

Polyols and Polyurethanes Prepared from Epoxidized Soybean Oil Ring-Opened by Polyhydroxy Fatty Acids with Varying OH Numbers

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ABSTRACT: Bio-based polyols from epoxidized soybean oil and different fatty acids were successfully prepared using a solvent-free method in order to investigate the effect of the polyols' OH numbers on the thermal and mechanical properties of the polyurethanes prepared using them. Epoxidized soybean oil/epoxidized linseed oil was ring-opened by methanol/glycol followed by saponification to prepare polyhydroxy fatty acids. These fatty acids and epoxidized soybean oil were then used for further solvent-free ring-opening reactions with DBU as catalyst, which facilitated the carboxylic ring-opening. Gel permeation chromatography revealed that a molar ratio of carboxylic acid from polyhydroxy fatty acids and epoxy group of 0.5 : 1 resulted in optimized polyols containing the smallest amounts of residual starting materials. The obtained polyols had varying OH numbers and the acquired polyurethane films were comprehensively characterized. With increasing OH number of the polyols the PUs displayed an increase in crosslinking density, glass transition temperature (T_g), tensile strength and Young's modulus, and a decrease in elongation and toughness. This work provides Supporting Information on the effect of OH number of polyols obtained via a solvent-free ring-opening method on the mechanical and thermal properties of polyurethanes, of particular interest when designing PU products for specific purposes. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41213.

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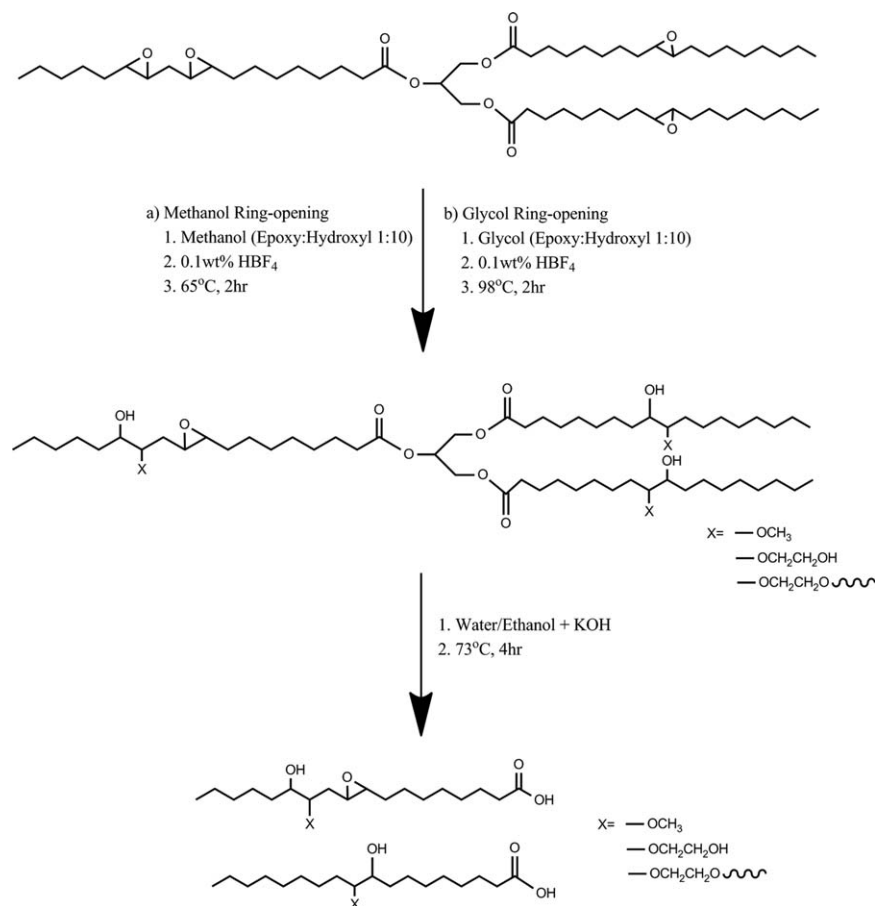
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INTRODUCTION

Polyurethanes (PUs), commercially available first in 1954, have been employed in a wide range of applications, such as coatings, adhesives, sealants, foams, elastomers, and others.¹ Polyurethane is known for its recurring urethane linkages in the main chain and is commonly synthesized by mixing two components: one hydroxyl-bearing monomer and a monomer with isocyanate groups. As the available choices of poly-functional isocyanates are relatively limited, significant research and development effort has been spent on polyols for the preparation of polyurethane with desired properties. The soaring price of crude oil and increasing environmental concerns spurred the exploration of bio-renewable alternatives for future plastic development in both academia and industry. Considering the fact that polyol contributes the majority of the weight of polyurethane, makes the full or partial substitution of polyols from bio-renewable resources in order to increase the bio-content of PUs a promising approach.

Vegetable oil has attracted increasing attention as one of the most promising options because of its ready availability, rela-

tively low cost, environmental sustainability, and low ecotoxicity. Vegetable oils, mainly triglycerides constituted by glycerol and three fatty acid chains, typically contain unsaturated carbon-carbon double bonds that are available for modification to form more reactive functional groups.² Epoxidation of double bonds followed by oxirane ring opening is commonly employed to graft attempted functional groups onto the vegetable oil molecules. Epoxidation is easily realized by *in situ* oxidation with peracids formed by a reaction of hydrogen peroxide with formic or acetic acid and catalysts with yields of 75–90%.³ Alcohols,^{4,5} amines,^{6,7} carboxylic acids,⁸ halogenated acids,⁹ and others have been reported as effective agents in the subsequent ring-opening step. Miao et al.¹⁰ successfully obtained polyols by ring-opening epoxidized soybean oil with isopropanol amine and hydrochloride. The effect of reaction time and temperature on the structure of the obtained polyols was studied thoroughly. Wang et al.⁴ prepared polyols by using methanol, glycol and 1,2-propanediol to ring open epoxidized soybean oil and studied the impact of their OH number on polyurethane properties. The reaction protocol was used for the preparation of fatty



Scheme 1. Preparation of fatty acids.

acids in the study presented here. Recently, a solvent-free method for the preparation of polyol from castor oil based fatty acid (COFA) and epoxidized soybean oil was published.⁸ This novel, green method is worth further systematic investigation, in particular the effect of fatty acids with different OH numbers on the properties of polyols and the resulting polyurethanes.

In this work, epoxidized soybean oil and epoxidized linseed oil were used as the starting materials and ring-opened by methanol and glycol. The OH numbers of the obtained fatty acids varied between 167.1 mg/KOH and 245.2 mg KOH/g while the fatty acids had similar acid numbers. Subsequently, the different fatty acids were used to produce polyols utilizing the solvent-free method reported in Ref. 8, where the molar ratio of carboxylic acid in fatty acid to epoxy group in epoxidized soybean oil was kept at 0.5 : 1. This molar ratio was determined as optimum by GPC, because it resulted in the least amount of residual unreacted epoxidized soybean oil and fatty acid. In addition, the OH numbers of the obtained polyols increased with the OH numbers of the fatty acids. Fatty acids and polyols were characterized by proton nuclear magnetic resonance (¹H NMR), Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and rheometry to determine their fundamental properties. Subsequently, the polyols were used to produce polyurethanes and the mechanical and thermal properties of their respective cast films were studied by differen-

tial scanning calorimetry (DSC), dynamic mechanical analysis (DMA), ethanol absorption and uptake, thermogravimetric analysis (TGA), and tensile tests. It was concluded that the crosslinking densities increased with increasing OH numbers of the polyols, which contributed to an increase in Young's modulus, tensile strength, and glass transition temperature (*T_g*).

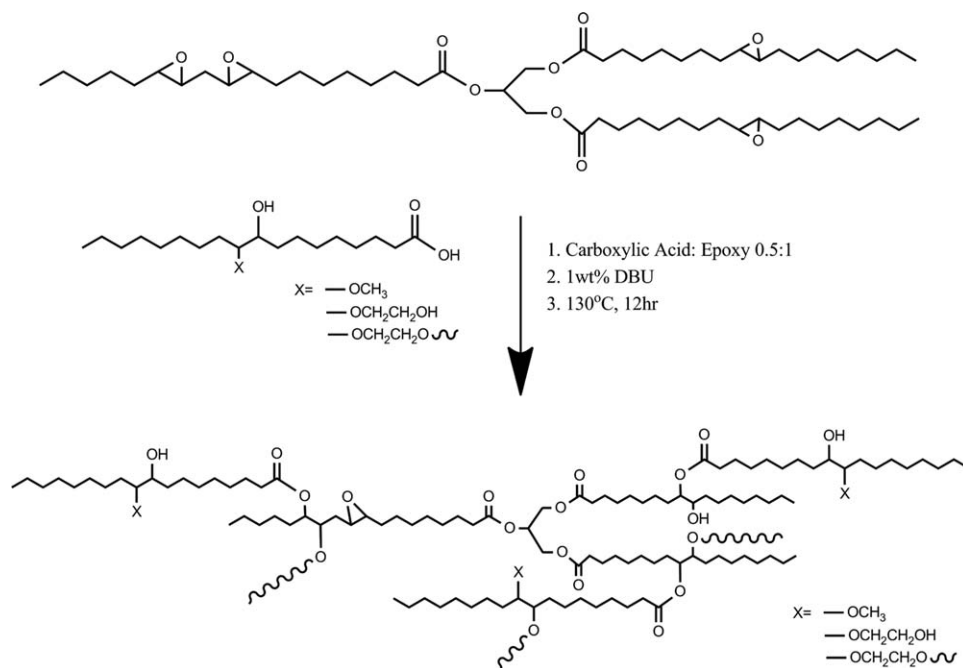
EXPERIMENTAL

Materials

Epoxidized soybean oil (ESBO) was purchased from Scientific Polymer, New York, NY. Epoxidized linseed oil (ELO) was kindly provided by American Chemical Service, Griffith, IN. Magnesium sulfate (MgSO₄), potassium hydroxide (KOH), methanol, ethylene glycol, hydrochloric acid (HCl), and methyl ethyl ketone (MEK) were purchased from Fisher Scientific Company (Fair Lawn, NJ). Tetrafluoroboric acid solution (48% in H₂O), isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were obtained from Sigma-Aldrich (Milwaukee, WI). Ethanol was purchased from Decon Laboratories, King of Prussia, PA. All materials were used as received without further purification.

Preparation of Fatty Acids

The initial step was the preparation of four different fatty acids from epoxidized soybean oil ring opened by (1) methanol and (2) glycol, and epoxidized linseed oil ring opened by (3)



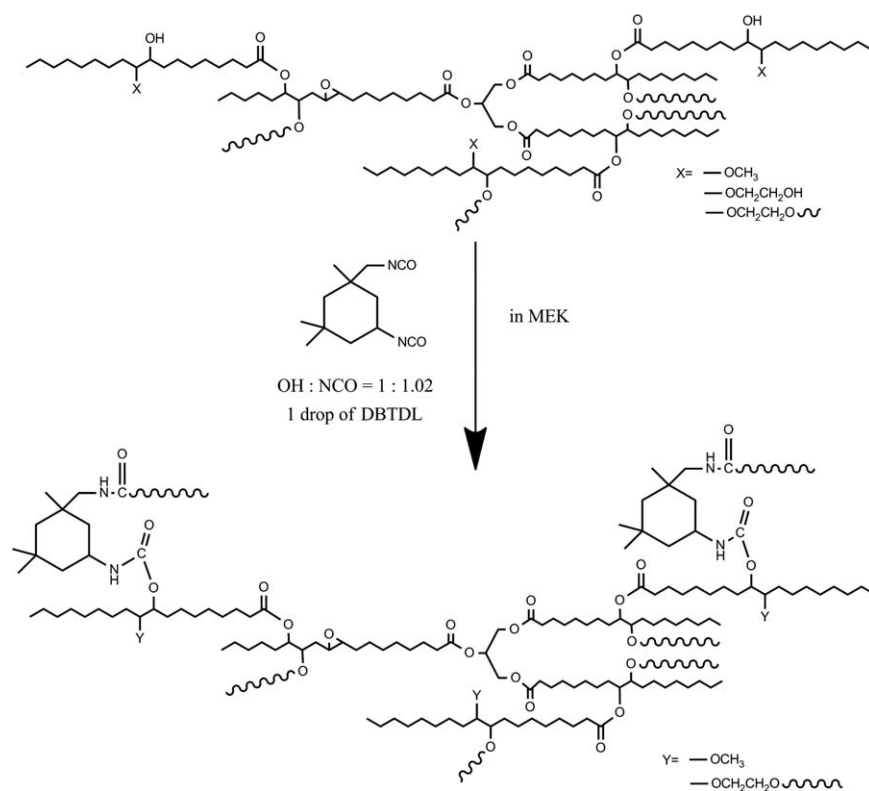
Scheme 2. Preparation of representative polyols.

methanol and (4) glycol.⁴ The ring-opened epoxidized oils were then saponified into fatty acids for later use.

Methanol Route. Nearly 100 g of epoxidized oil was dissolved in methanol (molar ratio of epoxy group of oil to hydroxyl group of methanol was 1 : 10) in the presence of 0.1 wt % tet-

rafluoroboric acid. The reaction was carried out in a two-necked round-bottom flask equipped with a condenser and mechanical stirrer at 65°C for 2 h.

Glycol Route. In a process similar to the methanol route, 100 g of epoxidized oil was mixed with glycol (molar ratio of epoxy



Scheme 3. Illustration of polymerization reaction.

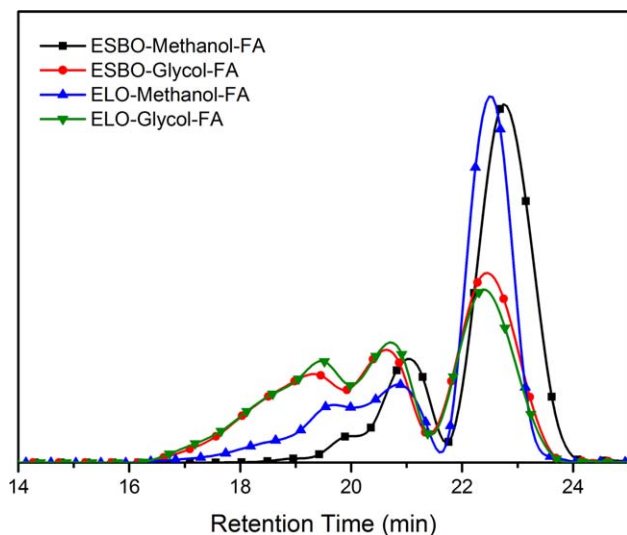


Figure 1. GPC curves for the fatty acids. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

group of oil to hydroxyl group of glycol was 1 : 10). The reaction proceeded at 98°C for 2 h in the presence of 0.1 wt % tetrafluoroboric acid.

After being cooled down to room temperature, the reacting mixtures were extracted by ethyl acetate and washed with saturated sodium chloride solution three times. Organic solvent was then removed at 70°C under reduced pressure. The obtained fatty alcohol was then saponified by KOH in a mixture of ethanol and water (50/50 v/v) at 73°C for 4 h, and then neutralized using HCl. Fatty acid precipitated out of the uniform solution and was subsequently extracted by ethyl acetate. The organic layer was washed three times and dried over MgSO₄. Pure fatty acid was obtained upon removal of the organic solvent by roto-evaporation. Scheme 1 shows the representative synthesis route.

Preparation of Polyols from Epoxidized Soybean Oil Ring-Opened by Fatty Acids with DBU Catalyst

Polyols were prepared by mixing fatty acids with epoxidized soybean oil in a flask under magnetic stirring at 130°C in the presence of DBU as catalyst. The weight ratio of fatty acid to epoxidized soybean oil was determined by an initial molar ratio of carboxylic acid group to epoxy group of 0.5 : 1.⁸ The reaction proceeded for 6 h and the obtained polyols were dark brown, viscous liquids. The four polyols were identified as SMS, SGS, LMS, and LGS, where the first letter “S” stands for ESBO and “L” stands for ELO, the second letter “M” represents ring-opened by methanol and “G” means ring-opened by glycol, and the last letter “S” refers to ESBO ring-opened by fatty acids. Scheme 2 depicts the synthesis of polyols.

Preparation of Polyurethanes Using Polyols

Scheme 3 shows the polymerization reaction creating polyurethanes, which was carried out in MEK as solvent at 60°C for 3 h by mixing polyol, IPDI (molar ratio of OH and NCO was 1 : 1.02) and one drop of DBTDL. The solution was then poured into an 80 × 80 mm² Teflon mold to produce thin films, which were post-cured and dried overnight at 80°C. The obtained PU films were sliced into specific dimension for tests.

Characterization

¹H NMR spectra of the polyols were recorded on a Varian spectrometer (Palo Alto, CA) at 300 MHz in chloroform-*d*. A Bruker IFS66V FT-IR spectrometer was used to characterize both fatty acids and polyols. The scanning resolution was 4 cm⁻¹ and the scanning range covered 4000 to 400 cm⁻¹. The hydroxyl numbers and the acid numbers of the fatty acids and polyols were determined using the Unilever method and the AOCs Official Method Te 1a-64, respectively. The average molecular weight was measured by a Thermo Scientific Dionex Ultimate 3000 GPC (Sunnyvale, CA) equipped with a Shodex Refractive Index (RI). The eluent solvent used was tetrahydrofuran with two Agilent PLgel 3μm 100 Å 300 × 7.5 mm (p/n

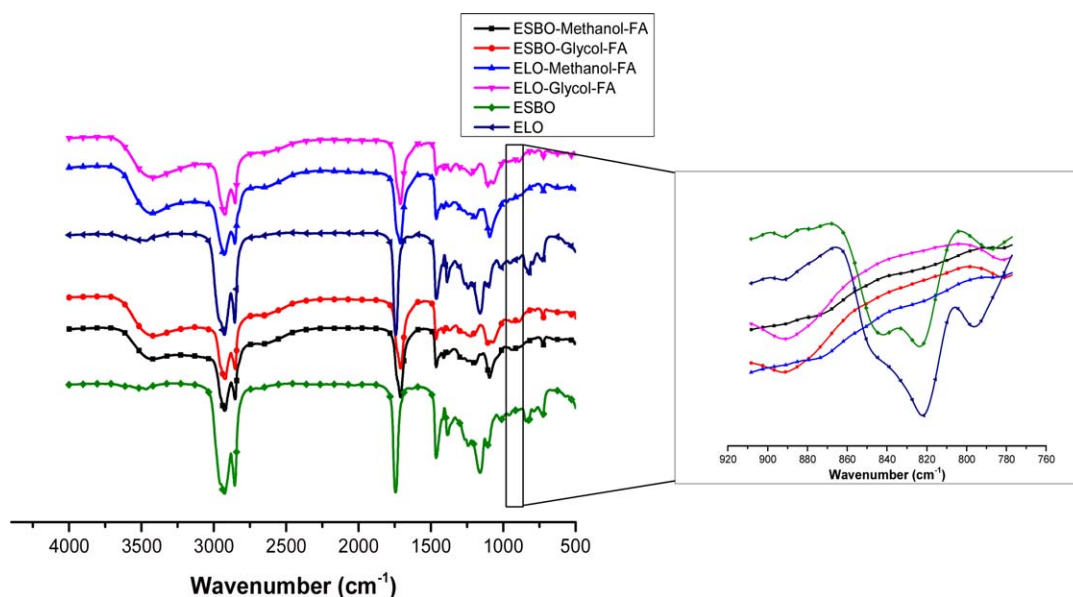


Figure 2. FTIR spectra of FA compared with ESBO and ELO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Properties of Fatty Acids

Fatty acid	OH number (mg KOH/g)	Acid number (mg KOH/g)	Viscosity (Pa s ⁻¹) at 40°C	M _n	M _w	PDI
ESBO-methanol-FA	167.1	160.7	0.28	568	664	1.17
ESBO-glycol-FA	186.0	151.4	1.15	889	1402	1.58
ELO-methanol-FA	202.4	145.5	0.71	705	955	1.36
ELO-glycol-FA	225.2	142.8	2.11	944	1476	1.56

PL1110-6320) and one Mesopore 300 × 7.5 mm² (p/n PL1113-6325). The flow rate of THF was 1.0 mL min⁻¹ and the measurement proceeded at 25°C. Rheological tests were performed using an AR2000 (TA Instruments). The rheological behavior of fatty acids and polyols was investigated by varying the shear rate from 10 to 1000 s⁻¹ at designated temperatures.

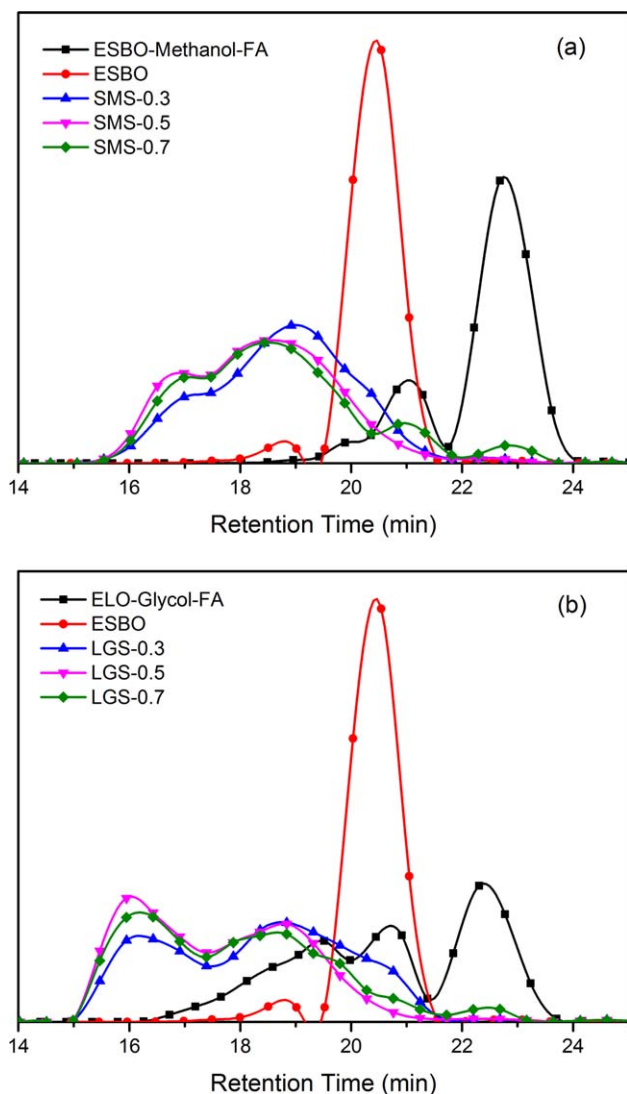


Figure 3. Effect of ratio between carboxylic acid and epoxy groups on GPC curves for (a) SMS (ESBO-Methanol-FA ring-opened ESBO) and (b) LGS (ELO-Glycol-FA ring-opened ESBO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Ethanol uptake and ethanol absorption tests were performed following reported methods.¹¹ W_0 was defined as the original weight of dry PU films with dimensions of 2 cm × 2 cm. Subsequently, the films were immersed in ethanol for 48 h, then towel-dried and their weight was recorded as W_1 . Then, the samples were re-conditioned in an oven at 70°C for 24 h and their weight was recorded as W_2 . The percentage of ethanol absorption (W_a) and the percentage of weight loss (W_d) are calculated as:

$$W_a = \frac{W_1 - W_2}{W_2} \times 100\%$$

$$W_d = \frac{W_0 - W_2}{W_0} \times 100\%$$

Dynamic mechanical analysis (DMA) of the polyurethane films was carried out on a TA Instruments DMA Q800 dynamic mechanical analyzer using a film-tension mode of 1 Hz. Rectangular samples with a length of 15 mm, a width of 10 mm, and a nominal thickness of 0.5 mm were used for the analysis. The samples were cooled and held isothermally for 3 min at -80°C before raising the temperature to 120°C at a rate of 3°C min⁻¹. The glass transition temperatures (T_g s) of the samples were obtained from the peaks of the $\tan \delta$ curves.

Thermogravimetric analysis (TGA) of the films was performed on a TA Instruments Q50 (New Castle, DE). The samples were heated from 25 to 650°C at a rate of 20°C min⁻¹ in air. The air flow rate was 60 mL min⁻¹. The remaining weight percentage was recorded as a function of temperature.

Differential scanning calorimetry (DSC) was conducted on a TA Instruments Q20. Samples with a weight of ~10 mg were heated to 120°C to eliminate their heat history. The samples were cooled down to -50°C by manually adding liquid nitrogen to the chamber and then heated to 120°C at a programmed rate of 10°C min⁻¹. The second heating ramp was recorded and the glass transition temperature was determined by the midpoint inflection method.

The tensile properties of the PU films (ca., 0.5-mm thick) were determined using an Instron universal testing machine (model 4502) with a crosshead speed of 100 mm min⁻¹. Samples were prepared in rectangular shape of 50 mm × 10 mm (length × width). At least three replicates were tested for each PU sample. The stress-strain curve was plotted and toughness, representing the ability of a material to absorb energy without fracturing, was calculated as the area beneath the curve.

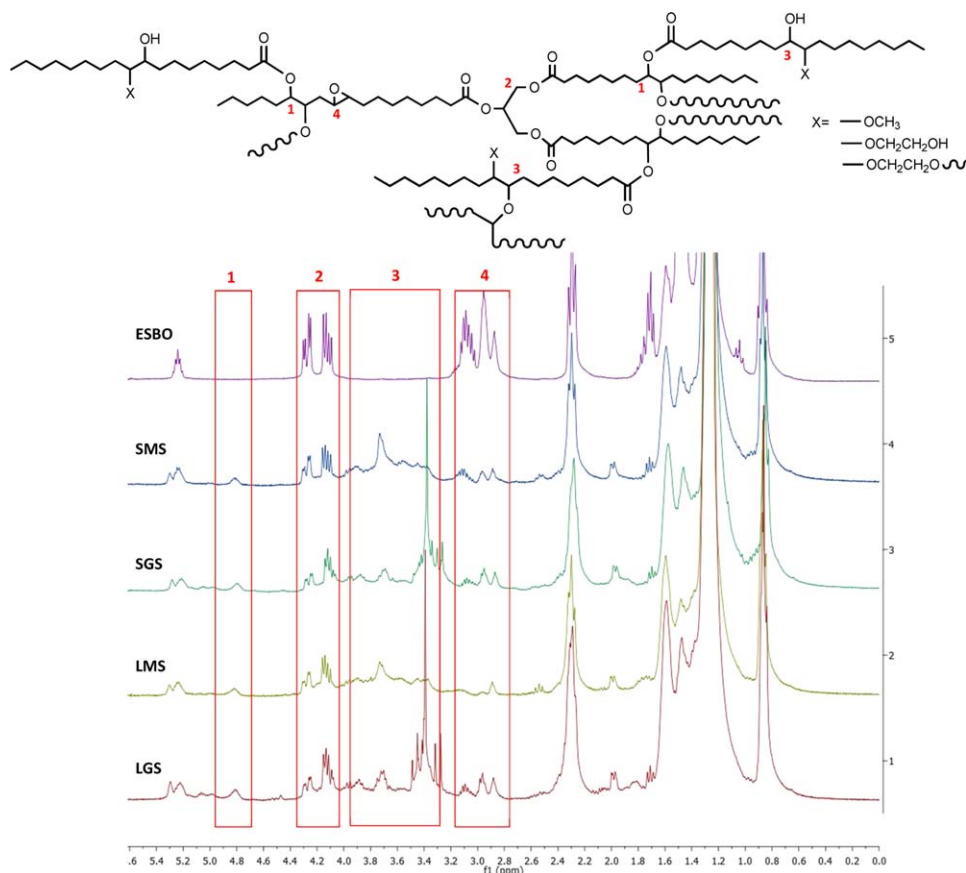


Figure 4. ^1H NMR spectra of polyols and ESBO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Preparation of Fatty Acids

Scheme 1 shows that the preparation of fatty acids involves the ring-opening of epoxidized vegetable oils by methanol/glycol followed by saponification. Neither methanol nor glycol was able to ring open all epoxy groups, which is in accordance with reported results.^{3,12} Additionally, oligomerization was observed for both methanol and glycol ring-opening systems. GPC curves are plotted in Figure 1, where shoulders to the left of the main peaks represented the presence of molecules of higher molecular weights. Ring-opening by alcohols yielded secondary hydroxyls which can further ring-open epoxy groups on other molecules, causing the oligomerization. It is worth noting that for the glycol ring-opening system, when one epoxy group is ring-opened by one hydroxyl group from glycol, the other primary hydroxyl group remains, and has a higher reactivity towards further ring-opening than the secondary hydroxyl groups from the methanol ring-opening reaction, resulting in even more highly oligomerized fatty acids. Molecular weights are summarized in Table I. SBO-methanol-FA and ELO-methanol-FA showed lower M_n and M_w than ESBO-glycol-FA and ELO-glycol-FA. In addition, oligomerization caused higher polymeric dispersion indices in the respective glycol ring-opened oils, and the viscosities at 40°C of ESBO-Glycol-FA and ELO-Glycol-FA (1.15 and 2.21 Pa s⁻¹, respectively) were higher than those of fatty acids derived by

methanol ring-opening. Figure 2 shows FTIR spectra of the obtained fatty acids, with ESBO and ELO as references. All fatty acids exhibited a new broad trough between 3600 to 2500 cm⁻¹, which was assigned to overlapped signal from the —OH stretching of the hydroxyl and the carboxylic groups.¹³ The peak at 823 cm⁻¹ was no longer observed for the fatty acids because most of the epoxy groups were reduced during the ring-opening step.¹⁴ These two changes confirmed the success of the preparation of fatty acids.

Preparation and Properties of Polyols

The polyols were prepared in a one-pot process, requiring neither solvent nor washing. Trace amounts of DBU as catalyst not only lowered both reaction temperature and time, but also promoted the reactivity of the carboxylic acid group toward ring-opening in competition with that of the hydroxyl group.⁸

The effect of the molar ratio between the carboxylic acid groups from fatty acid and the epoxy groups from epoxidized soybean oil was investigated by GPC. ESBO-methanol-FA with the lowest OH number and ELO-glycol-FA with the highest OH number were intentionally chosen as representatives. With increasing molar ratio (from 0.3 : 1 to 0.7 : 1) both systems showed similar GPC patterns. A low molar ratio of 0.3 : 1 did not provide the sufficient number of active functional groups to initiate ring-opening. Consequently, the spectra showed a shoulder in

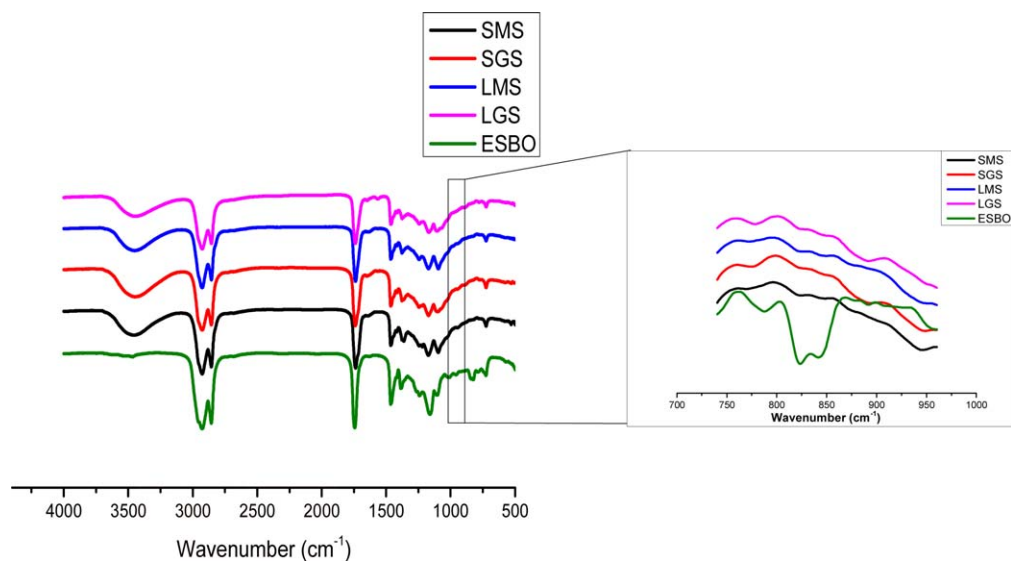


Figure 5. FTIR spectra of polyols and ESBO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the ESBO position, indicating the presence of remaining ESBO that was not ring opened, see Figure 3(a). As the ratio increased to 0.7 : 1, the shoulder in the ESBO position was suppressed as increasing numbers of epoxy groups were ring-opened, resulting in a prominent peak at the position of the corresponding fatty acids, indicating the presence of remaining fatty acids. As a conclusion, a molar ratio of 0.5 : 1 was determined as the optimized ratio with the lowest levels of unreacted fatty acid and ESBO. Same molar ratio was used for the polyol syntheses from ESBO-glycol-FA and ELO-methanol-FA.

^1H NMR spectra of the polyols and ESBO are shown in Figure 4. A representative structure of the polyol is embedded to illustrate the assignments of the peaks. The appearance of Peak 1, corresponding to $-\text{COO}-\text{CH}$, confirmed that carboxylic acid ring-opening had occurred and an ester group anchored on the fatty acid chains was formed. Broad peaks between 3.2 and 4.0 ppm were assigned to ether linkages formed by epoxy groups ring-opened by hydroxyl groups. The polyols did not show a noticeable Peak 4, which is assigned to the epoxy group, indicating that almost all epoxy groups were ring-opened.

FTIR spectra of the polyols are shown in Figure 5. Each ring opening of an epoxy group created one hydroxyl group. Together with the hydroxyl groups intrinsically present in fatty

acids, the polyols contain a considerable number of hydroxyl groups that contribute to the broad peak between 3600 and 3200 cm^{-1} . In the vicinity of 823 cm^{-1} , the polyol curves are wavy but show lower absorbance than the curve of ESBO, which matches the result from ^1H NMR.

Hydroxyl number, acid number, viscosity and molecular weight of the polyols are summarized in Table II. The acid numbers of the polyols indicated the presence of small amounts of fatty acids in the mixture. The viscosity of the polyols mirrored that of the fatty acids; those obtained from glycol ring-opening were more viscous because of oligomerization. The OH numbers of the polyols were lower than those of the fatty acids. This was explained by the fact that when a carboxylic acid group ring opened an epoxy, one net hydroxyl was generated, whereas when a hydroxyl group ring opened an epoxy, there was no net effect on the functionality. Because the molecular weight was increased significantly by the coupling of fatty acid and ESBO, and because the carboxylic acid involved had only half the number of epoxy groups, it is theoretically possible for the obtained polyols to have OH number lower than the fatty acids. Moreover, the OH number of the polyols increased with an increase in OH numbers of the fatty acids, which offers an important pathway for the preparation of polyols with tailored OH numbers.

Table II. Properties of the Polyols

Fatty acid	OH number (mg KOH/g)	Acid number (mg KOH/g)	Viscosity (Pa s^{-1}) at 60°C	M_n	M_w	PDI
SMS	150.4	1.2	1.17	2487	3389	1.36
SGS	168.5	0.8	3.72	2782	4434	1.59
LMS	190.8	0.7	1.77	2474	3402	1.37
LGS	211.3	1.5	5.54	3114	4715	1.51

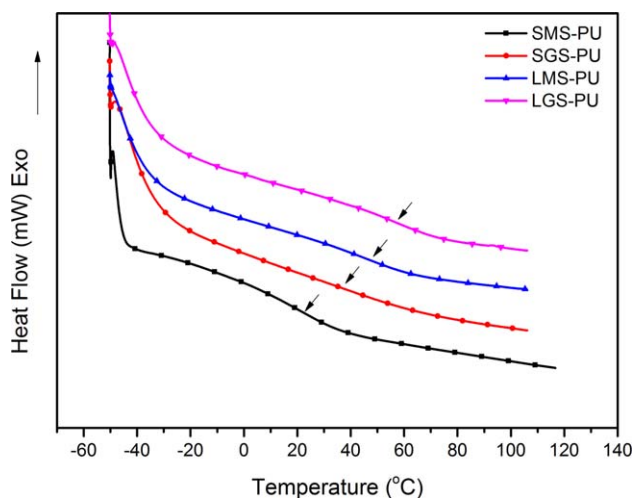


Figure 6. DSC scans of PU films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polyurethane Properties

Four polyols (SMS, SGS, LMS, and LGS) obtained from the previous step were subject to polymerization with IPDI catalyzed by DBTDL in the presence of MEK as solvent. Polyurethane films were acquired for thermo-mechanical tests. Differential scanning calorimetry (DSC) thermograms of the polyurethane films are shown in Figure 6. Each sample exhibited only one T_g and no melting or crystallizing peak, indicating that the samples had a homogenous, amorphous structure. With an increase in polyol OH number from 150.4 mg KOH/g to 215.3 mg KOH/g, the T_g increased from 19.0 to 56.3°C. The increase in T_g s was attributed to an increasing content of hard segments, higher crosslinking density, and less plasticizing effect of dangling chains.¹⁵ To compensate for the higher OH number of the polyols while maintaining a constant ratio between OH and NCO, higher levels of segment IPDI were used during polymerization. As summarized in Table III, the hard segment content increased from 22.9 to 29.9% with increasing polyol OH numbers. The OH number of the polyols also significantly influenced the crosslinking density of the PU network, which was formed by intermolecular urethane linkages between soft segments and hard segments. Higher polyol OH number, indicating higher functionality, led to more fatty acid chains being crosslinked and incorporated into the PU network. As a result, fewer free fatty acid arms, acting as plasticizers, were present in the material.

DMA was employed to study the temperature dependence of the storage modulus (E') and the loss factor ($\tan \delta$) of the PU

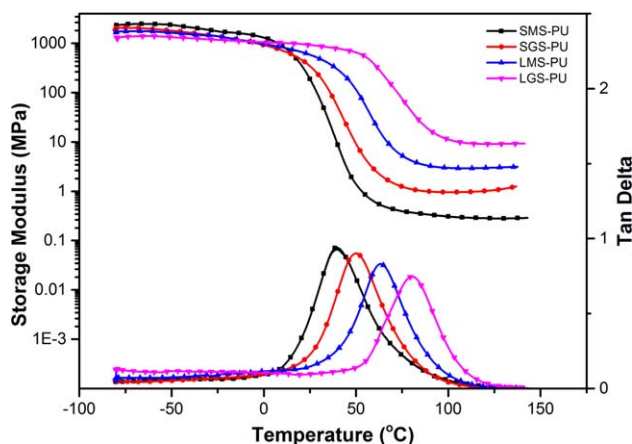


Figure 7. Storage modulus and loss factor of PU films as functions of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

films, see Figure 7. As the samples were heated through the glass transition temperature, which is defined by the peak of $\tan \delta$, the storage moduli of the samples dropped by approximately three orders of magnitude. Subsequently, all samples entered into the rubbery state and E' exhibited less dependence on temperature. The observed rubbery plateau was evidence of the presence of a crosslinked network in the PU films; the storage modulus in the rubbery state increased with the polyol OH number and determined the crosslinking density of the network structure.¹² According to the kinetic theory of rubber elasticity,¹⁶ crosslinking density (ν_e) can be quantitatively determined using the following equation:

$$E' = 3\nu_e RT$$

where E' is the rubbery storage modulus, typically at $T_g + 50^\circ\text{C}$, R is the universal gas constant, and T is the absolute temperature. The calculated crosslinking density of the PUs ranged from 37.4 to 911.9 mol m^{-3} with increasing polyol OH numbers, see Table III. The positive correlation between crosslinking density and polyol OH number revealed that an increasing fraction of fatty acid arms were incorporated into the network via urethane bonds as the OH number of the polyols increased. It is worth noting that the difference in T_g values obtained by DSC and DMA was mainly caused by the different nature of the two measurements. DSC measured the heat capacity change from frozen to unfrozen chains, while DMA measured the change in mechanical response of the polymer chains to heating.¹⁷ Only one $\tan \delta$ was observed for each material, indicating the homogeneous nature of all investigated PU samples. The height of $\tan \delta$

Table III. Physical and Thermal Properties of the Polyurethanes

	Hard segment content (%)	Gel content (%)	T_g (°C) DSC	T_g (°C) DMA	ν_e (mol m^{-3})	T_{10} (°C)	T_{50} (°C)
SMS-PU	22.9	88.2	19.0	39.3	37.4	305.2	383.5
SGS-PU	25.5	89.3	36.4	49.9	103.4	302.5	379.1
LMS-PU	27.6	94.2	46.9	63.4	305.7	301.32	376.6
LGS-PU	29.9	95.3	56.3	80.5	911.9	298.9	370.9

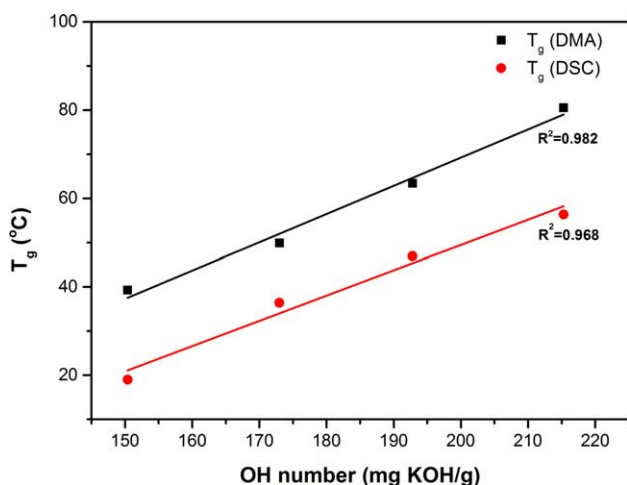


Figure 8. Dependence of glass transition temperature on OH number of polyols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased with increasing crosslinking density, matching reported properties of similar systems.^{8,11} With increasing OH numbers of the polyols, T_g increased from 39.3 to 80.5°C, which was explained by the fact that polymer chain motion was more restricted in a network with higher crosslinking density. Also, because the stoichiometric ratio of OH to NCO of 1 : 1.02 was strictly controlled during the polymerization step, higher content of hard segment IPDI was contained in PUs from polyol with correspondingly higher OH numbers, contributing to the stiffness of the material.

The Fox–Losheak equation relates the crosslinking density and T_g ^{12,18}:

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

Where $T_{g\infty}$ is the glass-transition temperature of the linear polymer of the same structure, v is the number of crosslinks per unit of volume (density/ M_c), and K and k are constants for a

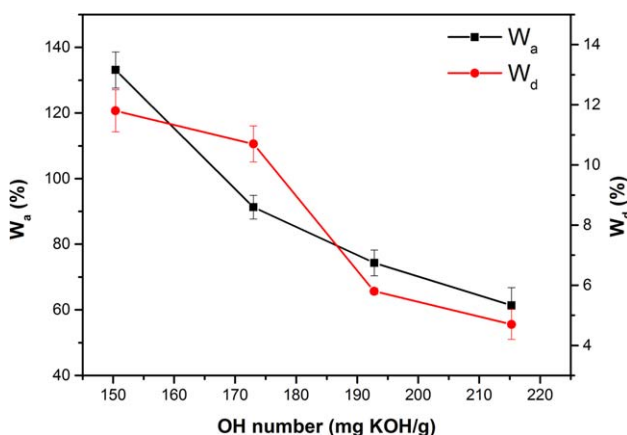


Figure 9. Dependence of ethanol absorption and uptake on OH number of polyols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

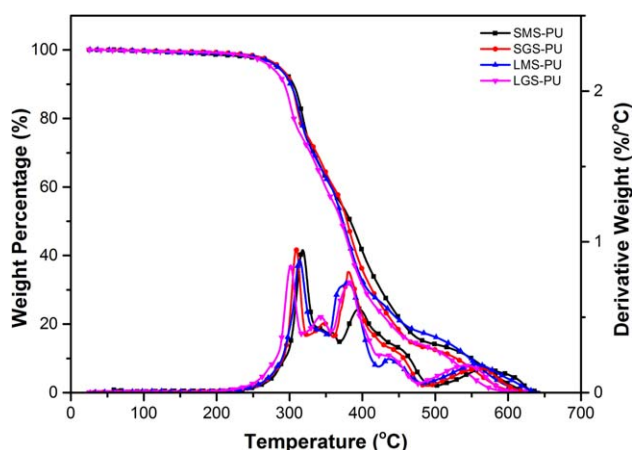


Figure 10. TGA curves and their derivative curves for PU films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

given system. It was reported previously that v is linearly proportional to the OH number of the polyol, assuming the monomer conversion is complete.^{12,19} The linear fit of the data points in Figure 8 shows the dependence of the T_g of the PU films on the OH number of the corresponding polyol, documented by R^2 values of 0.968 and 0.982 for DSC and DMA measurements, respectively.

Ethanol uptake and absorption experiments were performed to examine the degree of crosslinking for each PU film. Ethanol can dissolve oligomer/polymer chains which are not connected to the network. As discussed with the DMA results, the OH numbers of the polyols were linearly related to the crosslinking density of the PU network. Figure 9 shows that after immersion the amount of absorbed ethanol and the weight loss of the PUs decreased from 133.1 to 61.4% and from 11.8 to 4.7%, respectively, while the OH number of the polyols increased from 150.4 mg KOH/g to 215.3 mg KOH/g. This indicated that ethanol absorption and uptake were reduced as the degree of crosslinking increased.^{11,20}

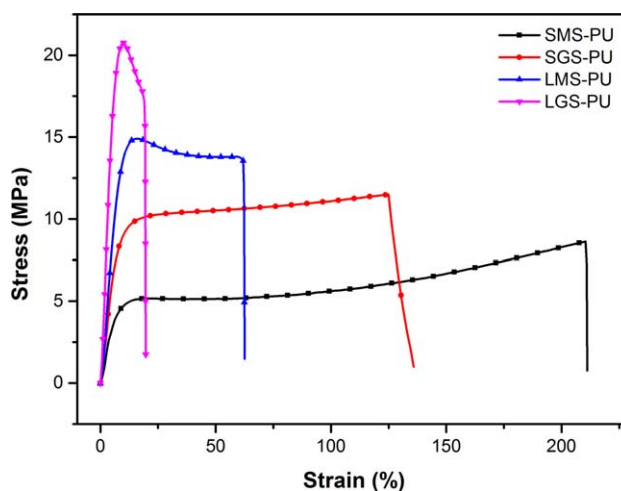


Figure 11. Stress–strain curves for PU films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Mechanical Properties of the Polyurethanes

	E (MPa)	σ_b (MPa)	ϵ_b (%)	Toughness (MPa)
SMS-PU	67.2	8.6	210.4	12.7
SGS-PU	123.4	11.5	124.9	13.5
LMS-PU	166.6	13.5	61.9	8.2
LGS-PU	315.0	17.2	19.1	3.2

TGA was conducted to investigate the thermal resistance of the PU films, see Figure 10. In general, PUs exhibit three stages of thermal decomposition in air atmosphere.⁴ The first weight loss domain observed in the range from 200 to 300°C is assigned to the dissociation of the labile urethane bonds. The dissociation of urethanes to isocyanates and alcohols, the formation of primary amines and olefins, and the formation of secondary amines were reported as three possible mechanisms.⁴ The second thermal degradation stage between 300 and 450°C is the result of chain scission in the soybean oil structure. The last stage, above 450°C, is attributed to further thermo-oxidation of the PUs in air. The content of urethane bonds within each sample increased when the OH number of the corresponding polyol increased from 150.4 mg KOH/g to 215.3 mg KOH/g, given a constant molar ratio of OH and NCO. Higher contents of labile urethane bonds caused the shift of T_{10} (temperature of 10% weight loss) and T_{50} (temperature of 50% weight loss) from 305.2 to 298.9°C and 383.5 to 370.9°C, respectively. Similar results regarding the effect of increasing fractions of urethane bonds were reported by Lu et al.¹²

Tensile properties of all PUs were measured and the stress-strain curves are plotted in Figure 11. Young's moduli, tensile strength at break, elongation at break and toughness are summarized in Table IV. In general, tensile strength and Young's modulus increased, while elongation decreased with increasing crosslinking density. The PU films with higher crosslinking densities had incorporated higher contents of hard segment IPDI, which contributed to their stiffness. At the same time, ductility dropped from 210.4 to 19.1% with increasing crosslinking density. The deformation profiles of the samples differed. For example, SMS-PU and SGS-PU deformed elastically before reaching their yielding point; then they exhibited strain hardening and finally broke at maximum strain. LMS-PU and LGS-PU exhibited strain softening in the plastic deformation domain, which occurred after yielding. Toughness was calculated by integrating the area below the stress-strain curve. SGS-PU exhibited the highest toughness (13.5 MPa), while LGS-PU, which had the highest tensile strength, was the least tough material among the examined PU films. Generally, brittle materials exhibit low toughness, while ductile materials are tough.¹¹

CONCLUSIONS

A series of fatty acids obtained from ESBO/ELO ring-opened by methanol/glycol were used to produce polyols using a solvent-free method. The fatty acids were reacted with ESBO at a ratio

of carboxylic acid to epoxy groups of 0.5 : 1. The resulting polyols exhibited increasing OH numbers with increasing OH numbers of the fatty acids. PU films prepared from these polyols exhibited significant differences in thermal and mechanical properties. With increasing OH number, crosslinking density was significantly increased, resulting in PU networks with fewer free-motion available to the chains. This allowed for the tailoring of the properties of the resulting PUs, ranging from rigid and brittle to soft and ductile. The choice of epoxidized vegetable oil as starting material clearly determined the OH number of the resulting polyols because of the different functionalities of the respective epoxy groups. Being able to use the OH number of the polyol to influence the properties of PUs provides a pathway for the design of materials with desired thermo-mechanical properties.

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