

Synthesis and Characterization of Novel Polyurethane Acrylates Based on Soy Polyols

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ABSTRACT: Novel polyurethane acrylates (PUAs) were prepared by the reaction of soy polyols with isophorone diisocyanate and hydroxyethylacrylate. FTIR results confirmed the formation of PUAs from different kinds of soy polyols. The glass transition, damping properties, thermal stabilities, and mechanical properties of PUAs were characterized by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and universal test machine. The morphology of PUAs was investigated by scanning electron microscope (SEM). The results of the swelling experiments showed that the crosslinking density of polyurethanes and PUAs directly correlated with the hydroxyl (OH) number of polyols. The DSC and DMA results displayed that the glass transition temperature of PUAs was higher than that

of polyurethanes and increased with OH number. Furthermore, the formation of PUA networks improved the damping properties of polyurethanes. TGA results demonstrated the acrylation of polyurethanes improved its thermal stability. The initial decomposition temperature of polyurethanes and PUAs also increased with OH number. When compared with polyurethanes, the tensile strengths of PUAs were improved by 118%, 39%, and 9%, respectively, with the increase of OH number of three soy polyols. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2449–2455, 2011

Key words: polyurethanes; renewable resources; structure–property relations; mechanical properties; thermal properties

INTRODUCTION

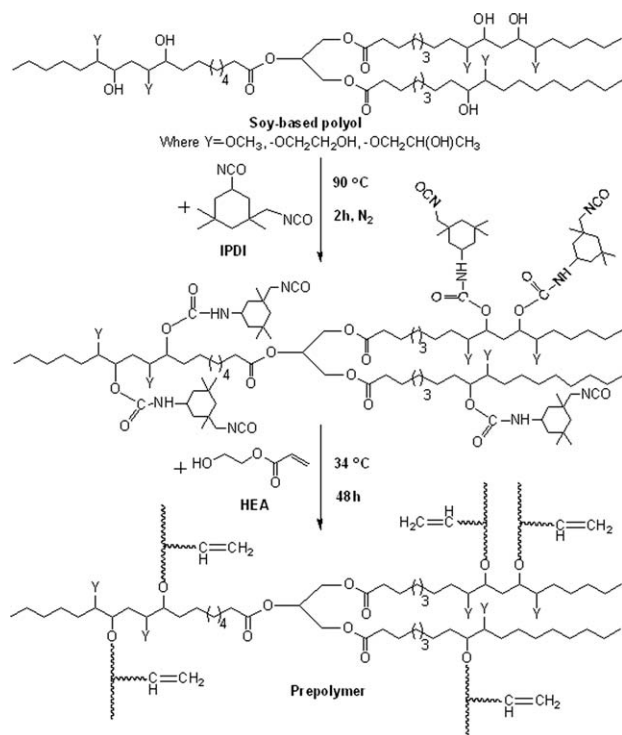
Vegetable-oil-based polymers from renewable resources are gaining popularity because of their attractive properties related to the specific structures of the oils, as well as concerns about the environment and sustainability. Among various vegetable-oil-based polymers, polyurethanes (PUs) have been successfully employed in many diverse applications such as thermoset and thermoplastic elastomers, adhesives, coatings, and foams (flexible, semirigid, and rigid).^{1–7} Comparing with PUs derived from petrochemical polyols, PUs from vegetable-oil-based polyols can potentially combine the high abrasion resistance, toughness, tear strength, and good low temperature properties of PUs with the biocompatibility and biodegradability of vegetable-oil-based polyols. In addition, PUs from vegetable-oil-based

polyols has better thermal, oxidative stabilities, and excellent weather stability.^{8,9}

Although many types of vegetable oils have been tested and reported for PU applications, soybean oil (SBO) is the most promising for partially replacing petroleum to make polyols due to its abundance and low price. Petrovic et al. have reported that SBO can be converted into polyols by various methods, such as hydroxylation,^{10,11} ozonolysis,¹² and hydroformylation.¹³ They had further extensively studied the use of various as obtained soy polyols to synthesize PUs and the effects of their structures on the properties of the PUs.^{11–14} Narine et al. developed an alternative method by using ozone to cleave and oxidize the double bonds in the vegetable oil and then various catalysts were chosen to reduce the ozonides to obtain polyols with terminal primary OH groups, which reduce the plasticizing effect in the subsequent formation of PU networks.^{15,16}

Recently, a great deal of effort has been devoted to the development of PUAs. PUAs are often used, in the liquid state, as precursors for products with desirable properties such as hardness, flexibility, abrasion resistance, good optical properties, and weatherability. The low viscosity liquid PUA

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Scheme 1 Synthesis of acrylated polyurethane prepolymer.

prepolymers possessed excellent processability keeping with the material requirements for various industrial sectors like aeronautic and automobile industries for composite materials and coatings.^{17–23} So far, there are few reports focused on the synthesis of PUAs from the soy polyols.²⁴ Besides, the comparing of the thermal and mechanical properties between PUs and PUAs originated from the polyols is rather limited.

Herein, three polyols based on epoxidized soybean oil (ESO) were prepared by oxirane ring opening with methanol, glycol, and 1,2-propanediol. PUs were obtained from these soy polyols with isophorone diisocyanate (IPDI).^{25–27} Furthermore, the prepolymers from polyols with IPDI were end capped by hydroxyethylacrylate (HEA) to form PUAs through a thermal polymerization process. The general procedure is given in Scheme 1. The objective of this work is to synthesis PUs and PUAs from polyols and then to compare their thermal and mechanical properties with DSC, DMA, TGA, and universal test machine.

EXPERIMENTAL

Materials

ESO 5.9 wt % oxygen content was kindly provided by Xiamen Vive Material Ltd Co., China. Analytical-reagent-grade toluene, methanol, glycol, 1,2-propanediol, ammonia (30%), and tetrafluoroboric acid (48%) were all purchased from Nanjing Chemical

Reagent Co., China. HEA was purchased from Aladdin Chemistry Ltd Co., China. IPDI was supplied by Crendva Speziaichemie, Germany. All chemicals were used without further purification.

Preparation of soy polyols

The details of the synthesis of soy polyols were described in previous reports.^{26,27} Three polyols-based ESO with 5.9 wt % oxygen content were prepared by oxirane ring opening with methanol, glycol, and 1,2-propanediol. The hydroxyl numbers of polyols were 173, 205, and 248 mg KOH/g, respectively, which were named as Polyol-173, Polyol-205, and Polyol-248 in the subsequent discussion. The OH number was determined by the reaction of OH groups with phthalic anhydride and then an alkaline titrimetric method was used to determine the residual content of phthalic anhydride according to GB 12008.3-89.²⁸

Synthesis of the PUs and PUAs

The PUs were synthesized from three polyols with IPDI using the method reported previously.^{25,26} The PUs derived from Polyol-173, Polyol-205, and Polyol-248 are designated as PU173, PU205, and PU248, respectively. The preparation procedures of PUAs were shown in Scheme 1. The oligomer was prepared with a reaction of a 2 : 1M ratio of -NCO and OH group at 90°C for 2 h in nitrogen. After cooling to room temperature, HEA was added to the oligomer and the mixture was stirred for 72 h. The molar ratio of IPDI to HEA was 1 : 1. The reaction was performed at room temperature to avoid thermal polymerization of the vinyl group. Then, the prepolymer were poured into a polytetrafluoroethylene mold, followed by sequential heat treatment at 70°C for 2 h, 90°C for 2 h, and 110°C for 24 h. The samples were then cooled down to room temperature. The PUAs prepared by Polyol-173, Polyol-205, and Polyol-248 were hereafter shortened as PUA173, PUA205, and PUA248, respectively.

Characterization

FTIR measurements were performed with a Thermo Nicolet iS10 FTIR spectrometer. Thermal properties were measured by differential scanning calorimetry (DSC) using a PerkinElmer Pyris 1 instrument with a heating rate of 20°C min⁻¹ from -50 to 120°C. Argon was used as purge gas at a flow rate of 20 mL/min. About 6 mg of sample was used in aluminum pan for each analysis. Thermogravimetric analysis (TGA) was performed on the PUs and PUAs using a Pyris 1 thermogravimetric analyzer (PerkinElmer) with a heating rate of 10°C min⁻¹ under a nitrogen atmosphere from 30 to 600°C. Dynamic mechanical analysis

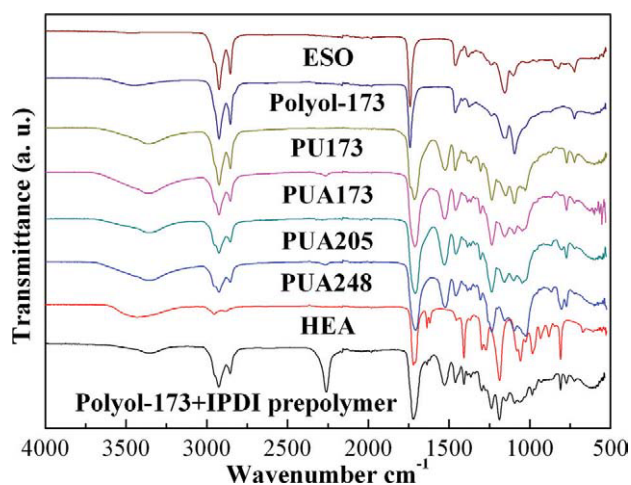


Figure 1 FTIR spectra of ESO, Polyol, PUs, and PUAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(DMA + 450, 01dB-Metravib) was employed for the PUs and PUAs studies. The measurements were taken under tension mode from -100 to 200°C at a heating rate of $2^{\circ}\text{C min}^{-1}$ using a frequency of 1 Hz.

Surface contact angle of the samples was measured by CAM 200 (KSV Instrument) at room temperature. The data was collected 1 min after the $5\ \mu\text{L}$ drop of twice-distilled water had been placed on the surface of the sample. Each measurement was repeated at least 10 times and the average contact angle was then calculated.

Square samples with 1–2 mm thickness and 1–2 g weight were chosen to complete swelling experiments. The samples were immersed in 50 mL toluene for 2 weeks to reach the constant weight at 25°C . After dried, the weight of the sample gel (W_{gel}) was recorded and sol fraction of the sample (W_{sol}) was expressed as follows:

$$W_{\text{sol}} = \frac{W_0 - W_{\text{gel}}}{W_0} \times 100\% \quad (1)$$

where W_0 is the initial weight of sample.

Tensile properties were measured with a universal testing machine (Instron 4466) with a strain rate of $10\ \text{mm/min}$ at 23°C according to GB/T 2567-2008. The results were averaged over at least six specimens. The morphology of the samples was observed by SEM (S-4800, Hitachi). The surface of the liquid nitrogen fractured samples was coated with gold before observation.

RESULTS AND DISCUSSION

FTIR spectra of PUs and PUAs

FTIR was employed to investigate the reactions among the soy polyols, IPDI, and HEA. As shown in

Figure 1, the ESO characteristic peaks at 822 and $842\ \text{cm}^{-1}$ attributed to the epoxy group disappeared after the epoxy group opening reaction. In contrast, the new characteristic absorption peak at $3435\ \text{cm}^{-1}$ in the spectrum of polyol (Polyol-173) corresponded to the OH group formed, implying the successful reaction between alcohol and ESO. After cure reaction with HEA, the characteristic peak of the PUAs at $2260\ \text{cm}^{-1}$ attributed to the $-\text{NCO}$ group almost disappeared, when compared with the neat PU. Besides, the characteristic peaks at $2959\ \text{cm}^{-1}$ attributed to the residual double bonds also disappeared, when compared with the spectrum of HEA. Obviously, the FTIR results indicated the formation of PUA networks were achieved between PU and HEA.

DSC and DMA characterizations of the PUs and PUAs

The DSC results provided the glass transition trends for the PUs and PUAs (Fig. 2). It can be observed that the glass transition temperature (T_g) of PUAs was higher than that of neat PUs and increased with OH number of soy polyols (also shown in Table I). Specially, the T_g of PUA173 increased 27°C when compared with that of neat PU.

The storage moduli (E') and loss tangent ($\tan \delta$) as a function of temperature for PUs and PUAs were shown in Figure 3. The behaviors of the E' versus the temperature were very similar in nature for PUs and PUAs [Fig. 3(a)]. T_g was defined as the temperature at which $\tan \delta$ was maximum. The T_g s of PUs and PUAs were collected in Table I. The T_g s of both PUs and PUAs increased with the OH number of soy polyols. In addition, the T_g s of PUAs were also greater than that of neat PUs. All these results were in good agreement with the results of DSC discussed above. On the molecular scale, T_g represented the

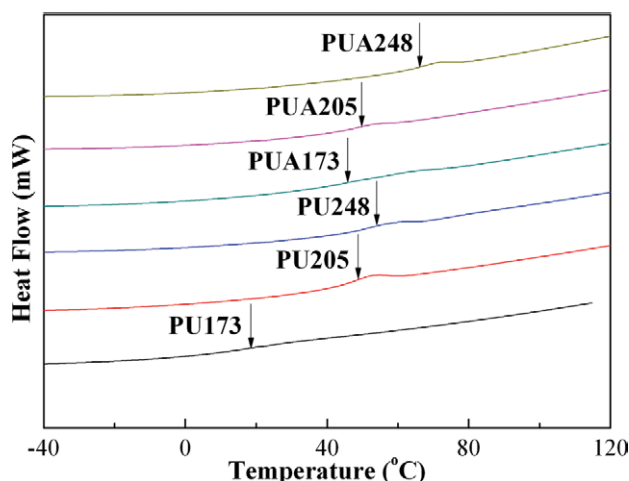


Figure 2 DSC curves of PUs and PUAs from different polyols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
DSC and DMA Results for PUs and PUAs

Sample	DSC		DMA			
	T_g (°C)	T_g^a (°C)	T_β^b (°C)	$(\tan \delta)_{\max}^c$	ΔT at $\tan \delta > 0.3^d$ (°C)	TA ^e (Height × K)
PU173	18.6	38.8	-38.4	1.06	18.3–56.9 (38.6)	50.4
PU205	48.8	58.4	-25.0	0.77	44.3–74.2 (29.9)	35.8
PU248	53.9	78.4	-21.9	0.83	60.0–94.8 (34.8)	42.0
PUA173	45.8	69.4	-22.3	0.41	54.0–95.0 (41.0)	56.6
PUA205	49.7	94.6	5.8	0.53	74.7–113.8 (39.1)	56.3
PUA248	66.2	114.0	6.9	0.56	90.9–130.1 (39.2)	35.9

^a Glass transition temperature (from $\tan \delta_{\text{peak}}$).

^b β transition temperature.

^c Loss tangent ($\tan \delta$) maximum.

^d Temperature range (ΔT) for efficient damping ($\tan \delta > 0.3$).

^e The area under the ($\tan \delta$) versus the temperature curve.

mobility level of polymer chains/network in the material. An increase in T_g corresponded to a decrease in mobility in the polymer.^{29,30} The formation of crosslinking networks between the PU and HEA would hinder the movement of polymer chains, resulting in the increase T_g of PUAs.

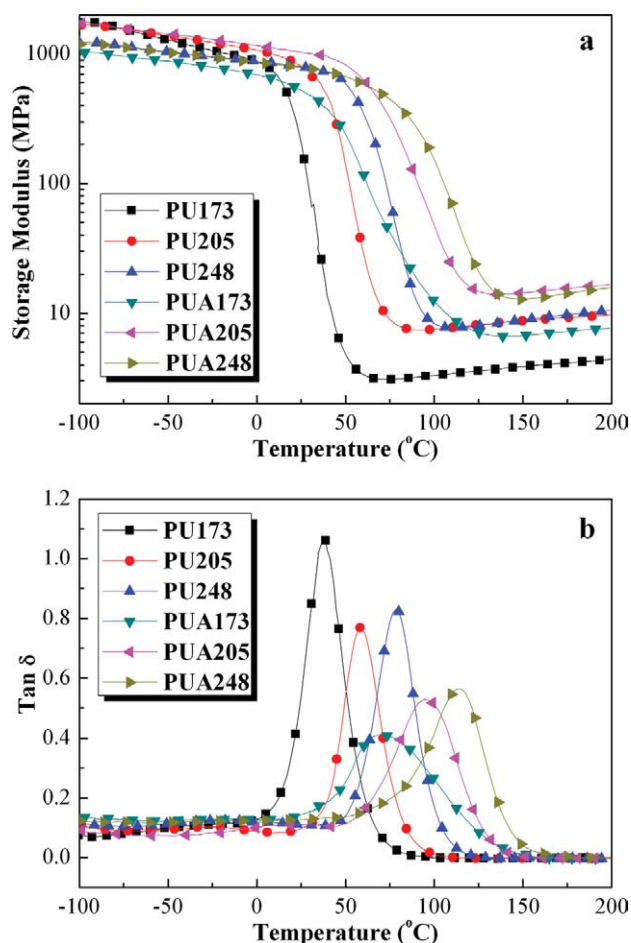


Figure 3 Temperature dependence of the E' (a) and $\tan \delta$ (b) for PUs and PUAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It should be noted that β transitions were existed in Figure 3(b), which could be attributed to the movement of polyol soft chains of polyols in the PUs and PUAs. The β transition temperature (T_β) of the samples was listed in Table I. It can be seen that the T_β of PUAs was higher than that of neat PUs and increased with the OH number. These results indicated that the more OH groups in the polyols, the better restrictions of chain mobility in the PUs and PUAs.

The damping properties of PUs and PUAs have been quantitatively evaluated by the loss tangent maximum, $(\tan \delta)_{\max}$, the temperature range (ΔT) for efficient damping ($\tan \delta > 0.3$) and the area under the $\tan \delta$ versus temperature curve (TA). All of these properties for PUs and PUAs were listed in Table I. The $(\tan \delta)_{\max}$ of PUs and PUAs were in the range of 0.77–1.06 and 0.41–0.56, respectively, revealing that the acrylation decreased the $(\tan \delta)_{\max}$ of PUs. It is noteworthy that the ΔT value of PUAs was higher than that of neat PUs. We deduced that this was because of the higher crosslinking densities of PUAs. The TA value, as defined, described the damping capability of PUs and PUAs over the whole temperature range. It can be seen that the TA values of PUs and PUAs were in the range of 35.8–50.4 K and 35.9–56.6 K, respectively. When compared with the neat PUs, PUAs had greater TA values except the sample with the highest crosslinking density (PUA248). Furthermore, the PUs and PUAs with lower OH number had better damping abilities when compared with PUs and PUAs with higher OH number, which agreed with the results of previous report.³¹ Therefore, it can be conclude that the

TABLE II
Swelling Results for PUs and PUAs

Sample	PU173	PU205	PU248	PUA173	PUA205	PUA248
Sol fraction (wt %)	3.17	1.88	1.02	2.14	1.19	0.6

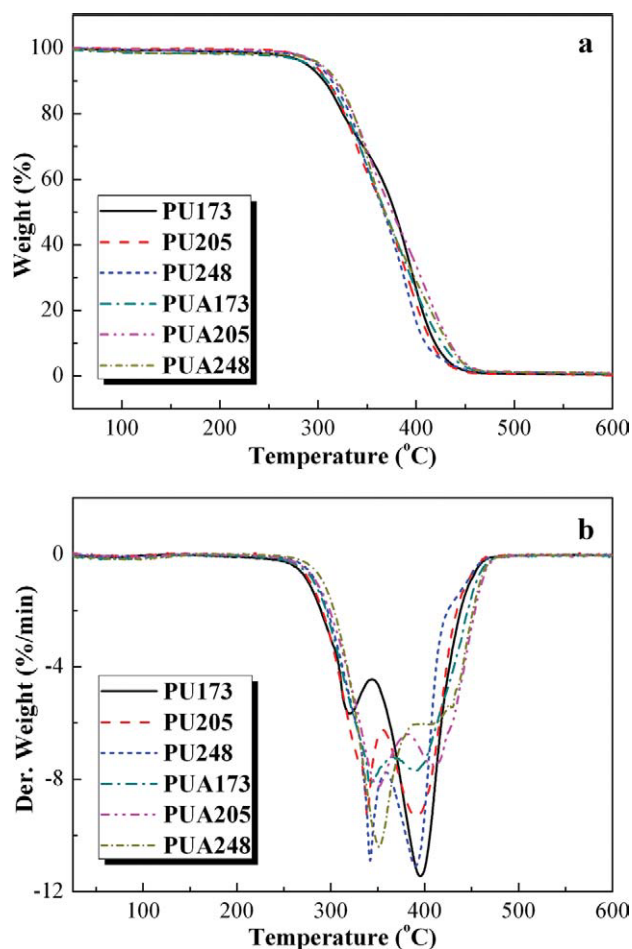


Figure 4 TGA (a) and DTG (b) curves of PUs and PUAs from different polyols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formation of PUA networks improved the damping properties of PU.

Swelling of the PUs and PUAs in toluene

To study the effect of crosslinking density on the glass transition of PUs and PUAs, the swelling experiments were carried out. The results of the swelling experiments were shown in Table II. It can be seen that none of the samples were completely soluble. Notably, the sol fraction of PUAs was lower than that of neat PUs. Moreover, the sol fraction of the PU networks decreased with the increase of OH number of polyols. The crosslinking density of the PUs and PUAs directly correlated with the OH number. PUA248 contained the lowest sol fraction (0.6 wt %), indicating the highest crosslinking den-

TABLE III
TGA and DTG Results for PUs and PUAs

Sample	IDT ^a (°C)	T_{max}		Residue at 600°C (%)
		1st step (°C)	2nd step (°C)	
PU173	288.6	320.9	396.7	0.4
PU205	295.2	338.8	394.7	0.3
PU248	299.3	341.6	389.9	0.9
PUA173	290.9	341.2	389.6	0.7
PUA205	300.6	347.4	410.9	0.9
PUA248	303.3	350.5	415.4	0.9

^a The initial decomposition temperature (from the temperature of 5% weight loss).

sity among the polymer networks. Obviously, with the increase of OH number, the crosslinking density of PUAs enhanced, leading to the increase of T_g of the PU networks.

Thermal properties of the PUs and PUAs

It is known that the thermal stability of PUs is not high in general, primarily due to the presence of labile urethane groups.³² TGA and derivative thermogravimetry (DTG) curves of PUs and PUAs in nitrogen were shown in Figure 4. The initial decomposition temperature (IDT), which was assumed to be the temperature of 5% weight loss, was shown in Table III. As observed, the IDT of PUAs was slightly greater than that of corresponding neat PUs, suggesting the crosslinking networks in the PUAs enhanced the thermal stability. For different polymer networks, the IDT increased with the rise of OH number of polyols. In addition, it can also be observed that the residues at 600°C of both PUs and PUAs were similar in Table III. As can be seen in the DTG curves [Fig. 4(b)], the decomposition processes of both PUs and PUAs were divided into two stages. First, urethane bonds as well as chain segments of polyols decomposed to form volatile products such as carbon dioxide. Second, the oxidative decomposition of isocyanates compound took place. Nevertheless, the changes in weight associated with each step and the residue at high temperature were very different. The temperatures of maximum rate of degradation (T_{max}) in the two stages for PUs and PUAs were also listed in Table III. It can be observed that in the first stage the T_{max1} of PUAs was greater than that of neat PUs. For the PUAs, both the T_{max1} and T_{max2} increased with the OH number in polyols.

TABLE IV
Water Contact Angle Results for PUs and PUAs

Sample	PU173	PU205	PU248	PUA173	PUA205	PUA248
Contact angle (°)	91.4 ± 1.8	93.5 ± 1.1	96.0 ± 0.7	77.0 ± 2.8	79.2 ± 2.6	81.8 ± 3.5

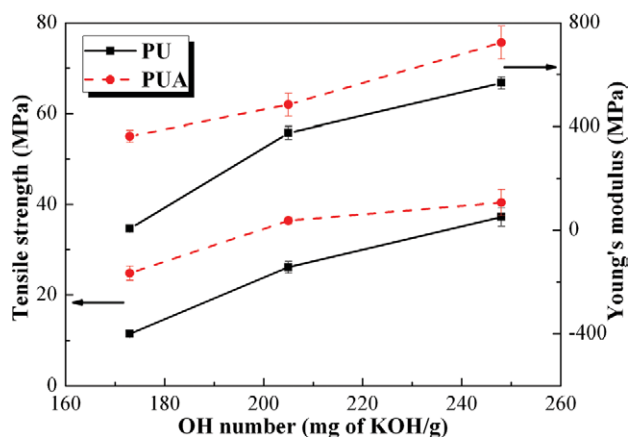


Figure 5 Mechanical properties of PUs and PUAs from different polyols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Surface contact angle measurement of the PUs and PUAs

The surface-water-air contact-angle measurements were more surface-sensitive and probably responded to the outermost monolayer of the surface.³³ The contact angles of PUs and PUAs were listed in Table IV. The water contact angle of PUAs increased from $77.0 \pm 2.8^\circ$ to $81.8 \pm 3.5^\circ$ with the increasing of OH number, indicating the decrease of the surface polarity. Furthermore, the water contact angle of PUAs was higher than that of neat PUs. It can be concluded that the PUAs became more hydrophilic with the acrylated reaction and the decrease of OH groups.

Mechanical properties of the PUs and PUAs

The mechanical properties of PUs and PUAs with different OH number were shown in Figure 5. The tensile strength and elongation at break and Young's modulus of PUs and PUAs were listed in Table V. The tensile strength and Young's modulus of PUAs were much higher than that of neat PUs, whereas the elongation at break of PUAs was much lower than that of neat PUs except the samples of PU205 and PUA205. Comparing with the neat PUs, the PUAs from Polyol-173, Polyol-205, and Polyol-248

TABLE V
Mechanical Properties of PUs and PUAs

Sample	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
PU173	11.4 ± 0.6	257.4 ± 6.2	6.2 ± 1.2
PU205	26.1 ± 1.3	11.6 ± 0.4	375.9 ± 25.6
PU248	37.2 ± 2.0	11.2 ± 0.7	567.4 ± 23.5
PUA173	24.8 ± 1.6	13.5 ± 0.9	362.7 ± 23.0
PUA205	36.4 ± 0.7	12.4 ± 1.3	484.3 ± 44.1
PUA248	40.4 ± 2.9	7.9 ± 0.8	724.0 ± 63.8

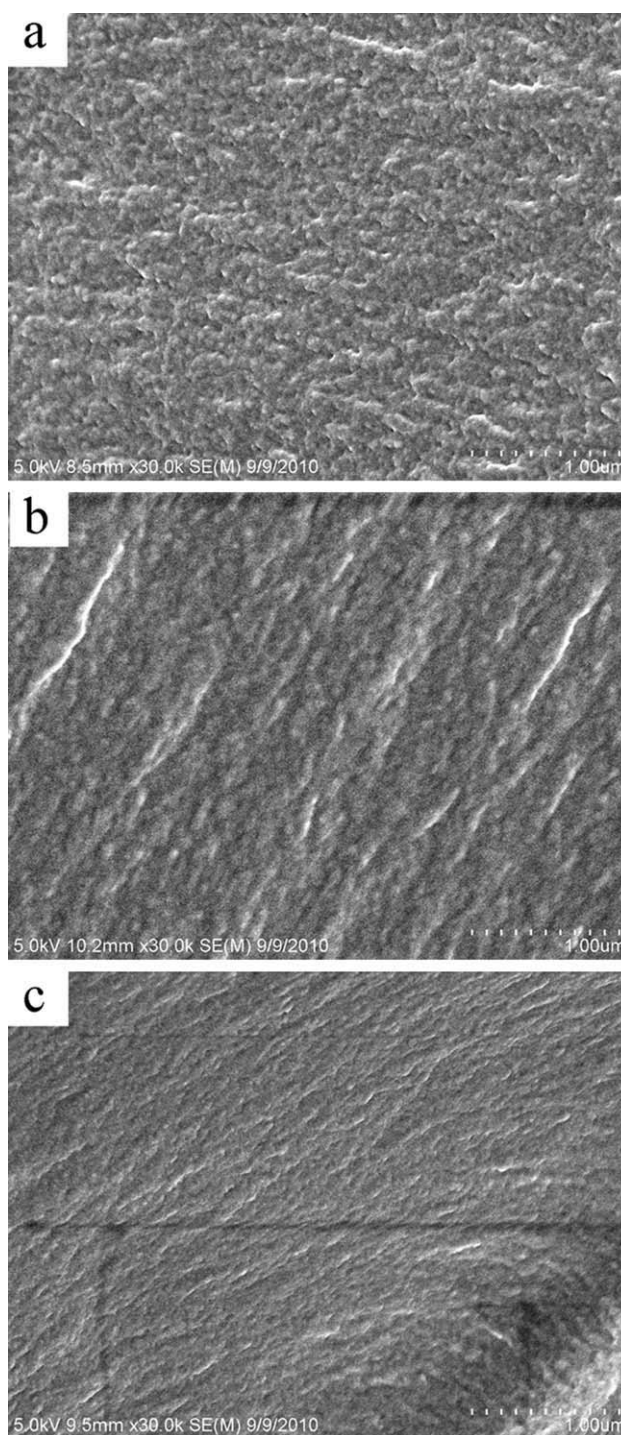


Figure 6 Scanning electron micrographs of (a) PUA173, (b) PUA205, and (c) PUA248.

had 118%, 39%, and 9% increase in the tensile strength. The Young's modulus of the samples PUA205 and PUA248 had increased 29% and 28% than that of neat PU, while the sample PUA173 was increased surprisingly about 59 times. The ultimate elongation decreased with increasing the OH number. It should be noted that the PUA248 appeared as a rigid plastic with the tensile strength higher than

40 MPa and the Young's modulus of 724 MPa. The good performance could be attributed to the highest crosslinking density in the sample PUA248.

SEM of the PUs and PUAs

The SEM micrographs of tested PUA specimens were considered for fractured surface analysis. Figure 6 showed fractured surfaces of PUAs. For the three PUAs, the micrograph of the PUA248 [Fig. 6(c)] showed the smoothest fractured surface, indicating the crosslinking density of PUAs increased with the OH number.

CONCLUSIONS

In this work, three polyols based on ESO were prepared by oxirane ring opening with methanol, glycol, and 1,2-propanediol. Novel PUAs were prepared by the reaction of these polyols with IPDI and HEA by a thermal polymerization process. Both DSC and DMA results showed that the acrylated reaction between PU and HEA increased the T_g of the polyurethane. Furthermore, the T_g of PUs and PUAs increased with the OH number. The damping properties of PUs and PUAs have also been evaluated by DMA. The results showed that the $(\tan \delta)_{\max}$ were in the range of 0.41–1.06; the TA values were from 35.8 to 56.6 K; and the ΔT value for effective damping ($\tan \delta > 0.3$) of PUAs was higher than that of neat PUs. TGA results showed that the thermal stability of PUAs was improved when compared with neat polyurethane and the initial decomposition temperature of PUAs increased from 290.9 to 303.3°C with the increase of OH numbers. The mechanical studies indicated that the tensile strength and Young's modulus also increased with the increase of OH number of polyols, whereas the ultimate elongation decreased with the OH number increasing. The tensile strength and Young's modulus of PUAs were much higher than that of neat PUs. Microstructure of the fractured surfaces examined by SEM technique revealed that the fractured surface of PUAs became smoother with the increase of OH groups.

This study showed that these novel PUAs synthesized from the soy polyols could be employed for green, inexpensive, biodegradable materials and thus reliable alternatives to currently available petroleum-based materials.

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