Polyurethane Networks from Different Soy-Based Polyols by the Ring Opening of Epoxidized Soybean Oil with Methanol, Glycol, and 1,2-Propanediol

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ABSTRACT: A series of polyols with a range of hydroxyl (OH) numbers based on soybean oil and epoxidized soybean oil were prepared by oxirane ring opening with methanol, glycol, and 1,2-propanediol. The polyols, with average functionalities varying from 2.6 to 4.9, were characterized. Novel cast polyurethane resins were synthesized from these polyols and 2,4-toluene diisocyanate. The sol fraction of the network decreased as the OH number of the polyol from which it was synthesized increased. None of the samples were completely soluble. The crosslinking density of the polyurethanes correlated directly with the functionality of the polyols. The thermal and mechanical properties of the cast resins were characterized with differential scanning calorimetry and thermogravimetry. The glass-transition temperature increased with the OH number increasing, and the thermal stability of the resins was slightly decreased with the OH number increasing. The tensile strength at break increased with the OH number increasing. Polyurethanes prepared from polyols with OH numbers higher than 170 mg of KOH/g were glassy, whereas those with OH numbers below that value were rubbery. Glassy polyurethanes displayed decent mechanical strength, whereas rubbery samples showed relatively poor elastic properties and were characterized by lower strength. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 125–131, 2009

Key words: biomaterials; networks; polyurethanes; renewable resources; resins

INTRODUCTION

Polyurethanes (PUs) have been successfully employed in many diverse applications such as elastomers, foams (flexible, semirigid, and rigid), coatings, adhesives, fibers, thermosets, and thermoplastics.[1] Vegetable-oil-based PUs from renewable resources are gaining in popularity because of some attractive properties related to the specific structures of the oils as well as concerns about the environment and sustainability. Vegetable oils are abundant and inexpensive raw materials offering some economic advantages.[2]

There has been renewed interest recently in developing new polymers from soybean and other plant oils.[3] Wool and coworkers[4–8] developed a family of chemically modified oils that can be polymerized with free-radical initiators into rigid composites, rubbers, and adhesives. Larock and coworkers[9–14] reported the preparation of polymers ranging from rubbers to hard plastics through the cationic polymerization of a variety of oils with petroleum-based comonomers such as styrene, divinyl benzene, and dicyclopentadiene in the presence of boron trifluoride diethyl etherate as the initiator. Petrovic and coworkers[2,15–22] recently developed methods for preparing soy polyols from epoxidized soybean oil (ESO) and for further reacting these with diisocyanates to form PUs. Such materials have applications as rigid materials or as foams for insulation, carpet backing, and so forth. Liu and coworkers[23–25] prepared soft-to-rigid composites of polyamine-cured ESO with fillers and fibers. Shogren[26] prepared citric acid cured ESO resins for use as coatings and showed that these disintegrate over time during soil burial.

Although many types of vegetable oils have been tested and reported for polyol and PU applications, soybean oil (SBO) is the most promising for partially replacing petroleum to make polyols because of its volume and price stability. Many innovative chemical and/or biological approaches are possible for converting SBO into polyols, but limited attention has been paid to the effects of different alcohols of low molecular weights, used as ring-opening reagents with ESO, on the properties of polyols and resulting PUs.[27]
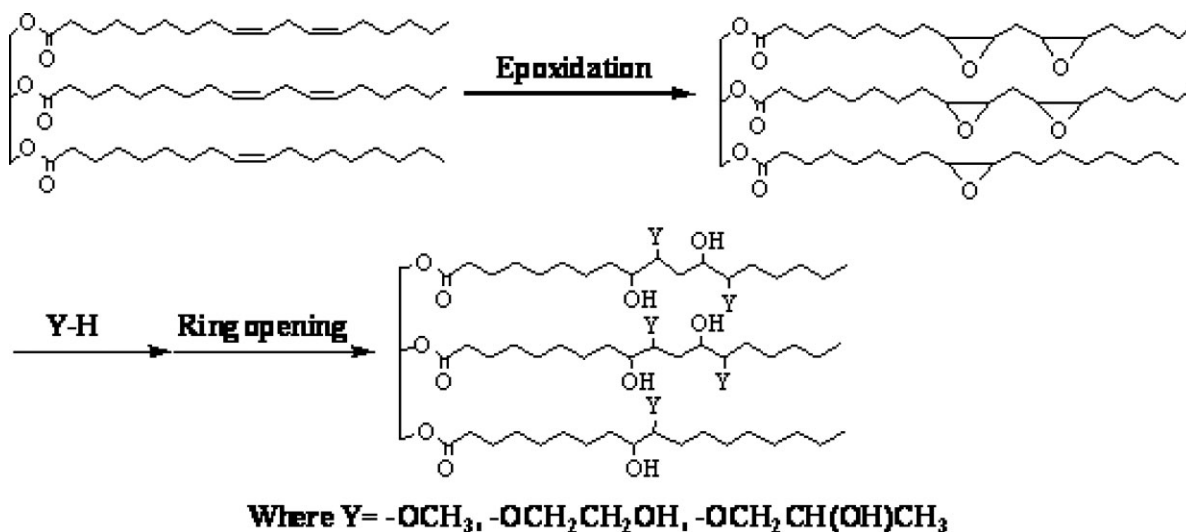
Figure 1 Schematic representation of the ring-opening reactions of ESO with various reactants [Y is the rest of the methanol, ethylene glycol, and 1,2-propane diol; i.e., $Y = -OCH_3$, $-OCH_2CH_2OH$, and $-OCH_2CH(OH)CH_3$].

In this study, a series of polyols with a range of hydroxyl (OH) numbers based on SBO and ESO were prepared by oxirane ring opening with methanol, glycol, and 1,2-propanediol. The general scheme for the epoxy group conversions is given in Figure 1.

It is obvious that all of these reactions yield a range of polyol structures that may have properties different from those of the final product. When these polyols are crosslinked with isocyanates, part of the chain is pendent. For saturated acid chains in the polyols (ca. 11% palmitic acid and 4% stearic acid in the glyceride), the whole acid chain becomes a pendent chain in the crosslinked network. Pendent chains do not support stress when a sample is under a load and may act as plasticizers, but this could result in their different thermal and mechanical properties. Our objective was to examine the effects of the structures of six types of polyols on their properties and the properties of the resulting PUs.

All polyols were fully characterized with Fourier transform infrared (FTIR) spectrometry and by the measurement of the OH number. The objective of this work was to synthesize cast PU resins from polyols reacted with 2,4-toluene diisocyanate (TDI). Swelling in toluene was used to estimate the crosslinking density. The effect of the OH number on the thermal and mechanical properties of the resins was studied with differential scanning calorimetry (DSC), thermogravimetry (TG), and mechanical tests.

EXPERIMENTAL

Materials

Refined SBO with an iodine value 127.23 g of I_2/100 g of oil and ESO with a 6.2% oxygen content and an iodine value of 1.62 g of I_2/100 g of oil were kindly provided by Nanhai Oil Co., Ltd. (Guangzhuo,

China). Analytical-reagent-grade glacial acetic acid (99.5%), sodium carbonate, sodium chloride, hydrogen peroxide (30%), sulfuric acid (98%), methanol, ammonia (30%), tetrafluoboric acid (48%), glycol, 1,2-propanediol, and TDI were all purchased from Guangzhou Chemical Reagent Co. (Guangzhou, China). They were used as supplied.

Methods

The OH numbers of the polyols were determined according to the ASTM E 1899-97 standard test method for OH groups via a reaction with p-toluene-sulfonyl isocyanate (TSI) and potentiometric titration with tetrabutylammonium hydroxide. The IR spectra were recorded on an FTIR spectrometer (IR Prestige-21, Shimadzu, Kyoto, Japan). The samples were prepared as thin films on KBr salt plates.

Thermal properties were measured on a differential scanning calorimeter (DSC 200PC, Netzsch, Selb, Germany) at a heating rate of 20 K/min from −80 to 120°C, and nitrogen was used as a purge gas at a 50 mL/min flow rate. Samples (10 mg) were placed in sealed aluminum pans for each analysis. The analysis of the TG behavior of the samples was performed on a TG instrument (TG STA 409PC, Netzsch) at a heating rate of 10 K/min from 50 to 700°C, and nitrogen was used as a purge gas at a 30 mL/min flow rate. Approximately 10-mg samples were used in each test. Swelling experiments were performed on square, 1–2-mm-thick samples weighing between 1 and 2 g. The samples were immersed in 50 mL of toluene for 2 weeks at 25°C. The sample weight was measured periodically, and the change with time was recorded. After reaching the maximum weight, the samples started losing weight because of the extraction of the sol fraction until constant values were obtained. The solvent

was replaced three times after the maximum swelling was obtained. The samples were dried, and the weight of the gel fraction was recorded. The sol fraction was the difference between the initial weight and gel weight divided by the initial weight expressed as a percentage. The tensile properties were measured according to ASTM D 882-97 on an RGB-1 tensile tester from Reger Instrument Co., Ltd. (Shenzhen, China). The extension rate was 100 mm/min, and five specimens were used for each sample. The impact properties were measured according to GB/T 2571-1995 on an XJJ-5 impact tester from Chengde Instrument Co., Ltd. (Chengde, China).

Synthesis of SBO-based polyols

SBO was epoxidized with Dai et al.'s method.[28] A series of ESOs with different epoxy values were obtained, and they were used to synthesize the SBO-based polyols. The polyols were prepared by complete epoxy ring opening in ESO with methanol in the presence of a tetrafluoboric acid catalyst at 65°C. The molar ratio of epoxy groups to OH was 1 : 11. The concentration of the catalyst was 0.2% of the total weight of the reaction mixture. Methanol and the catalyst were added to a 500-mL, three-necked flask equipped with a refluxing column, a mechanical stirrer, and a thermometer. The flask was heated with a water bath. ESO was then added to the mixture of the refluxing methanol and the catalyst. The reaction mixture was kept at 65°C for 2 h. After cooling to room temperature to avoid hydroxylation during the neutralization process, ammonia (30%) was added to neutralize the catalyst. The alcohol was extracted with water. The aqueous phase was then removed, and the sample was purified on a rotary evaporator under a low vacuum at 98°C for 1.5 h. The OH numbers of the polyols were determined according to the ASTM E 1899-97 standard test method for OH via a reaction with TSI and potentiometric titration with tetrabutylammonium hydroxide.

When methanol was substituted by glycol or 1,2-propanediol, the ring-opening reaction temperature should have been 98°C. The other procedure was the same as that previously mentioned.

Synthesis of ESO-based polyols[29]

The ESO-based polyols were synthesized from ESO with an oxygen content of 6.2% by oxirane ring opening with methanol, glycol, and 1,2-propanediol. The process was just a reference.[29]

Synthesis of PUs[30]

Twenty-four PUs were prepared via the mixing of the polyol with TDI with an NCO/OH molar ratio of 1.1 : 1. The polyol and the isocyanate components were stirred for 2 min, and then the mixture was poured into a mold; the unit was left *in vacuo* to evacuate bubbles (5 min at 60°C). The sample was put into an oven for 24 h at 110°C to complete the reaction. The sample was then cooled to room temperature and remolded.

RESULTS AND DISCUSSION

Characterization of the polyols

The reaction for the preparation of polyols through the epoxidation of SBO followed by ring opening is shown in Figure 1. The OH numbers and iodine values of the polyols are presented in Table I. SBO-Met is the polyol based on the epoxidation of SBO followed by ring opening of methanol, SBO-Gly is the polyol based on epoxidation of SBO followed by ring opening of glycol, and SBO-Prop is the polyol based on epoxidation of SBO followed by ring opening of 1,2-propanediol. The OH number of the polyols increases with the epoxidation time of SBO, whereas the iodine value decreases. This result shows that there still are double bonds in the polyol molecules, and this may result in the rubbery properties of PU. The chemical and physical properties of the ESO-based polyols and resins are presented in Table II. ESO-Met is derived from ESO with an oxygen content of 6.2% by oxirane ring opening with methanol, ESO-Gly is derived from ESO with an oxygen content of 6.2% by oxirane ring opening with glycol, and ESO-Prop is derived from ESO with an oxygen content of 6.2% by oxirane ring opening with 1,2-propanediol.

The FTIR spectra of SBO, ESO, SBO-based polyols, and ESO-based polyols are shown in Figure 2. The characteristic peak at 3012 cm^{-1} was attributed to the C—H stretching of SBO C=C—H in the spectra of SBO, SBO-Met148, and SBO-Gly187. The ESO characteristic peaks at 823 and 846 cm^{-1}, attributed to the epoxy group, disappeared after the epoxy group opening reaction. Also, there were new characteristic absorption peaks at about 3400 cm^{-1} in the spectrum of the polyol attributable to the OH group. The intensity of the characteristic peak at 1097 cm^{-1} was attributed to the stretching of the C—O bond associated with the ether groups. The peak at 1097 cm^{-1} for ESO-Prop246 was the highest, and this indicated that the number of OH groups in ESO-Prop246 was the highest among the samples.

Swelling of the networks in toluene

The results of the swelling experiments are shown in Tables I and II. None of the samples were completely soluble. The higher the OH number was of the polyol, the higher the sol fraction was of the PU. This is because the sol fraction of the higher

TABLE I
Properties of Polyols and PUs from SBO

SBO-Mets	Epoxidation time (h)	4	5.5	6	7
	Polyol OH number (mg of KOH/g)	148	155	161	174
	f_n	2.64	2.78	2.91	3.18
	Iodine value (g of I_2/100 g of oil)	35.71	28.52	21.13	16.29
	Sol fraction (%)	3.24	2.14	1.71	1.13
	Tensile strength at break (MPa)	6.37 ± 0.34	10.36 ± 0.68	14.02 ± 0.77	20.24 ± 0.90
	Elongation at break (%)	184.00 ± 5.07	122.00 ± 3.85	49.00 ± 1.72	31.00 ± 1.23
SBO-Glys	Epoxidation time (h)	2.5	3	4	5.5
	Polyol OH number (mg of KOH/g)	187	203	209	226
	f_n	3.35	3.68	3.81	4.18
	Iodine value (g of I_2/100 g of oil)	39.51	33.74	24.94	21.08
	Sol fraction (%)	3.14	2.06	1.71	0.83
	Tensile strength at break (MPa)	19.57 ± 0.75	25.40 ± 0.60	27.80 ± 0.72	33.21 ± 1.62
	Elongation at break (%)	18.28 ± 1.72	19.60 ± 0.92	15.18 ± 1.13	14.57 ± 1.61
	Impact strength (kJ/m^2)	29.52 ± 2.96	33.89 ± 2.16	39.65 ± 2.12	41.35 ± 4.38
SBO-Props	Epoxidation time (h)	2.5	3	4	5.5
	Polyol OH number (mg of KOH/g)	211	220	233	237
	f_n	3.80	4.18	4.49	4.58
	Iodine value (g of I_2/100 g of oil)	38.23	34.72	24.52	21.60
	Sol fraction (%)	1.18	0.80	0.48	0.42
	Tensile strength at break (MPa)	26.44 ± 0.76	33.32 ± 1.20	36.88 ± 3.44	38.14 ± 0.95
	Elongation at break (%)	18.40 ± 1.48	16.92 ± 1.98	17.37 ± 0.76	17.37 ± 0.89
	Impact strength (kJ/m^2)	40.03 ± 2.87	42.23 ± 2.39	40.31 ± 4.01	38.58 ± 1.03

Functionality f_n was calculated on the basis of OH under the assumption of total conversion.

functionality polyols has a greater chance of becoming incorporated into the network on account of more reactive sites in comparison with a lower functionality polyol. As shown in Tables I and II, ESO-Met144 with the lowest functionality contained about 6 wt % sol, and ESO-Prop246 with the highest functionality offered sol fractions of less than 0.2%.

Thermal and mechanical properties of PUs

The properties of PUs are related to the crosslinking densities of the networks, which correlate directly with the OH number of the polyols. Thus, the properties are discussed as a function of the OH number of the polyols.

TABLE II
Properties of Polyols and PUs from ESO

ESO-Mets	Polyol OH number (mg of KOH/g)	144	160	168	174
	f_n	2.60	2.92	3.09	3.21
	Oxygen content (mol/100 g)	0.060	0.031	0.028	0.010
	Sol fraction (%)	5.44	2.69	2.47	1.64
	Tensile strength at break (MPa)	5.42 ± 0.63	11.31 ± 0.84	14.96 ± 1.21	21.47 ± 1.97
	Elongation at break (%)	110.71 ± 6.86	71.70 ± 3.46	36.69 ± 2.06	31.00 ± 1.89
ESO-Glys	Polyol OH number (mg of KOH/g)	195	205	217	240
	f_n	3.63	3.84	4.10	4.60
	Oxygen content (mol/100 g)	0.055	0.023	0.021	0.019
	Sol fraction (%)	2.24	1.08	0.88	0.80
	Tensile strength at break (MPa)	24.01 ± 0.20	28.57 ± 2.56	30.85 ± 2.12	38.04 ± 1.58
	Elongation at break (%)	16.86 ± 2.06	19.76 ± 1.26	10.64 ± 0.97	11.14 ± 1.53
	Impact strength (kJ/m^2)	32.81 ± 1.41	34.67 ± 0.64	38.66 ± 0.48	36.43 ± 2.20
ESO-Props	Polyol OH number (mg of KOH/g)	200	215	235	246
	f_n	3.84	4.18	4.64	4.90
	Oxygen content (mol/100 g)	0.039	0.022	0.019	0.013
	Sol fraction (%)	0.83	0.63	0.46	0.15
	Tensile strength at break (MPa)	29.84 ± 1.40	33.04 ± 1.19	37.20 ± 0.82	38.88 ± 2.55
	Elongation at break (%)	16.65 ± 1.60	15.88 ± 1.87	10.80 ± 0.24	10.14 ± 0.61
	Impact strength (kJ/m^2)	37.48 ± 1.52	39.94 ± 3.98	40.18 ± 1.92	36.00 ± 2.84

Functionality f_n was calculated on the basis of OH under the assumption of total conversion.
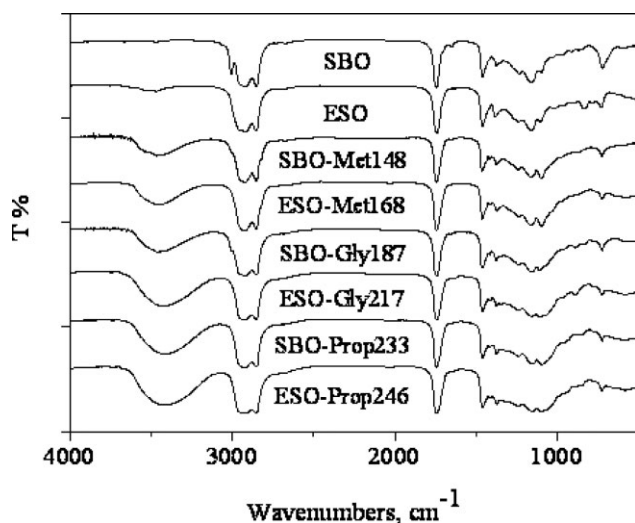
Figure 2 FTIR spectra of the polyols.

The properties of the PUs are listed in Tables I and II. Samples made from polyols with OH numbers higher than 174 mg of KOH/g were glassy, whereas all others were rubbery at room temperature. Glassy PUs prepared with polyols having OH numbers higher than 174 mg of KOH/g displayed moderate strength.

The DSC experiments also provided the glass-transition trends for these networks, which are shown in Figure 3. The glass-transition temperature (T_g) of the corresponding PU over the range of OH numbers correlates directly with the functionality of the polyols. As one can readily observe, SBO-Gly, ESO-Gly, SBO-Prop, and ESO-Prop fall closely on the trend. Despite the use of different ring-opening reactants to produce the polyols, the results still offer a linear relationship.
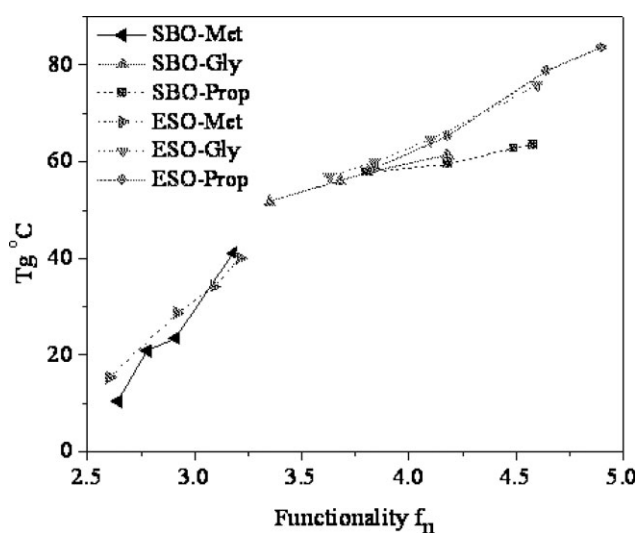

Figure 3 Effect of the OH number of polyols on the T_g values of PUs determined by DSC.
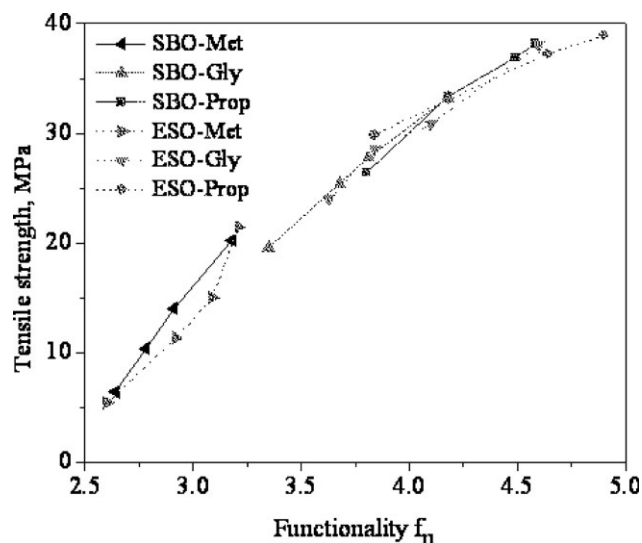

Figure 4 Effect of the functionality of polyols on the tensile strength of PUs.

Figure 3 displays the relationship between the functionality and T_g as expected from the Fox–Losheak equation[31] relating the crosslinking density and T_g:

$$T_g = T_{g\infty} + \frac{K}{M_c} = T_{g\infty} + kv \tag{1}$$

where $T_{g\infty}$ is the glass transition of the linear polymer of the same structure, M_c is the average molecular weight between crosslinks, v is the number of crosslinks per unit of volume (density/M_c), and K and k are constants for a given system. It can be shown that for a complete conversion, v is directly proportional to the functionality.

The tensile strength of the PUs increased with the crosslinking density and functionality, and the elongation decreased with the crosslinking density and functionality, as displayed in Figure 4. The strength was moderate for the sample with an OH number of 174 mg of KOH/g, and the strength was higher than 25 MPa for samples having an OH number of 200 or greater.

The elongation at break for the elastomer samples was relatively low, and this indicated that they were fairly imperfect networks because of the low average functionality of the polyols and the absence of oligomers.

As shown in Figure 4, the PUs made from SBO-Gly, ESO-Gly, SBO-Prop, and ESO-Prop, as expected, displayed higher tensile strength (20–38 MPa). They also displayed lower elongation at break (10–20%), as shown later in Figure 6. This was due to the high T_g values of the PUs and the higher average functionality of the polyols. The tensile strength of the PUs increased with the crosslinking density and functionality, and the elongation decreased with the crosslinking density and functionality.
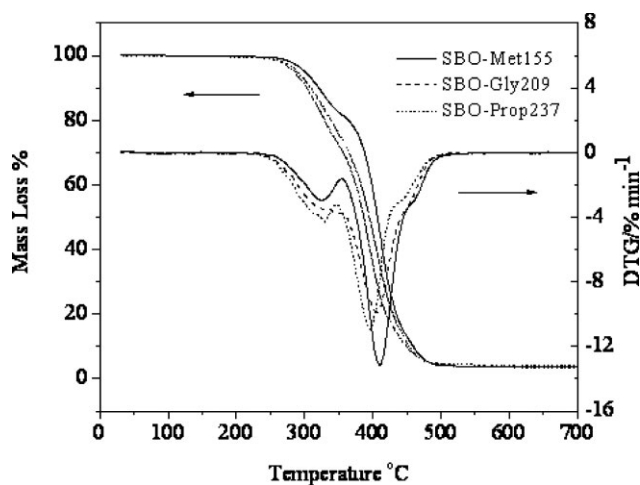
Figure 5 TG curves of cast PU resins made from SBO-based polyols in nitrogen (DTG = differential thermogravimetry).

As shown in Tables I and II, SBO-Gly and SBO-Prop displayed higher impact strengths than ESO-Gly and ESO-Prop. This could be attributed to the residual double bonds. The impact strength of the corresponding PUs over the range of OH numbers was affected not only by the crosslinking density but also by the high content of nonfunctional species acting as plasticizers. The impact strength of cast PU resins prepared from SBO-Gly226, SBO-Prop220, and ESO-Prop235 was higher than 40 kJ/m^2.

PUs generally have relatively low thermal stability. Three mechanisms of decomposition of urethane bonds have been proposed:[32]

1. Dissociation to isocyanate and alcohol:
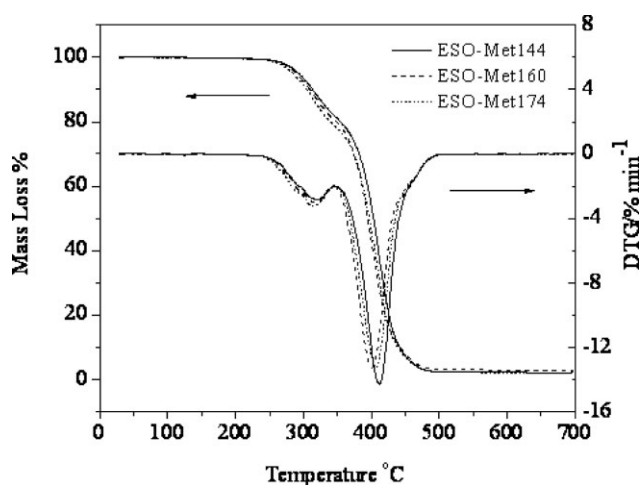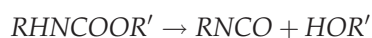
$$RHNCOOR' \rightarrow RNCO + HOR'$$

Figure 6 TG curves of cast PU resins made from ESO-Mets in nitrogen (DTG = differential thermogravimetry).
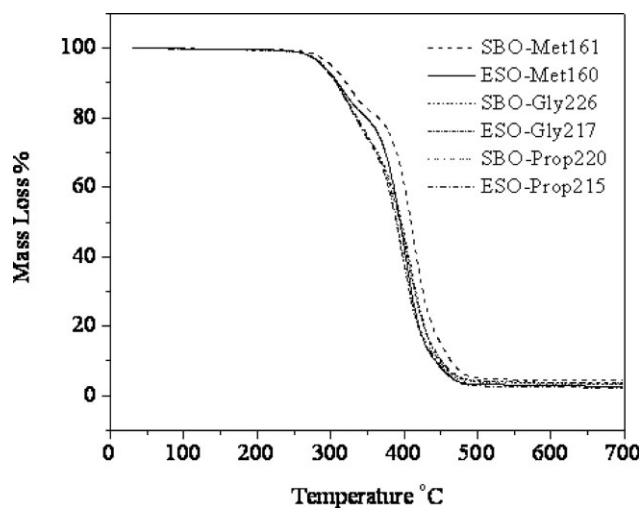
Figure 7 TG curves of cast PU resins in nitrogen.

2. Formation of a primary amine and olefin:

$$RHNCOOCH_2CH_2R' \rightarrow RNH_2 + CO_2 + R'CH = CH_2$$

3. Formation of a secondary amine:

$$RHNCOOR' \rightarrow RHNR' + CO_2$$
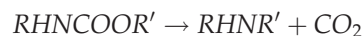
All three reactions may proceed simultaneously. PUs from vegetable-oil-based polyols with secondary OHs have been found to start degradation below 300°C with the loss of carbon dioxide from the urethane bond,[32] and this process is faster in PUs from secondary OHs as in our PUs. The thermal stability of PUs as measured by the initial weight loss (Figs. 5 and 6) shows a good correlation with the OH number of polyols, increasing with decreasing OH numbers but increasing with double bonds in the SBO-based polyols and with the epoxy content in the ESO-Mets. The iodine values of SBO-Met155, SBO-Gly209, and SBO-Prop237 were 28.52, 24.94, and 21.6 g of I$_2$/100 g of oil, respectively. The oxygen contents of ESO-Met144, ESO-Met160, and ESO-Met174 were 0.06, 0.031, and 0.01 mol/100 g of oil, respectively. The degradation of PUs with lower OH numbers was also faster at higher temperatures, leaving less char residue, possibly because of the lower crosslinking density and lower TDI content. It appears that the residual epoxy groups are good heat stabilizers, although the precise mechanism is not clear.

Figure 7 shows that the onset of degradation was about the same in all the polymers, but the initial loss of about 5% was higher in samples with higher double-bond contents and subsequently lower

crosslinking densities. The thermal stability of PUs from SBO-Met, as measured by the initial weight loss, was higher than that of PUs from ESO-Met, possibly because of the residual epoxy groups. The degradation of PUs with lower OH numbers was also faster at higher temperatures, leaving less char residue, possibly because of the lower crosslinking density and lower TDI content.

CONCLUSIONS

In this work, a series of polyols with a range of OH numbers based on SBO and ESO were prepared by oxirane ring opening with methanol, glycol, and 1,2-propanediol. The polyols, with average functionalities varying from 2.6 to 4.9, were characterized. These polyols were used to prepare PUs through their reaction with TDI and the application of heat to promote curing. The sol fraction of the network decreased with the OH number of the polyols. None of the samples were completely soluble. The crosslinking density of the PUs correlated directly with the functionality of the polyols. The PUs prepared from polyols with OH numbers greater than 170 mg of KOH/g were glassy, whereas those prepared from polyols with OH numbers less than 170 were rubbery. Glassy PUs displayed decent mechanical strength, whereas rubbery samples showed relatively poor elastic properties characterized by lower strengths. The cast PU resin prepared from ESO-Prop246 appeared as a rigid plastic with a T_g of 83.6°C. The cast resin could be molded into electro-insulating components.

The tensile strength of the PUs increased with the OH number increasing. However, the elongation and thermal stability of the PUs decreased with the OH number increasing. This could be caused by the low reduced crosslinking density of the resins due to the lower OH value of the polyols. The impact strength of the cast PU resins prepared from SBO-Gly226, SBO-Prop220, and ESO-Prop235 was higher than 40 kJ/m^2. The advantages of these PUs are their low cost, availability from a renewable natural resource, and possible biodegradability.

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