. For data collection and processing, VNMR 6.1 C software was used. Solutions were prepared with deuterated chloroform (CDCl₃, 99.8 atom% D) at 15% concentration by volume. MALDI-MS spectra were obtained using 2,5-dihydroxybenzoic acid as the MALDI matrix, acquired in linear modes with an average of 50 shots on a Bruker Daltonics Microflex mass spectrometer equipped with a nitrogen UV-Laser operating at 337 nm. DSC experiments were conducted on Mettler Toledo DSC1 200 W. Approximately 3 mg of samples were weighed in aluminium pans (40 μL) and were subjected to cooling-heating cycles from -90 to 25 °C at a heating rate of 10 °C min⁻¹ under nitrogen with 50 mL min⁻¹ flow rate. Thermogravimetric analysis was carried out using a Netzsch STA 44F1A analyzer. Samples (40–60 mg) were loaded in aluminium crucibles (0.3 ml). The change in weight loss of the samples was measured by heating in nitrogen atmosphere (20 mL/min) at a rate of 10 °C/min from 40 to 600 °C. Hydroxyl number was determined according to ASTM D-1957-86. In this method, a solution of acetic anhydride in pyridine was used to esterify the hydroxyl groups of polyol quantitatively and the released acetic acid was titrated with KOH. High hydroxyl value of polyol 1 indicated that thiol group is involved in hydroxyl determination as well, since they can also react with the anhydride and generate acetic acid. Acid value test was conducted according to ASTM D-4662. In this method, the solution of ESBO and polyols in ethyl alcohol was titrated with potassium hydroxide solution. Epoxide number was measured according to ASTM D 1652-04, Test Method B. In this method, the solution of ESBO in methylene chloride was titrated with standard perchloric acid in the presence of an excess amount of tetraethylammonium bromide. SV-10 Series Sine-wave Vibro

Viscometer of N&D Company was used to measure dynamic viscosity. Tuning fork vibration method with 30 Hz was applied and two points calibration was made before measurements. GPC analysis was performed at 30 °C on a Shimadzu Prominence GPC system equipped with a RID-10A refractive index detector, a LC-20AD solvent delivery unit, a CTO-10AS column oven and a set of two columns, PSS SDV 5 μ L 1000 A° and PSS SDV 5 μ L 50 A°. THF (HPLC grade) was used as the mobile phase at a flow rate of 1.0 mL/min. The sample concentration was 2 mg/mL, and the injection volume was 50 μ L. The calibration curve was made using seven polystyrene standards covering the molecular weight range from 162 to 33,500 Da (MW: 162, 690, 1470, 3250, 8900, 19,100, and 33,500 Da). An X-ray diffractometer (XRD-Rigaku D/MAX 2000) with Cu-K radiation was used to measure the crystalline properties. Microstructures of polyurethanes were evaluated using a scanning electron microscope (SEM, LEO 440i) at 10,000 \times magnifications at 20 kV electron beam (Carl Zeiss, Germany). Tensile properties were measured on a Shimadzu AG-IC 20 KN/50 KN tensile machine using 10 mm long, 10 mm width, 2 mm thick samples at the extension rate of 2 mm/min.

Synthesis of epoxidized soybean oil

Synthesis of epoxidized soybean oil (ESBO) was conducted according to the procedure reported in the literature [27]. Typically, a solution of soybean oil (103 g, 0.14 mol), glacial acetic acid (25.2 g, 0.42 mol), amberlite (25 g) and toluene (40 ml) were heated to a constant temperature of 55 °C by stirring in a four-necked, round-bottomed flask equipped with a thermometer, a stirrer and a reflux condenser. Epoxidation reaction was initiated by adding 30% H₂O₂ (79.4 g, 0.7 mol) to the above mixture and was allowed to react for 7 h at 55 °C. The solution was then filtered and washed with distilled water for four times to remove any unreacted H₂O₂. The oil phase was dried with anhydrous sodium sulfate and then filtered. Finally, toluene was removed in a vacuum oven at 80 °C. The yield of the reaction was determined as 88%.

Preparation of polyol 1 from ESBO and TGA

Ring opening reaction of ESBO was carried out following the procedure reported in our previous article [25]. Briefly, to a three-necked, 100 ml, round-bottomed flask equipped with a thermometer, a stirrer and a reflux condenser, epoxidized oil (24 g, 0.026 mol) and thioglycolic acid (12 g, 0.13 mol) were added; and the mixture was heated to 120 °C under nitrogen atmosphere. Ring opening reaction was initiated by adding 30% perchloric acid (2.63 g, 0.026 mol) slowly; and the mixture was allowed to react at 120 °C for 18 h. After cooling down to the room temperature, the solution was washed with sodium bicarbonate solution until pH 7 to remove unreacted perchloric acid. The organic phase was dried with anhydrous sodium sulfate. A viscous liquid was obtained. The hydroxyl value and acid value for polyol 1 were 283.74 and 3.31 mg KOH/g, respectively; and the yield was 81.7%.

Polyol 1. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm) δ 5.3 ppm (OH proton), δ 4.9 ppm (CH proton adjacent to $-\text{O}-\text{CO}-\text{R}$), δ 4.2 ppm (CH_2 protons of CH_2CHCH_2 glycerine backbone), δ 3.4–3.6 ppm (CH proton of $\text{CH}-\text{OH}$), δ 3.2 ppm (CH_2 protons α to $-\text{SH}$), δ 1.2–1.8 ppm (CH_2 protons of fatty acid chain), δ 0.8 ppm (CH_3 protons at the end of fatty acid chain).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.2 ppm (carbonyl carbon of triacylglycerol), δ 73.3 ppm ($-\text{HC}-\text{O}-$), 68.9 and 62.1 ppm (CH and CH_2 carbons of $-\text{CH}_2\text{CHCH}_2-$ glycerol backbone, respectively), δ 62.8 ppm ($-\text{CH}-$ carbon adjacent to $-\text{OH}$ group), 54.1 ppm (quaternary carboxylic carbon), 22.6–34 ppm (multiple singlets from the fatty carbon chain), 26.8 ppm (CH_2 carbon adjacent to $-\text{SH}$), 14.0 ppm (CH_3 end carbon of the fatty acid chain).

FTIR 3480 cm^{-1} (characteristic absorption peak due to hydroxyl groups), $2855\text{--}2926\text{ cm}^{-1}$ (methylene asymmetric stretching), 1734 cm^{-1} (triglycerides carbonyl stretching), 1463 cm^{-1} (CH_2 bending vibration), 1376 cm^{-1} (CH_3 bending vibration), $1159\text{--}1265\text{ cm}^{-1}$ (stretching vibrations of C–O group in esters), 734 cm^{-1} (CH_2 rocking vibration).

Preparation of polyol 2 from ESBO and GA

Synthesis of polyol 2 was carried out by modification of the procedure used for polyol 1. To a three-necked, 250 ml, round-bottomed flask equipped with a thermometer, a stirrer and a reflux condenser, was added 100 ml of ethyl acetate, epoxidized oil (24 g, 0.026 mol) and glycolic acid (8.4 g, 0.11 mol). The solution was heated to $77\text{ }^\circ\text{C}$ under nitrogen atmosphere. Subsequently, 30% perchloric acid (1.3 g, 0.7 mol) was added slowly from an addition funnel and allowed to react for 16 h at $77\text{ }^\circ\text{C}$. The solution was then washed with sodium bicarbonate solution until pH of water reached 7 to remove unreacted perchloric acid; and organic phase was dried with anhydrous sodium sulfate. Solvent was removed in a vacuum evaporator and a viscous liquid was obtained. The hydroxyl value and acid value for polyol 2 were 225.62 and 2.73 mg KOH/g, respectively; and the yield was 85.7%.

Polyol 2. **FTIR** 3474 cm^{-1} (characteristic absorption peak due to hydroxyl groups), $2855\text{--}2925\text{ cm}^{-1}$ (methylene asymmetric stretching), 1740 cm^{-1} (triglycerides carbonyl stretching), 1464 cm^{-1} (CH_2 bending vibration), 1374 cm^{-1} (CH_3 bending vibration), $1125\text{--}1237\text{ cm}^{-1}$ (stretching vibrations of C–O group in esters), 724 cm^{-1} (CH_2 rocking vibration).

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm) δ 5.3 ppm (OH proton), δ 4.9 ppm (CH proton adjacent to $-\text{O}-\text{CO}-\text{R}$), δ 4.2 ppm (CH_2 protons of CH_2CHCH_2 glycerine backbone and CH_2 protons of $-\text{CH}_2-\text{OH}$), δ 3.4–3.6 ppm (CH proton of $\text{CH}-\text{OH}$), δ 1.2–1.6 ppm (CH_2 protons of fatty acid chain), δ 0.8 ppm (CH_3 protons at the end of fatty acid chain).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.2 ppm (carbonyl carbon of triacylglycerol), δ 76.3 ppm ($-\text{HC}-\text{O}-$), 68.9 and 62.1 ppm (CH and CH_2 carbons of $-\text{CH}_2\text{CHCH}_2-$ glycerol backbone, respectively), δ 62.8 ppm ($-\text{CH}-$ carbon adjacent to $-\text{OH}$

group), 54.1 ppm (quaternary carboxylic carbon), 22.6–34 ppm (multiple singlets from the fatty carbon chain), 14.0 ppm (CH₃ end carbon of the fatty acid chain).

Preparation of polyol 3 from ESBO and MTGA

Ring opening reaction of ESBO was carried out following the procedure reported in our previous article [27]. Briefly, in a three-necked, 500 ml, round-bottomed flask equipped with a thermometer, a stirrer and a reflux condenser, epoxidized oil (24 g, 0.026 mol) and methyl thioglycolate (13.8 g, 0.13 mol) were dissolved in 250 ml of methylene chloride and the mixture was heated to 45 °C under nitrogen atmosphere. Ring opening reaction was initiated by adding 30% perchloric acid (2.63 g, 0.026 mol) slowly and allowed to react for 4 h at 45 °C. The solution was then washed with sodium bicarbonate solution until pH of water reached 7 to remove unreacted perchloric acid; and the organic phase was dried with anhydrous sodium sulfate. Solvent was removed in a vacuum evaporator and a viscous liquid was obtained. The hydroxyl value and acid value for polyol 3 were 158.93 and 4.56 mg KOH/g, respectively; and the yield was 78.4%.

Polyol 3. ¹H NMR (500 MHz, CDCl₃, ppm) δ 5.3 ppm (OH proton), δ 4.9–5.0 ppm (CH proton adjacent to –O–CO–R), δ 4.0–4.2 ppm (CH₂ protons of CH₂CHCH₂ glycerine backbone), δ 3.6–3.8 ppm (CH₃ protons at the acyl end), δ 3.4–3.6 ppm (CH proton of CH–OH), δ 3.2–3.4 ppm (CH₂ protons adjacent to –S–), δ 2.7 ppm (protons –CH–S–), δ 1.2–1.8 ppm (CH₂ protons of fatty acid chain), δ 0.8 ppm (CH₃ protons at the end of fatty acid chain).

¹³C NMR (125 MHz, CDCl₃, ppm) δ 173.2 ppm (carbonyl carbon of triacylglycerol), 68.9 and 62.1 ppm (CH and CH₂ carbons of –CH₂CHCH₂– glycerol backbone, respectively), 62.8 ppm (–CH– carbon adjacent to –OH group), 56.8 ppm (CH carbon α to –S–), 54.1 ppm (quaternary carboxylic carbon), 33.5 ppm (CH₂ carbon adjacent to –S–), 22.6–34 ppm (multiple singlets from the fatty carbon chain), 26.8 ppm (CH₂ carbon adjacent to –SH), 14.0 ppm (CH₃ end carbon of the fatty acid chain).

FTIR 3416 cm⁻¹ (characteristic absorption peak due to hydroxyl groups), 2855–2926 cm⁻¹ (methylene asymmetric stretching), 1739 cm⁻¹ (triglycerides carbonyl stretching), 1458 cm⁻¹ (CH₂ bending vibration), 1378 cm⁻¹ (CH₃ bending vibration), 1150–1265 cm⁻¹ (stretching vibrations of C–O group in esters), 734 cm⁻¹ (CH₂ rocking vibration).

Preparation of polyurethanes

Three cast polyurethanes PU-1, PU-2 and PU-3 were prepared by mixing polyol 1, polyol 2 and polyol 3, respectively, with 4,4'-methylenebis (phenyl isocyanate) (MDI) at 70 °C. Typically, 1 g of polyol was mixed for 3 min with MDI with an amount ranged from 0.1 to 1 g, and the mixture was poured on clean glass plates and left under vacuum to remove bubbles for 5 min. at 60 °C. PU-1 200, PU-2 200 and PU-3 200 were prepared with 200 mg MDI while PU-1 300, PU-2 300 and PU-

3 300 were prepared with 300 mg MDI. The amount of MDI required was calculated as follows:

$$\text{Mole of OH} = \text{Weight of polyol (g)} \times \text{OH functionality.}$$

$$\begin{aligned} \text{Mole of NCO} &= \text{Weight of MDI (g)} \\ &\times \text{number of isocyanate group in 1 g of MDI [28].} \end{aligned}$$

OH/NCO molar ratios can be seen in Table 1. The samples prepared with polyol 1 and polyol 2 with the amount of MDI more than 0.2 g became rigid immediately while the ones prepared with less than 0.2 g of MDI needed to be kept at room temperature for 24 h for completion of reaction and then peeled off from the glass mold.

FTIR 3320 cm^{-1} (characteristic stretching vibration peak due to N–H of urethane group), 1736, 1608, 1515 cm^{-1} (–C=O and N–H stretching of polymerized urethane), 1739 cm^{-1} (triglycerides carbonyl stretching), 1060 cm^{-1} (C–O stretching), 1217 cm^{-1} (N–H stretching), 1525, 1309 cm^{-1} (N–H vibrations of –O–CO–NH–).

The optimum polyol/MDI ratio was decided based on FTIR. When MDI was not sufficient, typical hydroxyl peak of polyol at 3416 cm^{-1} still exists and in the case of excess MDI, typical isocyanate peaks at 2250–2270 cm^{-1} did not disappear.

Results and discussion

Our aim in this study was to synthesize three new polyurethanes using three new soybean-based polyols obtained by epoxy ring opening using compounds bearing two different functionality, thiol (or hydroxyl) and carboxylic acid functionality. Ring opening reactions of ESBO with TGA, GA and MTGA took place as shown in Fig. 1.

As seen in Fig. 1, in the case of polyol 1 and polyol 2, ring was opened by carboxylic acid group of TGA and GA, respectively, while ring was opened by thiol group of MTGA in polyol 3.

Proposed chemical structures of polyurethanes synthesized by the reactions of polyol 1, polyol 2 and polyol 3 with MDI are shown in Fig. 2.

Table 1 OH/NCO molar ratios of PUs

PU	OH number (mg KOH/g)	OH functionality	OH/NCO molar ratio
PU-1 200	283.74	5.1	5.1/1.6
PU-1 300	283.74	5.1	5.1/2.4
PU-2 200	225.62	4.03	4.03/1.6
PU-2 300	225.62	4.03	4.03/2.4
PU-3 200	158.93	2.83	2.83/1.6
PU-3 300	158.93	2.83	2.83/2.4

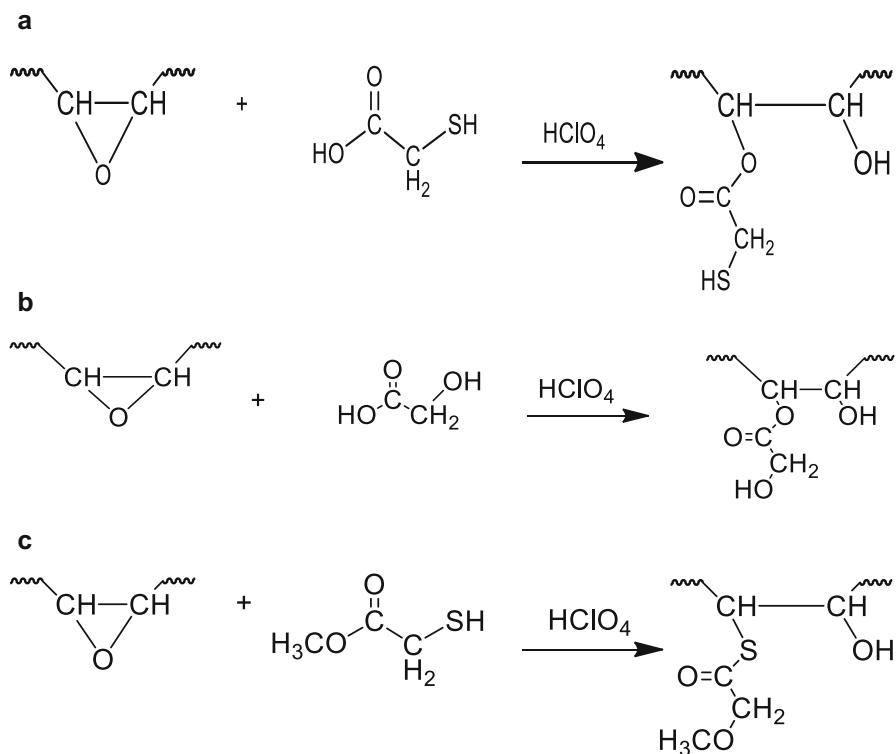


Fig. 1 Ring opening reactions of ESBO with **a** thioglycolic acid, **b** glycolic acid, **c** methyl thioglycolate

Hydroxyl and acid values

The hydroxyl and acid values of ESBO and polyols are presented in Table 2. Higher functionality of polyol 1 (5.1) and polyol 2 (4.0) compared to polyol 3 (2.8) can be attributed to additional hydroxyl and thiol group introduced through glycolic and thioglycolic acid. Acid value of ESBO, polyol 1, polyol 2 and polyol 3 were measured 1.21, 3.31, 2.73 and 4.56, respectively. This indicates the presence of some free fatty acids generated during the epoxy ring opening reaction.

FTIR analysis

The FTIR spectra of ESBO and soy-based polyols are shown in Fig. 3. Characteristic epoxy peaks of ESBO at 823 and 833 cm^{-1} , disappeared after the epoxy group opening reaction. The new characteristic absorption peaks at 3480, 3475, 3419 cm^{-1} in the spectrum of polyol 1, polyol 2 and polyol 3, respectively, were attributed to the hydroxyl groups. Characteristic peak at 1097 cm^{-1} was attributed to stretching of C–O bond associated with the hydroxy.

The FTIR spectra of polyurethanes are shown in Fig. 4. The peak at 1735 cm^{-1} was attributed to carbonyl stretching vibrations of polyols and polyurethanes, and

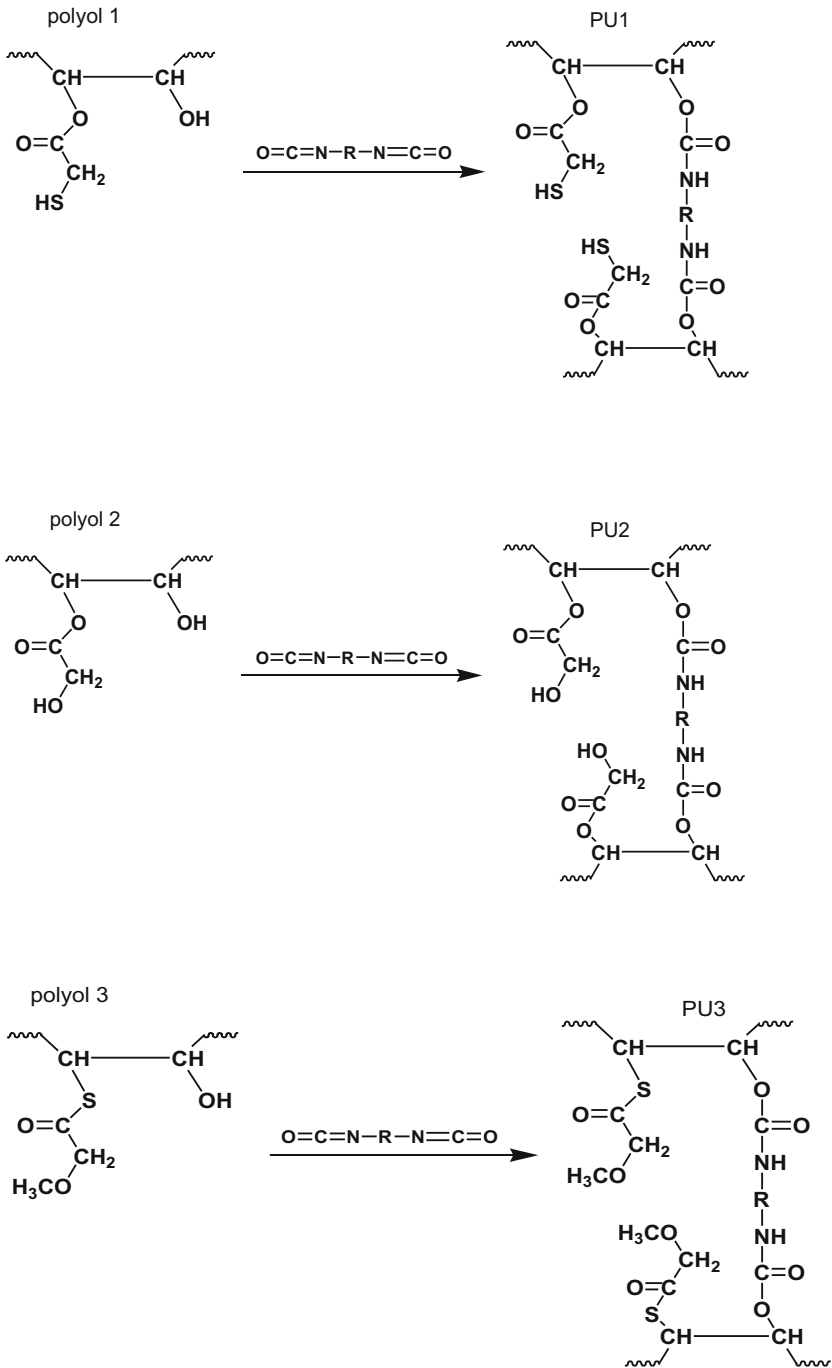
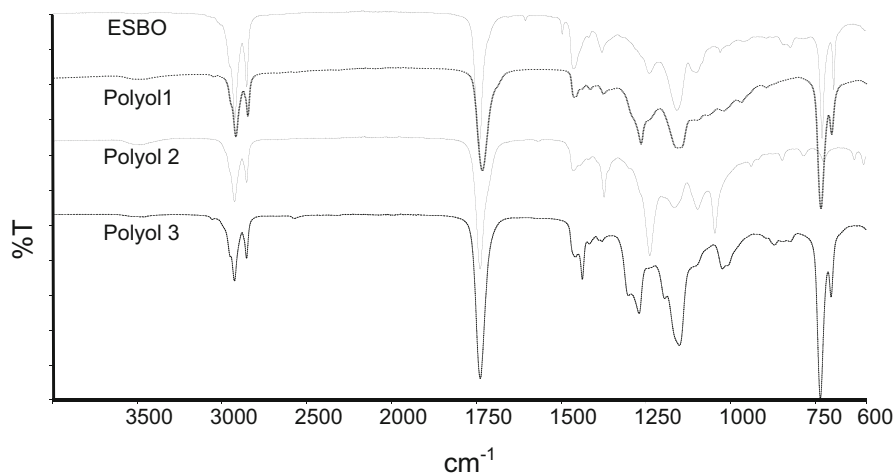


Fig. 2 Proposed route for PU1, PU2 and PU3 synthesis

Table 2 M_w , M_n , PDI, OH number and acid number of polyols

Polyol	M_w	M_n	PDI (M_w/M_n)	% of total	OH number (mg KOH/g)	Acid number (mg KOH/g)
Polyol 1	13,615	10,298	1.32	42.9	283.74	3.31
	3999	3898	1.03	19.7		
	1860	1792	1.04	37.9		
Polyol 2	9986	9080	1.10	2.0	225.62	2.73
	5047	4980	1.01	13.5		
	3248	3208	1.01	21.5		
	1636	1624	1.01	41.2		
Polyol 3	5548	4798	1.16	30.1	158.93	4.56
	1927	1811	1.03	55.8		
	501	515	1.03	14.1		

**Fig. 3** FTIR of ESBO and polyols

the new peaks appearing at 3321, 1217, 1060 cm^{-1} were attributed to N–H, C–N and C–O stretching vibrations, respectively. C=O and N–H stretching vibrations of polyurethanes appeared at 1608 and 1520 cm^{-1} , respectively. Appearance of CH–S bond and the disappearance of S–H bond could not be characterized from FTIR spectrum of polyol 1 because the intensities of their corresponding vibration bands at 600–700 and 2500–2600 cm^{-1} remained too weak [29].

NMR analysis

^1H NMR spectra of SBO, ESBO and the polyols are shown in Fig. 5. In the spectrum of ESBO, new peaks corresponding to the –CH– protons of the epoxy ring and –CH₂– protons alpha to the epoxy ring appeared at $\delta = 2.8\text{--}3.2$ ppm and

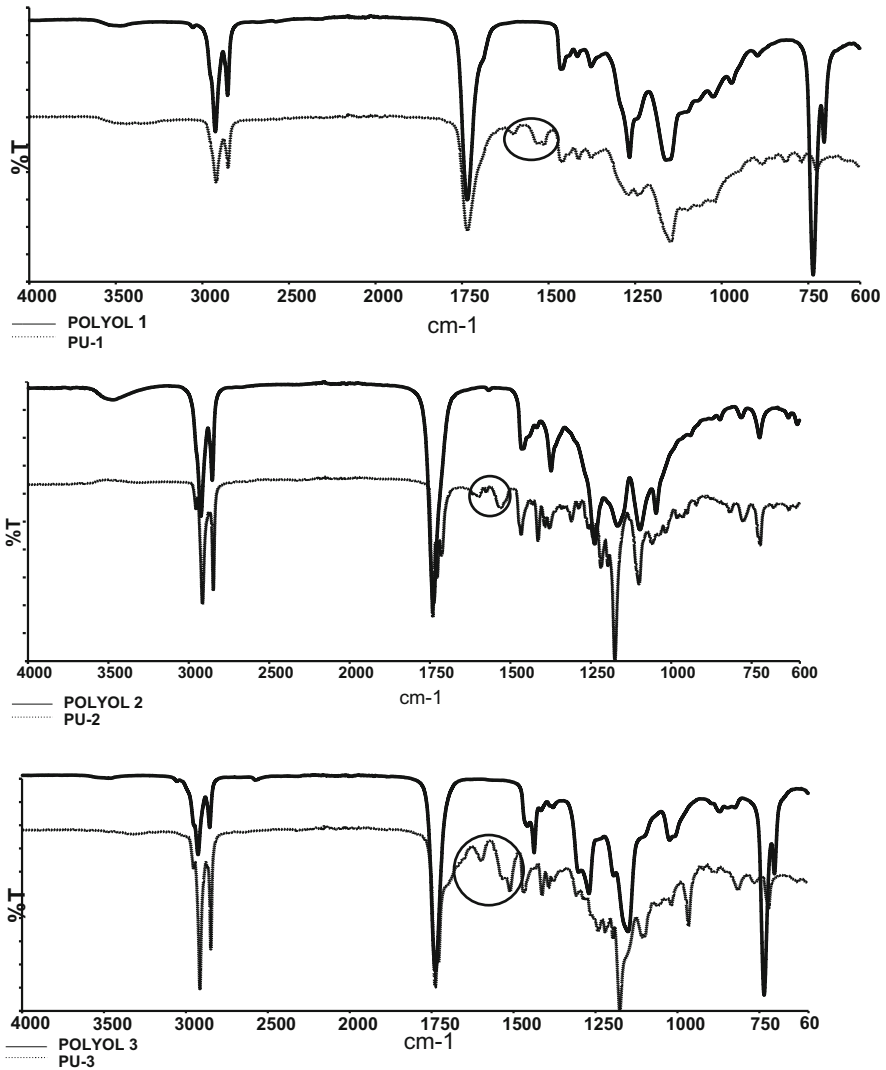


Fig. 4 FTIR of polyol-polyurethanes

$\delta = 1.4\text{--}1.6$ ppm, respectively. Moreover, the intensity of the peak at $\delta = 5.4$ ppm corresponding to methine protons in soybean oil decreased notably upon epoxidation [16]. However, low epoxy number (6.2%) indicated that some double bonds remained intact. The other peaks in the spectrum of ESBO, corresponded to terminal $-\text{CH}_3$ groups (at 0.8–0.1 ppm), saturated $-\text{CH}_2$ groups (at 1.1–1.4 ppm) and the protons of $(-\text{CH}_2-\text{CH}-\text{CH}_2-)$ (at 4.1–4.3 and 5.2 ppm).

The disappearance of the characteristic multiple peaks of epoxy groups at 2.8–3.2 ppm and at 1.4–1.6 ppm in the spectrum of ESBO and the appearance of OH proton at 5.3 ppm in the spectra of polyol 1, polyol 2 and polyol 3 confirmed

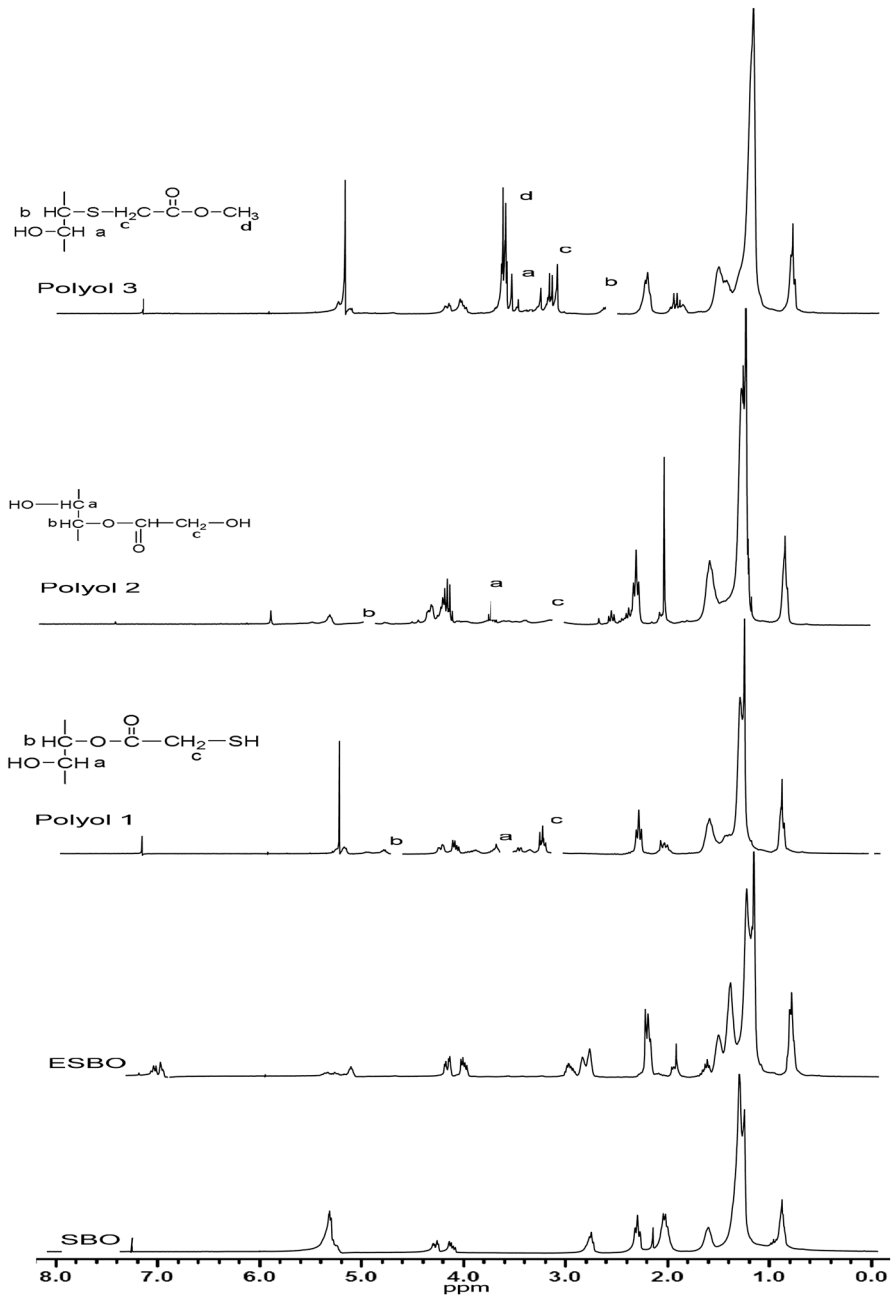


Fig. 5 ^1H NMR spectra of SBO, ESBO and polyols

epoxy ring opening reaction. The peak at 3.1–3.2 ppm in the spectrum of polyol 1 which was attributed to CH_2 protons of $-\text{CH}_2-\text{SH}$, and the $-\text{CH}-$ proton of $-\text{CH}-\text{O}-\text{CO}-\text{R}$ ester group appearing at 4.9–5.0 ppm confirmed that the ring was opened by

carboxylic acid group of TGA. The $-\text{CH}-$ proton of $-\text{CH}-\text{O}-\text{CO}-\text{R}$ ester group appearing at 4.9 ppm confirmed that the ring was opened by carboxylic acid group of GA in polyol 2. In the spectrum of polyol 3, the new peaks at 3.3–3.4 ppm and 3.4–3.6 ppm were attributed to methyl protons $[-\text{C}(\text{O})-\text{O}-\text{CH}_3]$ of TGAME and the protons adjacent to hydroxyl group ($-\text{CH}-\text{OH}$), respectively. The new peaks appearing at 3.2–3.4 and 2.7 ppm which were attributed to $-\text{CH}_2-$ and $-\text{CH}$ protons alpha to $-\text{S}-$, respectively, and terminal CH_3 peak at 3.6–3.8 ppm, confirmed that the epoxy ring was opened via SH group of TGAME.

Figure 6 shows ^{13}C NMR spectra of SBO, ESBO, polyol 1, polyol 2 and polyol 3. The appearance of new peak at 56 ppm confirmed epoxidation of SBO. New peaks in the spectra of polyol 1, polyol 2 and polyol 3 at 62.8 ppm were due to $-\text{CH}-$ carbons adjacent to hydroxyl groups. In the spectrum of polyol 1 and polyol 2, the appearance of new carbon peak at 73.3 ppm was attributed to $-\text{HC}-\text{O}-$ and this confirmed that the ring opened by carboxylic acid group of TGA and GA. The new peak at 60 ppm appeared on polyol 2 indicated that the OH adjacent to $-\text{CH}_2$ was not involved in epoxy ring opening. In the case of polyol 3, the new peak at 56.8 ppm corresponding to $-\text{CH}$ carbon alpha to $-\text{S}-$ confirmed that the ring opened via SH group of TGAME. The carbon peaks at 26.8 and 33.5 ppm were attributed to $-\text{CH}_2-$ adjacent to $-\text{SH}-$ and $-\text{S}-$ of polyol 1 and polyol 2, respectively. New carbon peak, which appeared at 176.1 ppm and did not exist on ESBO spectrum, can be attributed to carbonyl carbon of $-\text{C}(\text{O})-\text{O}-\text{CH}_3$ while the peak at 172.2 ppm can be attributed to $-\text{C}(\text{O})$ peak of soybean oil.

FTIR, ^1H NMR and ^{13}C NMR spectra are in agreement with the reported literature describing the ring opening reactions with chemicals that have thiol and carboxylic acid functional groups in their structure [7, 16, 17].

Figure 7 shows the mass spectra of polyol 3. As can be seen from the figure, there are presence of oligomers at 1408, 2089, 3135 and 4114 apart from main component at an MW of about 918.

GPC analysis

The GPC was conducted and molecular weights were determined as: polyol 1: 13,500 g/mol (30.0%, 15.3 min), 6400 g/mol (11.9%, 14.3 min), 3900 g/mol (20.2%, 13.7 min), 1800 g/mol (37.7%, 12.5 min); polyol 2: 9986 g/mol (17.0%, 13.3 min), 4980 g/mol (13.5%, 13.7 min), 3208 g/mol (21.5%, 14.3 min), 1624 g/mol (41.2%, 15.2 min); polyol 3: 4970 g/mol (10.1%, 14.6 min), 2995 g/mol (28.8%, 14.6 min), 1787 g/mol (59.1%, 15.4 min). Weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of polyols, and the GPC chromatograms of ESBO and polyols are shown in Table 1 and Fig. 8. High molecular weight products formed indicate the presence of epoxy ring opening polymerization and chain coupling. The formation of higher molecular weight products in polyol 1 and polyol 2 were probably due to higher extent of coupling which might result from the reaction of epoxy rings with thiol and hydroxyl groups some of which remained intact during the reaction of TGA and GA with ESBO. Low polydispersity indexes of polyols indicate that the

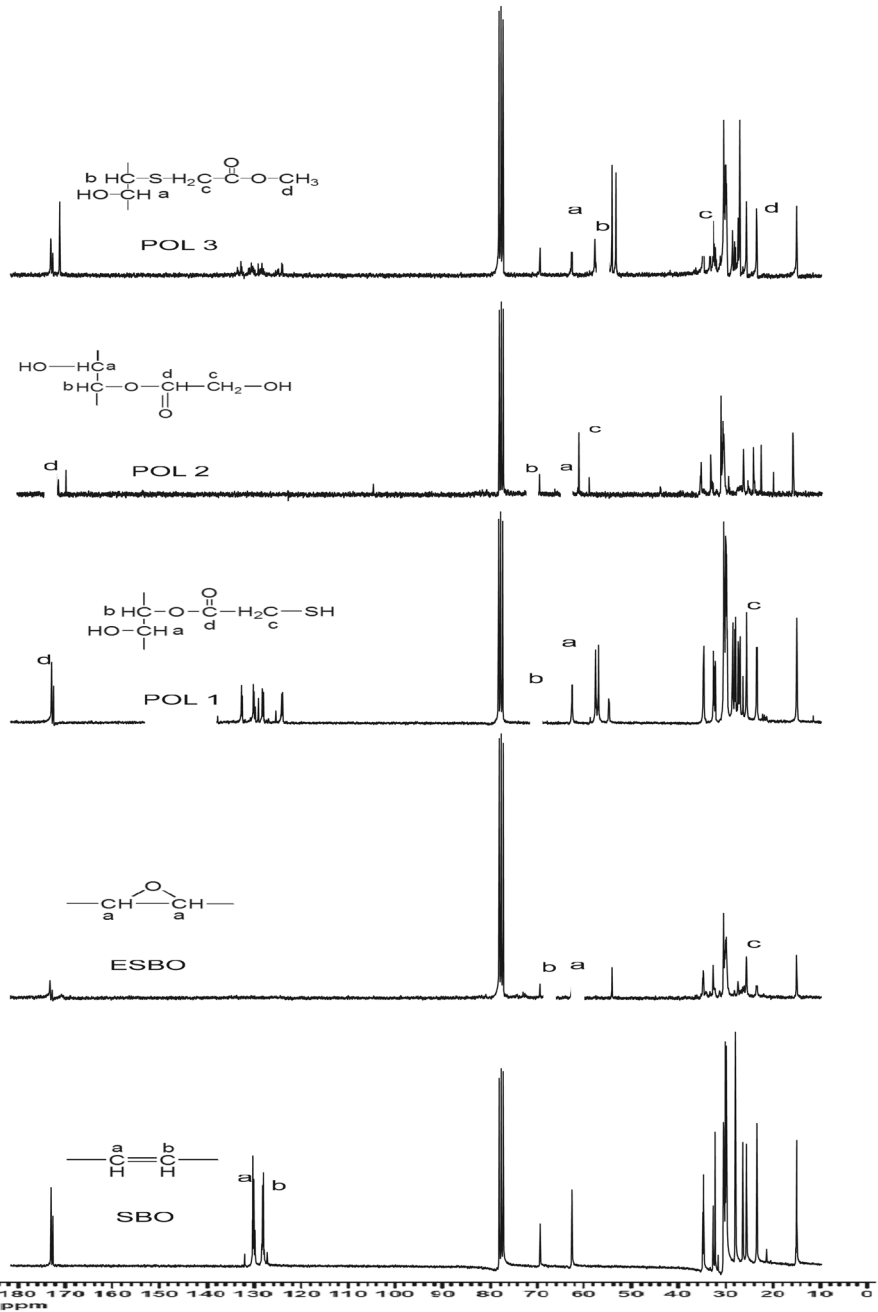


Fig. 6 ^{13}C NMR spectra of SBO, ESBO and polyols

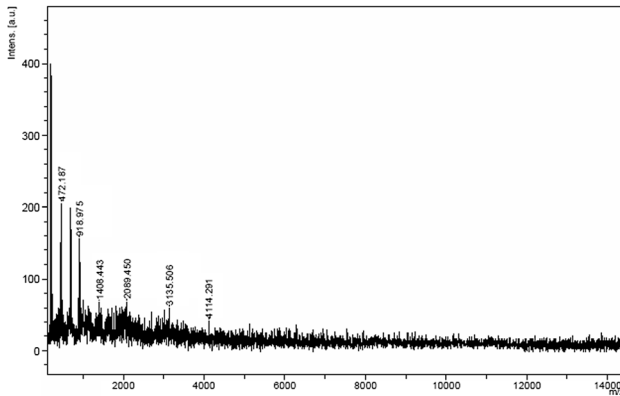


Fig. 7 Mass spectrum of polyol 3

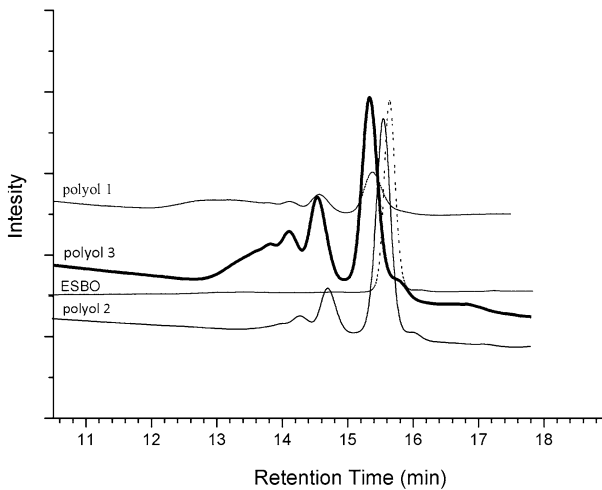


Fig. 8 GPC chromatograms of ESBO and polyols

existence of narrow monodisperse and moderate polydisperse distribution is valid for oligomeric chains.

Viscosity measurement

It can be seen from the viscosity data (Table 3) that viscosity order is: polyol 1 > polyol 2 > polyol 3 > ESBO. This viscosity increase may be due to higher molecular weight resulting from the ring opening polymerization of polyols and may also be due to the free hydroxyl groups. Polyol 1 and polyol 2 have higher viscosity than polyol 3 due to its higher molecular weight resulting from the high degree of chain coupling. GPC analysis confirms higher molecular weights of polyol 1 and polyol 2 compared to polyol 3.

Table 3 Dynamic viscosity of ESBO, polyol 1, polyol 2 and polyol 3

Samples	Dynamic viscosity (mPa s)
ESBO	37.5
Polyol 1	9020
Polyol 2	8030
Polyol 3	6880

Differential scanning calorimetry analysis

DSC analysis of polyols is shown in Fig. 9. Multiple peaks indicating melting points can be attributed to different crystalline structures. It can be seen in Table 4 that freezing points of polyols shifted to higher temperatures and structural regularity increased due to intramolecular interaction of OH groups of polyols. As a result, structural regularity of polyols was highest while their melting points were highest compared to ESBO.

Glass transition temperature (T_g) curves of polyurethanes are shown in Fig. 10. As seen from the Table 5, the T_g of PU products increase with increasing OH functionality and increasing MDI/polyol ratio. This suggests that the properties of soy-based polyurethanes associate with the structure of soy-based polyols and MDI/polyol ratio. Higher glass transition temperatures observed at 62 and 44 °C show that crosslinking density of PU-1 300 and PU-2 300 were higher than the other polyurethanes.

Thermogravimetric analysis

Polyurethanes exhibit relatively low thermal stability, mainly due to the presence of urethane bonds. Vegetable oil-based polyurethanes show three-step decomposition, whereas oxypropylene-based polyurethanes degrade in a single step [30]. The first decomposition step at temperatures between 300 and 340 °C can be attributed to the

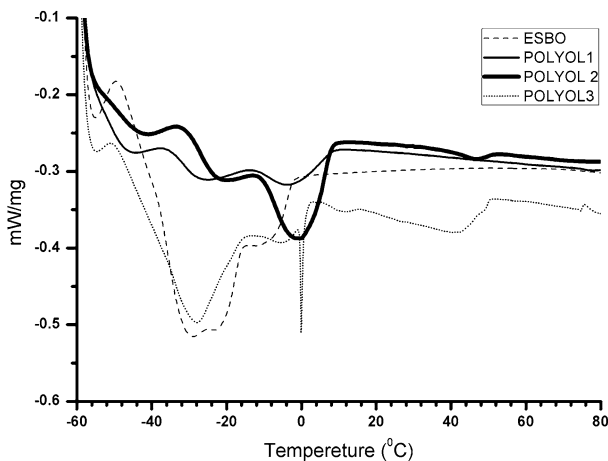
**Fig. 9** DSC thermograms of ESBO and polyols

Table 4 Freezing points of ESBO, polyol 1, polyol 2 and polyol 3

	Temperature (°C)			
	ESBO	Polyol 1	Polyol 2	Polyol 3
Peak 1	-56	-42	-44	-55
Peak 2	-32	-22	-26	-28
Peak 3	-12	0	-28	0

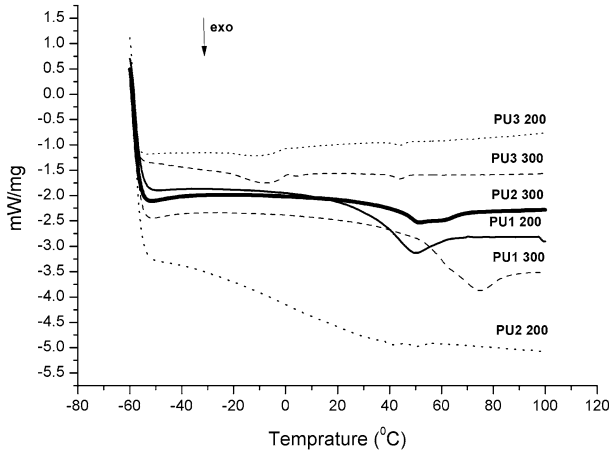


Fig. 10 DSC thermograms of polyurethanes

Table 5 OH number, OH functionality, OH/NCO molar ratio and glass transition temperature of PUs

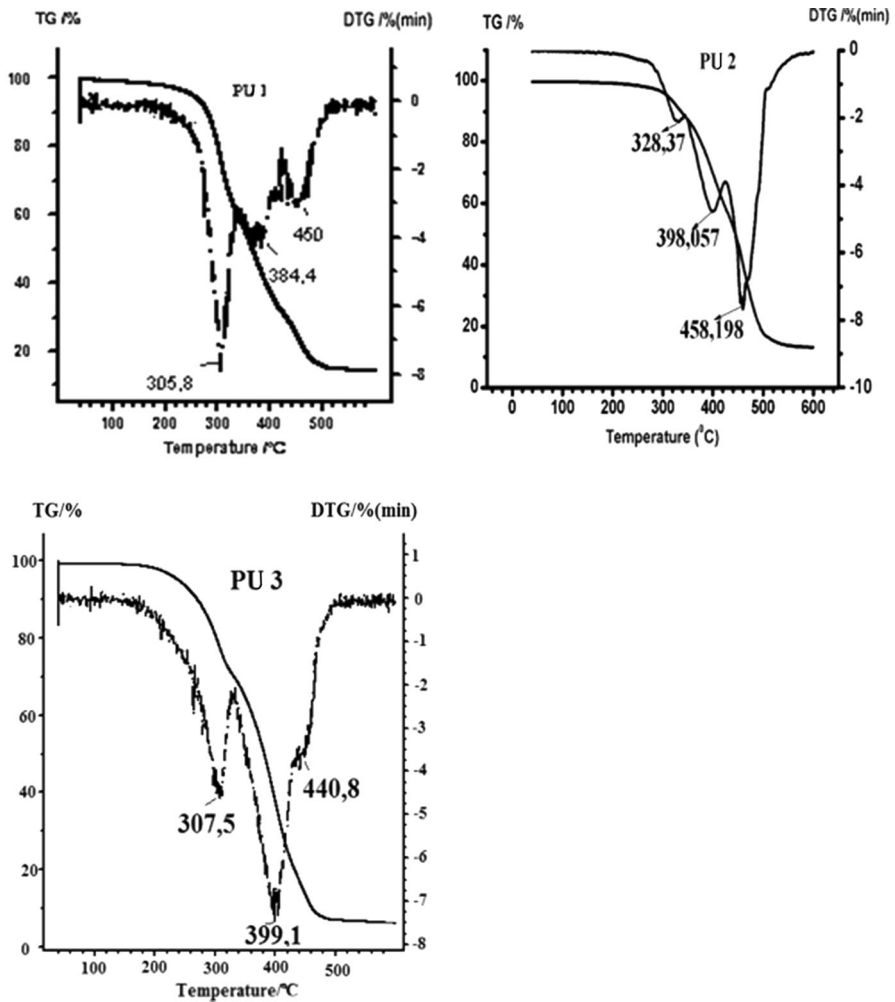
PU	OH number (mg KOH/g)	OH functionality	OH/NCO molar ratio	T _g from DSC (°C)
PU-1 200	283.74	5.1	5.1/1.6	32
PU-1 300	283.74	5.1	5.1/2.4	62
PU-2 200	225.62	4.03	4.03/1.6	38
PU-2 300	225.62	4.03	4.03/2.4	44
PU-3 200	158.93	2.83	2.83/1.6	22
PU-3 300	158.93	2.83	2.83/2.4	22

decomposition of weak urethane bonds. This decomposition takes place through the dissociation to isocyanate and alcohol, the formation of primary amines and olefins, or the formation of secondary amines. The second decomposition temperature taking place at 380–410 °C was mostly due to decomposition of polymer networks. The third peak observed at 440–460 °C could be related to gasification of any remaining components [31]. Table 6 shows thermogravimetric parameters of polyurethanes.

It can be seen from the Fig. 11 that PU-1 has a lower decomposition temperature at 306 and 384 °C, whereas PU2 has 328.4 and 458 °C. This can be explained by higher crosslinking density of PU-1. The main degradation process is observed at temperatures around 450 °C for PUs.

Table 6 Thermogravimetric parameters of polyurethanes

Sample	T_{onset} (°C)	$T_{50\%}$ (°C)	T_{offset} (°C)	Char residue (wt%)
PU-1 200	305.8	431.5	450.0	12.3
PU-2 200	327.4	422.9	458.2	6.8
PU-3 200	307.5	407.9	440.8	1.7

**Fig. 11** TG and DTG curves of polyurethanes

X-ray diffraction analysis (XRD)

As can be seen from the Fig. 12, no crystallinity was observed and amorphous shoulder around $2\theta = 50$ exists. This is in line with DSC result.

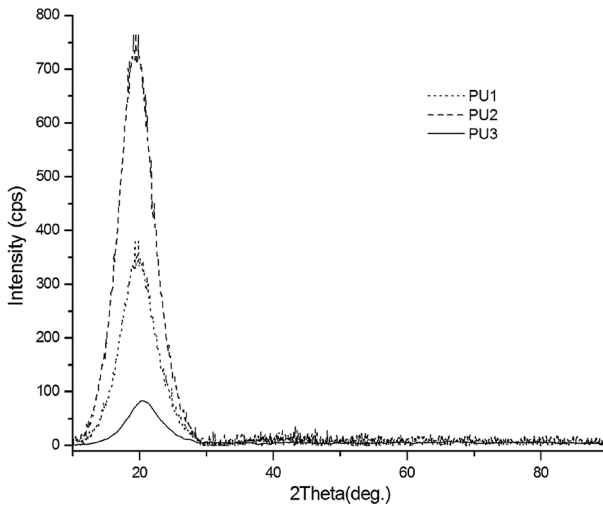


Fig. 12 X-ray diffraction of polyurethanes

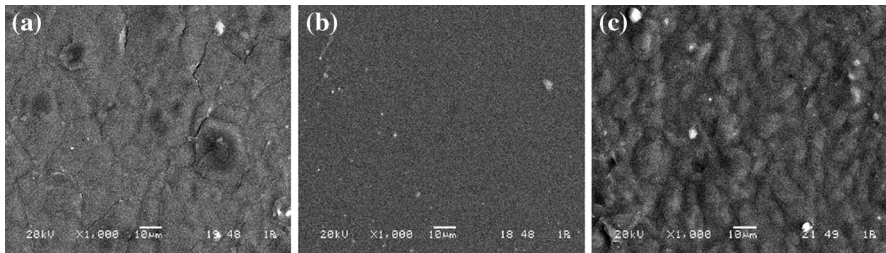


Fig. 13 SEM micrograph of polyurethanes. **a** PU1, **b** PU2 and **c** PU3

Scanning electron microscopy (SEM)

Figure 13 shows the SEM micrograph of polyurethanes. It revealed that the surfaces of polyurethanes were not smooth. There was a degree of non-homogeneity, which may be attributed to the presence of soft and hard segments.

Mechanical properties of polyurethanes

As seen in Table 7, tensile strength of PUs increase with increasing OH value of polyols from which PU was synthesized and increasing MDI/polyol ratio. PU-1 showed the highest rigidity while PU-3 showed the most flexibility.

Table 7 Tensile properties of PUs

Polyurethane	Young's modulus (MPa)	% Elongation at break	Ultimate tensile strength (MPa)
PU-1 200	117.3	35	18.9
PU-1 300	351.6	15	35.7
PU-2 200	35.4	35	10.5
PU-2 300	64.2	30	12.1
PU-3 200	32.5	25	5.9
PU-3 300	48.2	24	8.2

Conclusions

This is the first synthesis of polyurethanes utilizing soy-based polyols, which are prepared by epoxy ring opening reactions with chemicals bearing two different functionalities. In addition to the polyols reported in our previous work, another novel polyol having hydroxyl and carboxylic acid functionality was synthesized by the ring opening reaction with GA having hydroxyl and carboxylic acid functionality. As FTIR and NMR spectra indicate, epoxy ring was opened by carboxylic acid group and hydroxyl group did not participate in the ring opening reaction. DSC analysis and tensile tests showed that physical properties of polyurethanes were associated with OH functionality of polyols and MDI/polyol ratio. The ranking based on T_g and tensile strength was: PU-1 300 > PU-1 200 > PU-2 300 > PU-2 200 > PU-3 300 > PU-3 200. In this way, the synthesized PUs were comparable to petroleum-based PUs in tensile strength which ranged from 5.9 to 35.7 MPa.

Acknowledgements The authors acknowledge the financial support of The Research Fund of Sakarya University (BAP) (Project No: 2013-02-04-054).

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