J Am Oil Chem Soc (2009) 86:261–267
DOI 10.1007/s11746-008-1342-7

ORIGINAL PAPER

Synthesis and Characterization of the Different Soy-Based Polyols by Ring Opening of Epoxidized Soybean Oil with Methanol, 1,2-Ethanediol and 1,2-Propanediol

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Received: 4 March 2008 / Revised: 3 October 2008 / Accepted: 10 December 2008 / Published online: 6 January 2009

Abstract Three soy-based polyols intended for application in polyurethanes were prepared by ring opening the epoxy groups in epoxidized soybean oil (ESO, 0.385 mol/100 g epoxy rings) with methanol, 1,2-ethanediol and 1,2-propanediol in the presence of tetrafluoroboric acid catalyst. The effect of the different opening reaction reagents, different low molecular weight alcohols, on the polyols was investigated by spectroscopic, chemical and physical methods. The viscosities, viscous-flow activation energies, molecular weight and melting point of the samples increased in the following order: polyol (3) > polyol (2) > polyol (1) > ESO [polyol (1); polyol (2) and polyol (3) represented the samples synthesized from the same epoxidized soybean oil generated by opening reactions with methanol, 1,2-ethanediol and 1,2-propanediol, respectively]. All the samples were crystalline solids below their melting temperature, displaying multiple melting point peaks. Compared with polyol (1), polyol (2) had a primary hydroxyl group, promoting the reactive activity of the polyol with isocyanates; polyol (3) contained large numbers of hydroxy groups, improving the properties of polyurethanes.

Keywords Soybean oil · Polyol · Properties

Introduction

The preparation of polymers from renewable resources is of significant economic and scientific importance. Vegetable oils have a number of excellent properties that can be utilized in producing valuable polymeric materials. The oils are characterized by their hydroxyl values and fatty acid compositions. The modified oils have higher hydroxyl values and a lower number of unsaturated acids than regular unmodified oils. The modified soy-based vegetable oil polyols can be used as a replacement for conventional polyols, reacting with isocyanates to produce flexible slabstock polyurethane (PU) foams, elastomers, and coatings. Soybean oil (SBO) is highly hydrophobic, thus excellent weather stability of the soy-based PUs can be expected. The thermal and oxidative stability of the SBO-based PUs are comparable with those of polypropylene oxide-based PUs [1–7].

The preparation of polyols from oils has been the subject of many studies [8–11], but limited attention has been paid to the effect of different alcohols of small molecular weight, used as the ring opening reagents with epoxidized soybean oil (ESO), has on the properties of the polyol and the resulting polyurethanes. Polyol from SBO can be prepared by the ring opening of epoxy groups from ESO or by hydroformylation of the oil itself and the subsequent reduction of the aldehyde to hydroxyls. The SBO triglycerides are of heterogeneous structure, that is, there is variation in the fatty acid type from molecule to molecule. In SBO, the concentration of saturated acid is about 13.5%, the concentration of oleic (one double bond), linoleic (two double bonds) and linolenic (three double bonds) acids is 23.1, 56.5 and 6.5%, respectively. The average number of double bonds per molecule is 4.6 [12, 13]. When double bonds are converted into hydroxyls, they are located in the middle of the fatty acid chains of the triglyceride (as shown in Scheme 1). Consequently, when the polyols react with isocyanates, part of the chain is pendant. For saturated acids, the whole acid becomes a pendant chain in the crosslinked network. Pendant chains do not support stress

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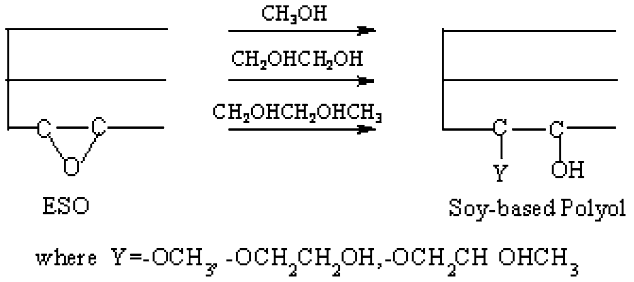


Scheme 1 Schematic of the reaction used for the synthesis of polyol

when the samples are under load and may act as plasticizers, but can significantly improve the hydrophobicity and the weather stability of polyurethanes.

In the present work, some soy-based polyols were synthesized by epoxy ring opening reaction of ESO with different alcohols of small molecular weight. These epoxy ring opening reactions gave a range of different structures, which when converted to polyurethanes imparted different properties to the final products. Scheme 1 shows the schematic of the reaction used for the synthesis of polyol.

Experimental

Materials

The refined SBO was kindly provided by Nanhai Oil Co. Ltd, epoxidized soybean oil was prepared according to our previous work [14] and the EOC (epoxy oxygen content) is 0.385 mol/100 g. Glacial acetic acid (99.5%), sodium carbonate, sodium hydroxide, hydrogen peroxide (30%), sulfuric acid, methanol, ammonia (30% in water), tetrafluoroboric acid (48% in water), 1,2-ethanediol and 1,2-propanediol used were all AR grade and tetrahydrofuran was HPLC grade. All were purchased from Guangzhou Chemical Reagent Co. and used as supplied.

Methods

The epoxy oxygen content (EOC) was determined using the AOCS method (Cd9-57). The hydroxyl value determinations were carried out according to ASTM D 1957–86. This method used a solution of acetic anhydride in pyridine and was generally expected to esterify quantitatively all of the OH groups in a polyol. The IR spectra were recorded on a Fourier transformation infrared (FTIR) spectrometer (IR Prestige-20, Shimadzu, Japan). The samples were prepared as thin films on KBr salts plates. The GPC chromatograms were acquired on a Waters model 1515 pump system equipped with a model 2414 differential refractometer using THF as the eluent operating at 1.00 mL/min at 40 °C. Three Styragel HR columns from Japan covering a molecular weight range of 1×10^3–10^6 Da were used and calibrated using five polystyrene narrow standards from BF Goodrich (Richfield, OH).

The viscosities of the samples were measured at different temperatures on a rheometer (MPJ-5S, Shanghai Dixue apparatus institute, Shanghai China) controlling the temperature very carefully (±0.1 °C). Thermal properties were measured on a differential scanning calorimeter (DSC 200PC NETZSCH, Germany) with a heating rate of 10 K/min from −80 to 100 °C. In the test process, nitrogen was used as the purge gas at a flow rate of 50 mL/min. Ten-milligramssamples were used in sealed aluminum pans for each analysis.

^{1}H-NMR spectra were recorded on a Bruker ARX-400 spectrometer (Bruker, Rheinstetten, Germany). The samples were dissolved in deuterated chloroform and ^{1}H-NMR spectra were obtained at room temperature. Electrospray ionization mass spectra were obtained on a LCQ Deca XP Max instrument (Thermo Finnigan, San Jose, CA). The samples were dissolved in methanol.

The tensile properties were measured according to ASTM D 882–97 on a tensile tester model RGB-1 from Reger instrument Co. Ltd (Shenzhen, China). The extension rate is 100 mm/min and five specimens were used for each sample. The reported results are an average of the five runs per sample.

Preparation of Polyol (1)

Epoxidized soybean oil was synthesized according to reference [13]. Polyol (1) was synthesized from ESO (100 g) with an EOC of 0.385 mol/100 g, by oxirane ring opening with refluxing methanol (136 g) in the presence of a tetrafluoroboric acid catalyst. The molar ratio of epoxy groups to methanol was 1:11. The concentration of the catalyst was 1% of the total weight of the ESO and methanol. Methanol and catalyst were added into a 500 ml three neck flask which equipped a refluxing column, a mechanical stirrer and a thermal meter. The flask was heated using a water bath. Epoxidized soybean oil was then added to the refluxing methanol and the catalyst. The reaction mixture was kept refluxing for 1 h. After cooling to room temperature to avoid hydrolysis during the neutralization process, ammonia (30% in water) was added to neutralize the catalyst. The solvent was removed on a rotary evaporator under a low vacuum at 60 °C for 0.5 h, followed by 95 °C for 1 h, respectively. The hydroxyl value of the products was 180.34 mg KOH/g and the yield was 98%.

Preparation of Polyol (2) and Polyol (3)

Polyol (2) and polyol (3) were synthesized from ESO (EOC 0.385 mol/100 g), by oxirane ring opening with 1,2-ethanediol and 1,2-propanediol, respectively, in the presence of a tetrafluoroboric acid catalyst at 95 °C. The molar ratio of epoxy groups to OH groups was 1:11. The concentration of the catalyst was 1% of the total weight of the ESO and alcohol. Alcohol and catalyst were placed in a 500-ml three neck flask which was equipped with a refluxing column, a mechanical stirrer and a thermal meter. The flask was heated using a water bath. Epoxidized soybean oil was then added to the mixture of the alcohol and the catalyst. The reaction mixture was kept at 95 °C for 2 h. After cooling to room temperature to avoid hydrolysis during the neutralization process, ammonia (30% in water) was added to neutralize the catalyst. The 1,2-ethanediol or 1,2-propanediol was extracted five times using 300 ml water each time. The sample was purified on a rotary evaporator under a low vacuum at 98 °C for 1.5 h. The hydroxyl values of polyol (2) and polyol (3) were 253.33 mg KOH/g and 289.31 mg KOH/g and the yield was 95, and 98%, respectively. The samples were transparent liquids at room temperature.

Preparation of Polyurethanes

Three cast PUs were prepared by mixing the soy polyol with 2,4-toluene diisocyanate (TDI) with a CNO/OH ratio of 1:1. The polyol and the isocyanate components were stirred for 2 min and then the mixture was poured into a mold and the unit was left under vacuum to remove bubbles (5 min at 60 °C). The samples were put in an oven for 24 h at 110 °C to complete the reaction and then cooled to room temperature and remolded.

Results and Discussion

FITR Analysis

The FTIR spectra of ESO and soy-based polyols are shown in Fig. 1. The ESO characteristic peaks at 823 and 833 cm^{-1} (indicated by an arrow), attributed to the epoxy group, disappeared after the epoxy group opening reaction. Also, there were new characteristic absorption peaks at 3,480 cm^{-1} in the spectrum of polyol (1), 3,419 cm^{-1} in the spectra of polyol (2) and polyol (3), respectively, attributed to the hydroxy groups. The intensity of the characteristic peak at 1,097 cm^{-1} was attributed to stretching of C–O bond associated with the hydroxy group, and that of polyol (3) was the highest, indicating that the number of hydroxy groups in polyol (3) was the highest among the samples.

GPC Analysis

The GPC chromatograms of ESO and the prepared soy-based polyols are shown in Fig. 2. A shoulder on the left-side appeared in the GPC chromatograms of the products, indicating that some oligomerization side reactions occurred during the ring opening reactions. Oligomerization occurred when the newly formed hydroxyl reacted with existing epoxy groups. The amount of multiple oligomer of polyol (2) was the largest among the products, because it was formed by primary hydroxyl and the reactivity of the primary hydroxyl is higher than that of the secondary hydroxyl. GPC analysis of ESO did not show the presence of oligomers. The retention time of the samples decreased in the following order: ESO > polyol (1) > polyol (2) > polyol (3), indicating that the molecular weight of the samples increased in the following order: ESO < polyol (1) < polyol (2) < polyol (3). This may be due to the molecular weight of the ring opener which is in the order: methanol < 1,2-ethanediol < 1,2-propanediol. Compared with the peaks of ESO, the peaks of the products did not broaden, indicating that these soy-based polyols kept the integrity of the triglyceride structures during the ring opening reaction. In conclusion, after epoxy opening reaction of ESO with methanol, 1,2-ethanediol and 1,2-propanediol, the hydroxyl group has been incorporated in the samples successfully.

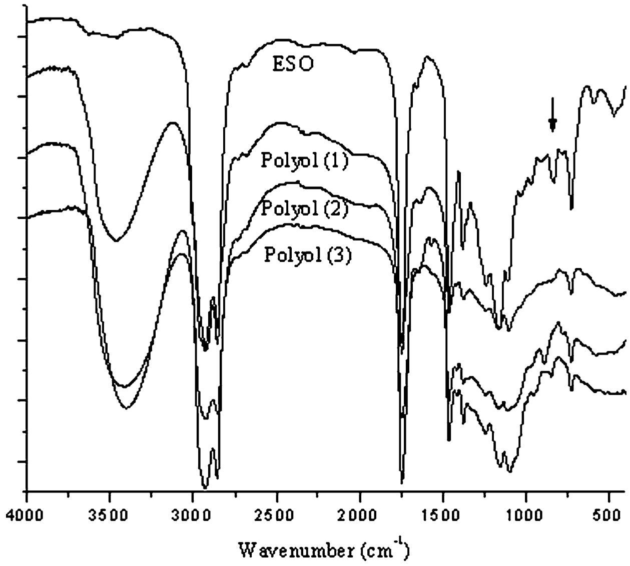


Fig. 1 FTIR spectra of ESO and soy-based polyols

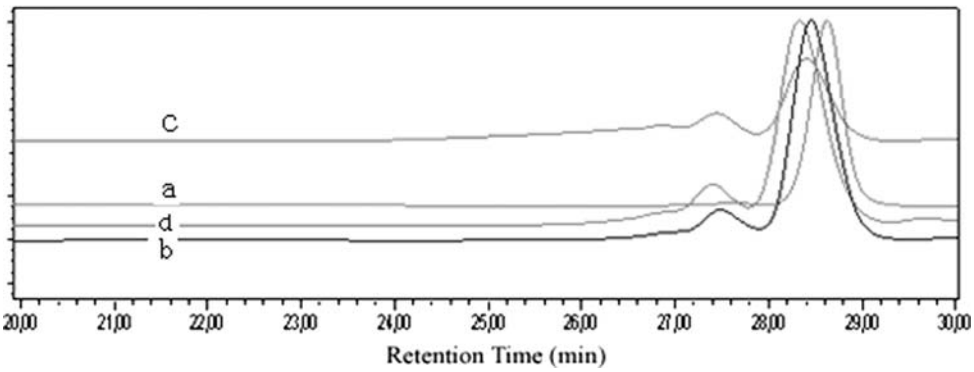
Rheological Behavior of Soy-Based Polyols

The rheological behavior of soy-based polyols as a function of temperature was also examined in the present work. The viscosities plotted against the reciprocal temperature, as described in Fig. 3, obeyed the Andrade dependence:

$$\eta = A \times e^{E/RT},$$

where A is a reference viscosity, E is the viscous-flow activation energy, R is the universal gas constant, and T the

Fig. 2 Chromatograms of ESO and soy-based polyols. **a** ESO, **b** Polyol (1), **c** Polyol (2), **d** Polyol (3)



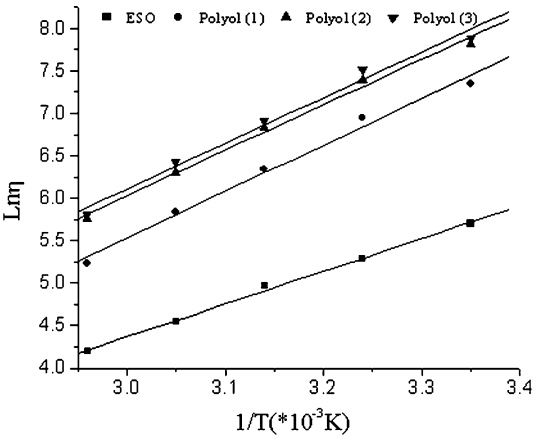


Fig. 3 Viscosity–temperature relationship for ESO and soy-based polyols

Table 1 Viscosity at 45 °C and the activation energy of the viscous-flow (E) for the SBO and soy-based polyols

Samples	Viscosity at 45 °C (mPa s)	E (kJ/mol)
ESO	144.6 (±1.5)	29.56 (±0.35)
Polyol (1)	567.0 (±1.6)	39.99 (±0.22)
Polyol (2)	935.5 (±2.3)	38.80 (±1.12)
Polyol (3)	1003 (±3.5)	49.88 (±1.36)

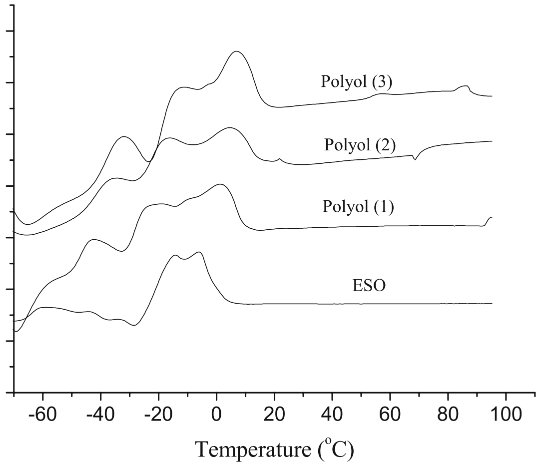


Fig. 4 Differential scanning calorimetry thermograms of ESO and soy-based polyols

Table 2 Melting points of SBO and soy-based polyols

Peak	Temperature (°C)			
	ESO	Polyol (1)	Polyol (2)	Polyol (3)
1	−58.8	−42.5	−34.6	−31.7
2	−14.1	−19.7	−16.5	−11.1
3	−6.1	1.0	4.7	6.9

absolute temperature (K). Activation energies were calculated from the slopes of these straight lines and are summarized in Table 1. The activation energies of the soy-based polyols were higher than those of ESO. The reason is that soy-based polyols form hydrogen bonds more easily than ESO. With an increase in the hydroxyl content, the viscosity of the soy-based polyols increased significantly at the same temperature. Because the reactivity of primary hydroxy groups is significantly higher than secondary hydroxy groups, polyol (2) forms oligomers more easily than polyol (1) and polyol (3) during the epoxy ring opening reaction, which leads to a decrease in the number of hydroxy groups. As a result, the viscosity of polyol (3) was higher than that of polyol (2). Polyols of industrial importance are commonly required to have low viscosity and high hydroxyl value.

Differential Scanning Calorimeter Analysis

The differential scanning calorimeter thermograms of the prepared soy-based polyols are depicted in Fig. 4. There are multiple melting point peaks in the samples, attributed to the different crystalline polymorphs. For example, there were three crystalline forms in the 18:0 triglyceride melt: at 54.9 °C for the α form (loosely hexagonally packed triglyceride), 64.0 °C for the β' form (a less stable crystal with orthorhombic packing) and 73.1 °C for the *β* form (the most stable triclinic subcell) [15]. The cooling (crystallization) rate of the samples was controlled at a constant value. Whereas the peak size was controlled by the cooling rate, and the physical properties of the soy-based polyols were related to the structural order and the physical state (above or below the melting point) of the samples, the physical state of the samples was largely determined by hydrogen bonding [12]. Compared with the differential scanning calorimeter thermograms of ESO, the melting point of the prepared soy-based polyols shifted to a higher temperature. Although the structural regularity of ESO was higher than that of the products, hydroxy groups could increase the intermolecular interactions and eventual

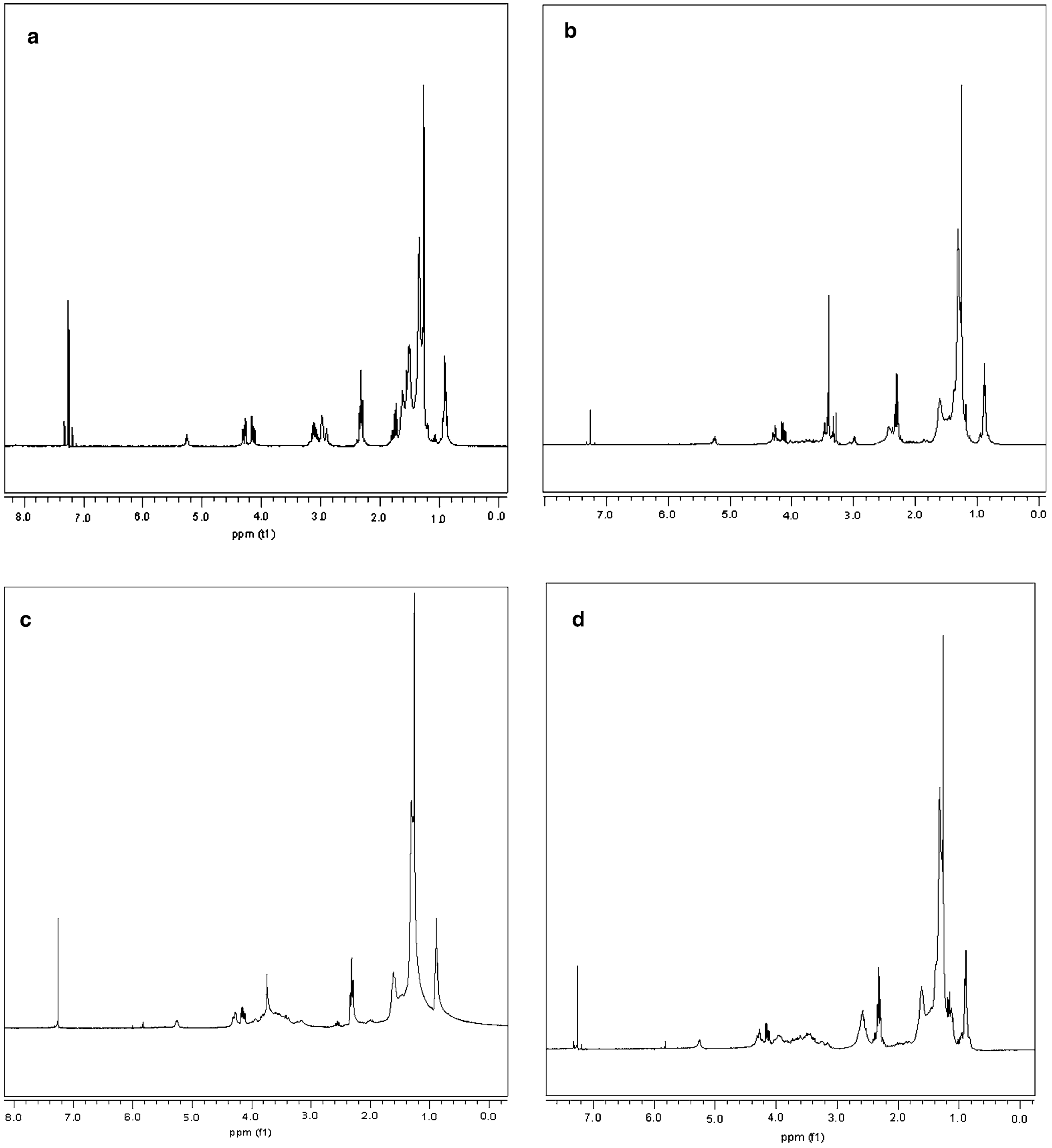


Fig. 5 **a** ^{1}H-NMR of ESO. **b** ^{1}H-NMR of polyol (1). **c** ^{1}H-NMR of polyol (2). **d** ^{1}H-NMR of polyol (3)

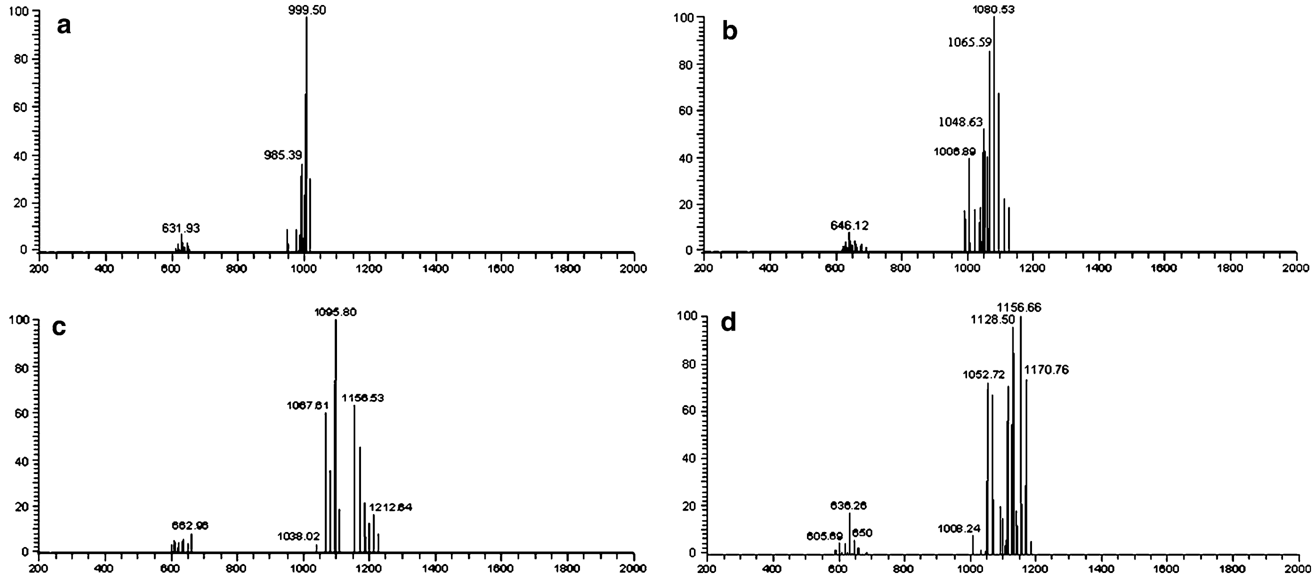


Fig. 6 **a** Mass spectrum of ESO. **b** Mass spectrum of Polyol (1). **c** Mass spectrum of Polyol (2). **d** Mass spectrum of Polyol (3)

transition into grease. As a result, among the products, the structural regularity of polyol (3) was the lowest, but the melting point was the highest and the melting point peaks were most clearly defined, indicating that the crystal structure of polyol (3) was the most compact [16]. The melting points of the samples are shown in Table 2.

^{1}H-NMR Analysis

Further confirmation of the soy-based polyol structure was obtained from the ^{1}H-NMR spectra in Fig. 5a–d. As can be seen from the ^{1}H-NMR spectrum of ESO (Fig. 5a), the epoxy protons are observed in the δ 3.0–3.2 ppm region. The methane protons of $–CH_2–\mathbf{CH}–CH_2–$ backbone at δ 5.1-5.3 ppm, methylene protons of $–\mathbf{CH_2}–CH–\mathbf{CH_2}–$ backbone at δ 4.0–4.4 ppm, $\mathbf{CH_2}$ protons adjacent to two epoxy group at δ 2.8–3.0 ppm, $–\mathbf{CH}–$ protons of the epoxy ring at δ 3.0–3.2 ppm, α-$\mathbf{CH_2}$ to >C=O at δ 2.2–2.4 ppm, α-$\mathbf{CH_2}$ to epoxy group at δ 1.7–1.9 ppm, β-$\mathbf{CH_2}$ to >C=O at δ 1.55–1.7 ppm, β-$\mathbf{CH_2}$ to epoxy group at δ 1.4–1.55 ppm, saturated methylene groups at δ 1.1–1.4 ppm and terminal $–\mathbf{CH_3}$ groups at δ 0.8–1.0 ppm region. This result is the same as A. Adhvaryu's result [17]. As can be seen from the ^{1}H-NMR spectra of polyols in Fig. 5b–d, the characteristic multiple peaks of epoxy groups at δ 3.0–3.2 ppm and δ 2.8–3.0 ppm, α-$\mathbf{CH_2}$ to epoxy group at δ 1.7–1.9 ppm, β-$\mathbf{CH_2}$ to epoxy group at δ 1.4–1.55 ppm in the spectrum of ESO, did not appear in the soy-based polyol spectra, indicating complete cleavage of the epoxy group after the epoxy group opening reaction. The new peak at δ 3.4–3.6 ppm is the protons of $–\mathbf{CH}–OH$ and the new peak at δ 3.3–3.4 ppm is the protons of $–\mathbf{CH}–O–CH_3$.

Table 3 Properties of soy-based PUs

Samples	OH value (mg KOH/g)	*Tg* by DSC (°C)	Tensile strength (MPa)
Polyol (1)	180.34	40	21.47 (±1.97)
Polyol (2)	253.33	75.8	38.04 (±1.58)
Polyol (3)	289.31	83.6	38.88 (±2.55)

It was apparent from the ^{1}H-NMR data that the hydroxylation of ESO progressed as expected to yield the desired polyols.

Figure 6a–d is the mass spectra of ESO and the polyols. As can be seen from the Figures, the main components at an MW of about 1,000 increase with the molecular weight of the ring opener. This result is the same as the GPC result. Apart from the main component at an MW of about 1,000, there was a small presence of diglycerides (MW about 600) as well as a variety of components differing in MW by a CH_2 group.

The Glass Transition Temperature and Tensile Strength of PUs

Three cast polyurethanes were prepared by mixing the soy polyol with 2,4-toluene diisocyanate (TDI) with an CNO/OH of 1:1. The glass transition temperature (*Tg*) and tensile strength at yield were summarized in Table 3. As seen from Table 3, the glass transition temperature and tensile strength increase with the increasing of OH value. This result suggests the properties of soy-based polyurethanes associate with the structure of soy-based polyol.

Conclusions

Three products were synthesized by ring opening of ESO (EOC 0.385 mol/100 g) with methanol, 1,2-ethanediol and 1,2-propanediol in the presence of a tetrafluoroboric acid catalyst. The ESO and the products were characterized by chemical and physical methods. The ranking based upon molecular weight, viscosity at the same temperature, viscous-flow activation energy and melting point was: ESO $<$ polyol (1) $<$ polyol (2) $<$ polyol (3).

Acknowledgments The authors are grateful to the Natural Science Foundation of Guangdong Province (No. 06025028) for financial support. Thanks Dr. David E. Finlow for the English correction.

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