Polyurethane Networks from Formiated Soy Polyols: Synthesis and Mechanical Characterization

Luciane L. Monteavaro, Eduardo O. da Silva, Ana Paula O. Costa, Dimitrios Samios, Annelise E. Gerbase, and Cesar L. Petzhold*
Instituto de Química, Universidade Federal do Rio Grande do Sul, 91501-970, Porto Alegre, Brazil

ABSTRACT: Polyurethanes can be prepared using polyols obtained from vegetable oils *in natura*, such as castor oil, or from functionalized vegetable oils, such as hydroxylated soybean oil. These polyurethanes have different valuable properties, determined by their chemical composition and cross-linking density. In this study, soy epoxy polyols with different OH contents were prepared through a one-step reaction using the method of *in situ* performic acid generation. Polyols with OH functionalities from 1.9 to 3.2 were reacted in bulk with different diisocyanates at a NCO/OH molar ratio of 0.8 and 60°C for 24 h. Mechanical properties of the polyurethanes were determined by dynamic mechanical thermal analysis, hardness (Shore A), and swelling measurements. Polymer networks with glass-transition temperatures (T_g) from –13 to 48°C were obtained. We observed that the higher the OH functionality of the polyols, the higher the T_g and cross-linking density of the polyurethane network. The influence of diisocyanate structure (rigid or flexible chain), curing temperature, and curing reaction time on mechanical properties was also investigated.

Paper no. J10956 in *JAOCS 82*, 365–371 (May 2005).

KEY WORDS: Hydroxylated soybean oil, mechanical properties, polyurethane, soy epoxy polyol.

The use of renewable resources has attracted the attention of many researchers because of their potential to replace petrochemical derivatives (1–3). Soybean oil is an inexpensive, readily available, renewable resource and provides an excellent platform for polymeric materials. Soybean oil is mainly composed of TG molecules derived from unsaturated FA such as oleic acid (22%), linoleic acid (55%), and linolenic acid (7%). Although they possess double bonds, which are the reactive sites for coatings and paints, they need to be functionalized to prepare polymers (4). Polyurethanes (PU) have been prepared from vegetable oils *in natura*, such as castor oil, or from polyols obtained from vegetable oils, such as corn, sunflower, and soybean oils, and show a number of excellent properties because of the hydrophobic nature of TG (5,6). To use natural oils as raw materials for PU production, multiple hydroxyl functionalities are required. Usually these are obtained by reacting epoxidized oils with low-M.W. mono- or polyfunctional alcohols or acids.

Recently, Petrovic *et al.* (7) reported the effect of the NCO/OH molar ratio on soy-based PU network properties using a methoxylated soy polyol (OH functionality = 3.7) and 4,4′-methylenebis(phenyl isocyanate) (MDI). Glassy polymers were produced when the NCO/OH ratio was between 0.8 and 1.05. Higher cross-linking densities, glass-transition temperatures (T_g), and tensile strengths were observed as the NCO/OH ratio increased. The influence of the diisocyanate structure on the properties of these soy-based PU was also investigated (8).

Guo *et al.* (9) reported the physical and mechanical properties of soy polyol-derived PU prepared by the hydrogenation of hydroformylated soybean oil. When the hydroformylation reaction was rhodium catalyzed, an OH functionality of 4.1 was obtained, yielding a rigid PU after reaction with MDI. On the other hand, a cobalt-catalyzed hydroformylated polyol presented an OH functionality of approximately 2.7, resulting in a polymer with poorer mechanical properties.

Javni *et al.* (10) also prepared a series of PU from halogenated, hydrogenated, methoxylated, epoxidized soybean oil with an average OH functionality of 3.8. PU based on nonhalogenated soy polyols showed higher thermal stability but lower T_g and mechanical properties.

Our group has studied different methods of functionalizing vegetable oils to obtain new raw materials for the preparation of biorenewable materials (11,12). In this study, we prepared formiated epoxy soy polyols in a one-step synthesis and investigated their influence on the mechanical properties of PU networks. Soy polyols having OH functionalities from 1.9 to 3.2 were reacted with different diisocyanates at a constant NCO/OH molar ratio. The effect of the diisocyanate structure and the PU curing conditions (time and temperature) also were investigated.

EXPERIMENTAL PROCEDURES

Materials. 2,4-Toluene diisocyanate (TDI) was purified by distillation under reduced pressure. MDI and 1,6-hexamethylene diisocyanate (HDI) were used as received but were degassed. All diisocyanates were supplied by Bayer AG (Leverkusen, Germany). The NCO index was determined according to ASTM D5155-96 (13). Toluene (Merck, Darmstadt, Germany) was dried under sodium and distilled before use under a nitrogen atmosphere.

Soy polyol synthesis. Fifty grams (0.26 mol of double bonds) of degummed soybean oil (MM = 868 g/mol and 4.5

---

*To whom correspondence should be addressed at Instituto de Química–UFRGS, CP 15003, 91501-970, Porto Alegre, RS, Brazil.
E-mail: petzhold@iq.ufrgs.br

mol of double bonds) supplied by Oleoplan Ltda. (Veranópolis, Brazil) was mixed with 13 mL (0.78 mol) of formic acid (Synth, São Paulo, Brazil). A solution of 30% H_2O_2 (29 mL, 0.39 mol; Nuclear, São Paulo, Brazil) was slowly added to the mixture at room temperature for 30 min under strong mechanical stirring. When the H_2O_2 addition was completed, the mixture was heated to 65°C for different lengths of time, depending on the hydroxylation level to be reached. After the required time, heating was removed and a 10% wt/vol sodium bisulfide solution was added to the mixture and stirred for at least 30 min to eliminate excess peroxide. Ethyl ether (from Nuclear) was then added, and the organic layer was washed with a 10% wt/vol sodium carbonate solution until neutralized. The organic layer was dried with sodium sulfate overnight, and the solvent was removed under vacuum.

PU preparation. The soy polyols were maintained under vacuum for 2 h before polymerization. PU were prepared by mixing the soy polyols with diisocyanate at a NCO/OH ratio of 0.80 at 60°C and placed into molds. Samples were then maintained at 60 or 100°C for 24 h to complete curing. The PU curing reaction was monitored by the disappearance of isocyanate absorption at 2270 cm^{-1} in the IR spectrum.

Characterization methods. The soy polyols were analyzed by IR and ^1H NMR spectroscopy. The IR spectra were obtained with a Shimadzu FTIR spectrophotometer, Model 8300, using KBr crystals. The ^1H NMR spectra were obtained with a Varian Inova 300, 300 MHz, using $CDCl_3$ as solvent and tetramethylsilane as standard. The viscosity was measured at 30°C in a Brookfield viscometer, model LVDV-II, serial no. RT57729. The OH content of the soy polyol was determined according to AOCS Official Method Tx 1a-66 (14).

The PU obtained from soy polyols were characterized by the following methods and techniques: DSC experiments were carried out using a PerkinElmer DSC-4 differential scanning calorimeter in a nitrogen atmosphere at a heating rate of 10°C/min.

Size exclusion chromatography (SEC) was performed in THF as the eluent on a Waters GPC equipped with a differential refractometer detector (Waters 410) and PS/DVB columns (linear, 10^5, 10^4, and 10^3 Å Waters Styragel; Waters, Milford, MA). A calibration curve with polystyrene standards was used.

Dynamic mechanical measurements were carried out on PL-DMTA MKII equipment. The storage modulus, E', and loss modulus, E'', as well as the loss factor, tan δ, were determined from −100 to 200°C at a heating rate of 2°C/min at 1 Hz. T_g was determined as the temperature at the maximum of the tan δ vs. temperature curve.

PU densities were measured by immersion in butyl acetate according to the method ASTM D 792-91 (15).

Network cross-linking density (ν_e) was calculated by the following equation, derived from the theory of rubber elasticity (16):

$$E' = 3\nu_e RT \qquad [1]$$

where E' is the storage modulus of the thermoset in the rubbery plateau region at T_g + 40°C, R is the gas constant, and T is the absolute temperature.

From the cross-linking density, the number-average M.W. between cross-linking (M_c) can be determined through the equation

$$M_c = \rho/\nu_e \qquad [2]$$

Swelling experiments were performed in toluene at 30°C. Three weighed and previously dried samples of each PU were placed in excess of dry toluene for 4 d at room temperature. On day 5, the samples were maintained at 30°C for 8 h, then removed from the toluene and weighed. The soluble fraction (W_s) for each sample was calculated by the weight difference between the dry sample before (w_1) and after (w_2) toluene extraction, according to the following equation:

$$W_S = (w_1 - w_2)/w_1 \qquad [3]$$

The volume fraction of the polymer in the swollen sample, Φ_2, was calculated as

$$\Phi_2 = \frac{(W_2/\rho_2)}{\frac{W - W_2}{\rho} + \frac{W_2}{\rho_2}} \qquad [4]$$

where w is the weight of the solvent absorbed by the sample, ρ is the solvent density, and ρ_2 is the density of the PU.

The degree of swelling was then determined from the inverse of the volume fraction of the polymer in the swollen sample:

$$\text{Degree of swelling} = \frac{1}{\Phi_2} \qquad [5]$$

Hardness was determined with a Shore A Durometer according to the method ASTM D 2240-97 (17). Measurements were made at 3, 15, and 30 s at six different points on the sample surface. The average value was taken as the hardness value.

RESULTS AND DISCUSSION

Soy polyol synthesis. Low-M.W. liquid epoxy polyol esters or ethers from vegetable oils can be used as polyols for PU systems. Usually, hydroxyl groups have been introduced through a two-step synthesis involving the epoxidation of the unsaturated sites with formic acid and hydrogen peroxide, followed by epoxy ring opening with mono- or polyfunctional alcohols, amino alcohols, or acids (5). Depending on the reaction conditions, polyols with high OH functionality (complete reaction) or epoxy polyol esters with remaining epoxy groups (partial conversion) are obtained. The latter (epoxy polyol esters) are also interesting because of their better oxidative stability (18).

In this study, formiated epoxy soy polyols were prepared by a one-step synthesis using the formic acid/H_2O_2 system. Initially, the best molar proportion of soybean oil double bonds/formic acid/H_2O_2 (1:3:1.5) was determined in order to

TABLE 1
Characterization of Formiated Epoxy Soy Polyol as a Function of Reaction Time[a]

Reaction	Time (min)	Acid value (mg KOH/g)	OH number (mg KOH/g)	Viscosity (cP at 30°C)
1	20	1.8	53	230
2	60	1.8	64	621
3	80	1.8	98	1398
4	100	2.2	125	3617
5	120	1.8	137	2933
6	150	2.0	158	5718
7	240	1.2	162	9844

[a] 1 mol of double bonds/3 mol of formic acid/1.5 mol of H_2O_2, at 65°C.

have a total conversion of the double bonds. The hydroxylation reaction was carried out at a constant temperature (65°C), and by increasing the reaction time, it was possible to prepare soy polyols with OH numbers from 53 to 162 mg KOH/g, as can be seen in Table 1.

Figure 1 shows the IR and ^{1}H NMR spectra of the soy polyol with an OH value of 162 mg KOH/g. In the IR spectrum, besides the appearance of a large band around 3400 cm^{-1}, assigned to OH stretching, and two small bands at 877 and 925 cm^{-1}, assigned to the epoxy groups, the disappearance of the 3010 cm^{-1} band, corresponding to the hydrogen of the =CH group, also can be observed.

In the ^{1}H NMR spectrum, the major changes observed were the appearance of hydrogen signals assigned to the formiate group ($\underline{H}$COO–, 8.15 ppm) and epoxy groups [–C$\underline{H}$(O)C$\underline{H}$–, 2.8–3.2 ppm], and methinic protons attached to the hydroxyl and formiate groups (–C$\underline{H}$(OH), 3.8–4.2 ppm). In the characteristic unsaturated bond region (5.2–5.5 ppm), only the signal corresponding to the methinic proton of the glycerol unit $(ROOCH_2)_2C\underline{H}(OOR)$ was observed.

The increase in viscosity was also expected since the presence of polar groups increases interaction between the molecules.

It is important to point out that in epoxy polyol esters from vegetable oils, the distribution of OH groups is not homogeneous. In fact, the OH value determined for each sample is an average distribution of OH groups present in the TG, which are composed of glycerol triesters of different saturated and unsaturated FA. This nonhomogeneous distribution is responsible for the different properties and characteristics of the vegetable polyols compared with petrochemical ones. Figure 2 shows the idealized structure of a formiated epoxy soy polyol with an OH functionality of approximately 3.0 having a saturated hydrocarbon structure, with one OH and one formiate group per double bond and one residual epoxy group.

Table 2 shows the characterization of formiated epoxy soy polyol used in PU preparation. Soy polyols having OH functionalities between 1.9 and 3.2 and acid values lower than 2.5 mg KOH/g were obtained. The OH functionality was calculated based on the OH number and the extension of the epoxy ring opening, p (hydroxylation reaction), as follows:

$$[\text{OH functionality}] = \text{OH number}/56{,}100 \times [\text{MM (soybean oil)} + 4.5(46 + 16) \times p + 4.5 \times 16 \times (1 - p)] \tag{6}$$

The number-average M.W., M_n, determined by SEC measurements, increases with the OH functionality and is higher than the calculated MM. However, these values should be viewed

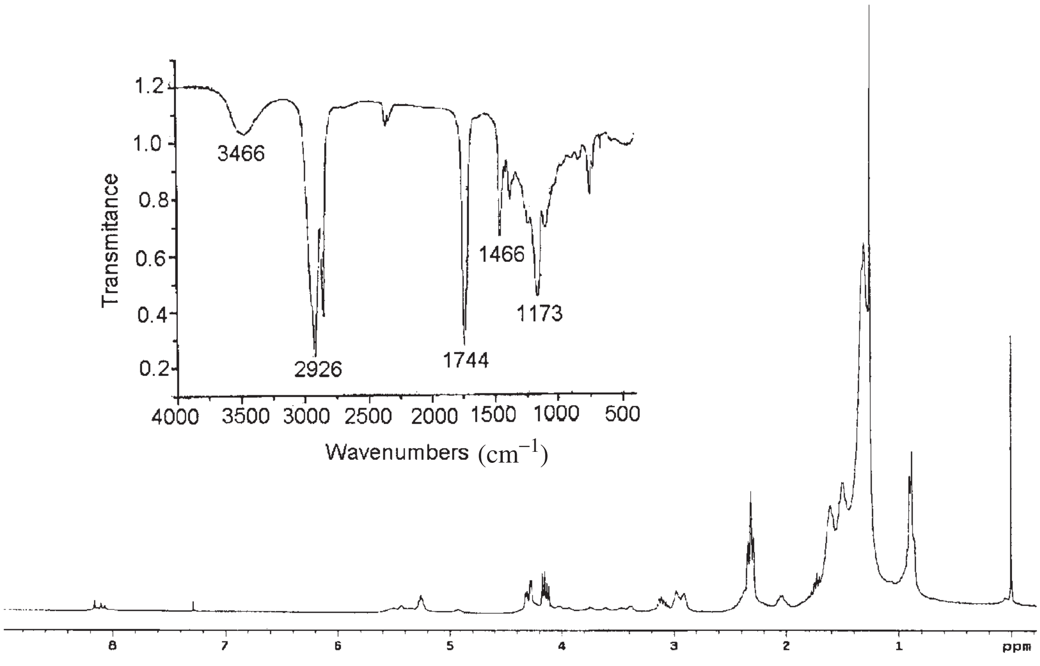

FIG. 1. FTIR (KBr film) and ^{1}H NMR ($CDCl_3$, 300 MHz) spectra of the formiated epoxy soy polyol (162 mg KOH/g).

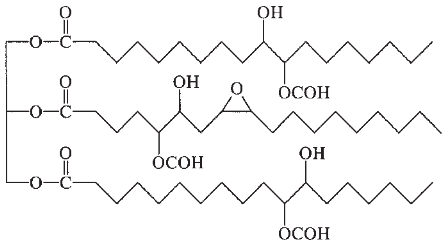

FIG. 2. Idealized structure of a formiated epoxy soy polyol.

with caution since they are obtained using a polystyrene standard calibration curve and also because TG are not linear molecules.

The soybean oil used in this work had 4.5 mol of double bonds, and after the reaction they were totally converted—part of them in OH/formiate groups and the rest in epoxy groups—resulting in a formiated epoxy polyol. Polymerization of the epoxy groups was not observed by SEC measurements. However, etherification and esterification of the epoxide groups cannot be ruled out, since the epoxide contents of the polyols, determined by ^{1}H NMR measurements, were lower than the theoretical ones.

PU preparation and characterization. PU were prepared by curing soy epoxy polyols with three diisocyanates in different conditions, as shown in Table 3. We used a NCO/OH ratio of 0.8 (excess of OH groups) to guarantee that the NCO groups reacted to completion. In this way, the known difference in NCO reactivity, in the case of TDI, would not significantly affect the properties of the resulting material. The parameters investigated were the influence of the OH functionality (PU01–PU04), the effect of the diisocyanate structure (PU01, PU05, and PU06), the influence of the curing temperature (PU01, PU08), and the effect of the curing time (PU07–PU09) on the properties of PU. The complete curing of PU was monitored by IR, through the disappearance of the isocyanate absorption band at 2270 cm^{-1}, and was confirmed by DSC analysis, where the exothermic curing reaction peak was not observed after the curing treatment.

Table 3 also shows the characterization data of the prepared PU, namely, glass-transition temperature (T_g), density (ρ), storage modulus (E'), cross-linking density (ν_e), M.W. between cross-linking (M_c), soluble fraction (W_s), degree of swelling (DS), and hardness (H).

We observed that the T_g and ρ of the PU increased with the increase in the polyol functionality. Petrovic *et al.* (6) reported a similar result for different vegetable polyols.

TABLE 2
Characterization of the Formiated Epoxy Soy Polyols Used in Polyurethane Preparation

Soy polyol	OH number (mg KOH/g)	Epoxide content[a] (%)	Acid value (mg KOH/g)	Average functionality (*f*)	MM[b] (g/mol)	M_n[c] (g/mol)
01	104	49	2.0	1.9	1027	1882
02	136	27	1.8	2.5	1055	2075
03	152	7	2.1	2.9	1073	2306
04	162	ND[d]	2.5	3.2	1086	2404

[a] Determined by ^{1}H NMR.
[b] Calculated according to the relation: $MM = 868 + f(46 + 16) + (4.5 - f)(16)$.
[c] Determined by size-exclusion chromatography using a polystyrene standard calibration curve.
[d] Could not be determined.

TABLE 3
Curing Conditions and Characterization of Polyurethanes (PU) Prepared from Soy Epoxy Polyols

	Soy polyol		Curing conditions		Characterization Data[b]							
PU	Average functionality	Isocyanate[a]	Temp (°C)	Time (h)	Tg (°C)	E' (MPa)	ρ (g/cm^3)	ν_e (mol/m^3)	M_c (g/mol)	W_s (%)	DS	H
01	1.9	TDI	60	24	1	0.678	1.052	87	12100	23.6	3.62	29
02	2.5	TDI	60	24	21	1.426	1.076	171	6300	13.3	2.56	44
03	2.9	TDI	60	24	42	3.754	1.096	424	2600	5.2	2.09	55
04	3.2	TDI	60	24	48	3.978	1.102	442	2500	0.2	1.95	74
05	1.9	HDI	60	24	−13	0.539	1.032	73	14100	33.2	4.25	26
06	1.9	MDI	60	24	4	0.800	1.050	101	10400	28.2	3.21	35
07	1.9	TDI	100	15	7	1.406	1.056	176	6000	20.2	3.21	45
08	1.9	TDI	100	24	6	1.441	1.051	181	5800	18.2	3.09	46
09	1.9	TDI	100	48	9	1.412	1.050	176	6000	15.4	3.02	48

[a] TDI, 2,4-toluene diisocyanate; MDI, 4,4′-methylenebis(phenyl isocyanate); HDI, 1,6-hexamethylene diisocyanate; NCO/OH ratio, 0.80.
[b] T_g, glass-transition temperature; E', storage moduli at $T = T_g + 40°C$; ρ, density; ν_e, cross-linking density; W_s, soluble fraction; DS, degree of swelling; H, hardness (Shore A, 15 s).

As expected, the PU based on polyols with higher OH functionalities presented a higher ν_e and consequently a smaller M_c value. T_g values of the soy polyol networks increased linearly with the logarithm of ν_e, according to Nielsen's empirical equation (19):

$$T_g - T_{go} \approx \frac{3.9\times10^4}{M_c} \qquad [7]$$

where T_{go} is the glass-transition temperature of a non-cross-linked polymer with the same chemical composition as the cross-linked polymer. In the present study, a linear relation was obtained, with a correlation parameter of 0.995. It is known that the higher the ν_e, the higher the T_g of the polymer, because of the restrictions imposed on the molecular chain motions.

The content of W_s was only 0.2% for PU04 but increased with decreasing OH functionality. The soluble fraction was also investigated by NMR, IR spectroscopy, and SEC and was characterized as a urethane with a weighted-average M.W. (M_w = 4100 g·mol^{-1}) higher than the soy polyol weight (M_w = 2800 g·mol^{-1}).

The DS values observed in toluene are consistent with the results obtained for the ν_e, since lower DS would be expected at higher ν_e. The *H* values are also consistent with the results obtained, since higher OH-functionality PU showed higher ν_e and were therefore stiffer.

The nature of the diisocyanate also influenced the T_g, as can be seen by comparing the data obtained for PU01, PU05, and PU06. Networks prepared from aromatic diisocyanates (TDI, MDI) showed higher T_g than those prepared from HDI, which has a more flexible chain.

On the other hand, the ν_e increased moderately. We observed that the PU obtained from MDI (PU06) had a higher ν_e than the PU obtained from TDI (PU01) or HDI (PU05).

As noted previously, PU networks with higher ν_e have lower DS. PU prepared from MDI (PU06) presented lower DS than those from TDI or HDI. It is important to mention here that the presence of aromatics in the PU can contribute to a higher elastic modulus because of their more rigid structure, resulting in a higher ν_e, as obtained experimentally. However, higher aromatic contents are also expected to increase the solubility in toluene, giving higher DS at the same ν_e, which was not observed in this work.

Figure 3 shows the dependence of temperature on the storage modulus (*E*′) for the PU obtained at 60°C (PU01–PU06). As observed, *E*′ remained constant at lower temperatures for all PU. As the temperature increased, the *E*′ dropped abruptly, between –40 and 80°C, according to the material. Even at higher temperatures, the apparent constant modulus indicated the existence of stable cross-linked networks in the bulk polymer. All samples showed an increase in the rubbery modulus with temperature because of the contraction of molecular coils (8). As expected, the rigidity of the PU increased with increasing polyol OH functionality. For example, PU04 (OH functionality = 3.2) had an elastic plateau at *E*′ of 4 MPa, whereas PU01 (OH functionality = 1.9) showed poor thermomechanical properties and a lower *E*′ (0.7 MPa). Despite this polyol having an average OH functionality lower than 2, it also had a thermoset mechanical behavior, which we attributed to the heterogeneous composition of the TG molecules of the soybean oil.

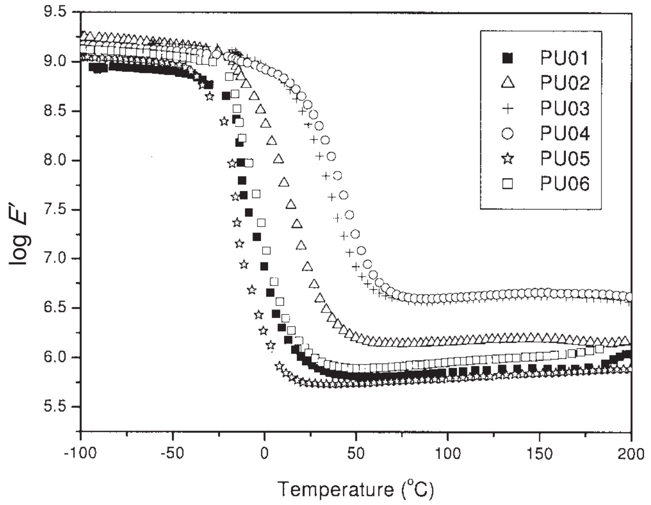

FIG. 3. Temperature dependence of the storage modulus (*E*′) for polyurethane (PU) networks (PU01–PU06) cured at 60°C for 24 h. PU01 (soy polyol OH number = 104 mg KOH/g and TDI), PU02 (soy polyol OH number = 136 mg KOH/g and TDI), PU03 (soy polyol OH number = 152 mg KOH/g and TDI), PU04 (soy polyol OH number = 162 mg KOH/g and TDI), PU05 (soy polyol OH number = 104 mg KOH/g and HDI), PU06 (soy polyol OH number = 104 mg KOH/g and MDI). TDI, 2,4-toluene diisocyanate; MDI, 4,4′-methylene-bis(phenyl isocyanate); HDI, 1,6-hexamethylene diisocyanate; NCO/OH ratio, 0.80.

Zlatanic *et al.* (20) prepared PU with MDI and triolein polyols with an OH functionality of 3.14, having a higher *E*′ (6.17 MPa) than that of the PU04 (3.98 MPa) prepared in this study using a soy polyol with almost the same OH functionality (3.2). The higher *E*′ obtained by Zlatanic *et al.* can be attributed to the use of MDI as the diisocyanate, the homogeneous polyol composition, and the different curing conditions, such as a higher NCO/OH ratio and temperature.

Very similar mechanical behavior was observed in the PU obtained from polyol with an average OH functionality of 1.9 and diisocyanates TDI, HDI, and MDI (respectively, PU01, PU05, and PU06). The networks prepared from MDI and TDI showed an elastic plateau at a higher *E*′ than that prepared from HDI, which has a more flexible chain. The same influence was verified recently by Javni *et al.* (8), although in this study we did not observe an increase in *E*′ at T_g in the samples prepared with aromatic diisocyanates (PU05 and PU06).

Figure 4 presents the tan δ vs. temperature curves for PU01–PU06. A tan δ peak was observed for all networks and was associated with the α relaxation temperature corresponding to the T_g of the cross-linked polymer network. A less pronounced peak around –70°C, corresponding to molecular motions in the polyol chains (β transition), was observed only in the log *E*″ plot. For PU01, PU05, and PU06, prepared from soy polyol of a 1.9 OH functionality, a shoulder was observed at a lower temperature, which can be attributed to the presence of nonreticulated PU, according to the higher values of the W_s for these PU (Table 3).

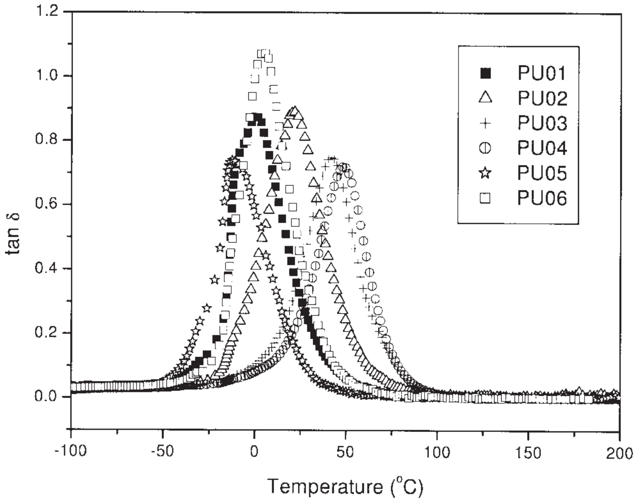

FIG. 4. Temperature dependence of the loss factor, tan δ, for the PU networks (PU01–PU06) cured at 60°C for 24 h. PU 01 (soy polyol OH number = 104 mg KOH/g and TDI), PU 02 (soy polyol OH number = 136 mg KOH/g and TDI), PU 03 (soy polyol OH number = 152 mg KOH/g and TDI), PU 04 (soy polyol OH number = 162 mg KOH/g and TDI), PU 05 (soy polyol OH number = 104 mg KOH/g and HDI), PU 06 (soy polyol OH number = 104 mg KOH/g and MDI). NCO/OH ratio, 0.80. For abbreviations, see Figure 3.

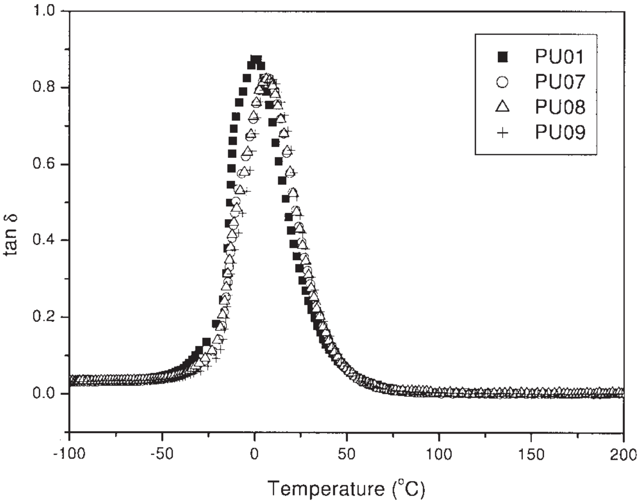

FIG. 6. Temperature dependence of tan δ for PU networks cured at 100°C for 15 (PU07), 24 (PU08), and 48 h (PU09). For comparison, the curve corresponding to PU01 (cured at 60°C, 24 h) was also included. The PU were prepared from a soy polyol with OH number = 104 mg KOH/g and TDI using an NCO/OH ratio of 0.80. For abbreviations, see Figures 3 and 4.

Comparing the data obtained for PU01 and PU08, we can see the remarkable effect of increasing the curing temperature from 60 to 100°C. The PU network obtained from the same polyol and diisocyanate but at a higher curing temperature (PU08) had a much higher E' and ν_e than PU01, cured at 60°C for 24 h. Consequently, the PU08 had a lower M_c, W_s, and DS and greater H. This result could be attributed to a polymerization reaction that could occur at a higher temperature between the remaining epoxy groups of the soy polyol.

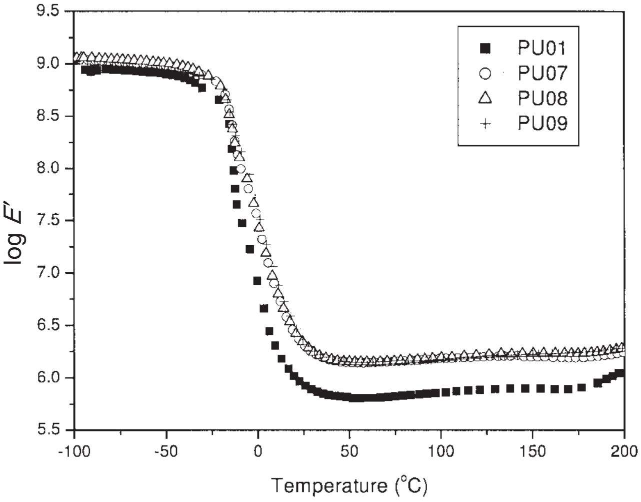

FIG. 5. Temperature dependence of E' for PU networks cured at 100°C for 15 (PU07), 24 (PU08), and 48 h (PU09). For comparison, the curve corresponding to PU01 (cured at 60°C, 24 h) was also included. The PU were prepared from a soy polyol with OH number = 104 mg KOH/g and TDI using an NCO/OH ratio of 0.80. For abbreviations, see Figure 3.

The reaction time showed a slight influence on the mechanical properties of the PU systems cured at 100°C, as can be seen in Table 3 when comparing the data for the PU07, PU08, and PU09 systems.

Figures 5 and 6 show the temperature dependence of E' and tan δ for the networks cured at 100°C and reaction times of 15, 24, and 48 h. As mentioned, no significant variation of T_g was observed for PU cured at different reaction times. When the T_g values of PU01 and PU08 are compared, however, one can see that a higher T_g was obtained for the polymer cured at the highest temperature. Also, in comparison with the PU cured at 100°C, the shoulder in the tan δ vs. temperature curve for PU08, cured at 60°C, was not more pronounced (Fig. 6), which could be evidence of a polymerization reaction between the residual epoxy groups.

ACKNOWLEDGMENTS

This work was supported by research grants from CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico–nr. 472525/03-4, Brazil) and Oleoplan–Óleos Vegetais Planalto Ltda. (Veranópolis, Brazil). L.L.M. is grateful to CAPES (Coordenadoria de Aperfeiçoamento de Pessoal de Ensino Superior, Brazil) and E.O.S. to FAPERGS (Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul, Brazil) for scholarships.

REFERENCES

1. Zhang, Y., and D.J. Hourston, Rigid Interpenetrating Polymer Network Foams Prepared from a Rosin-Based Polyurethane and an Epoxy Resin, *J. Appl. Polym. Sci. 69*:271–281 (1998).
2. Roy, T.K., V.M. Mannari, and D.A. Raval, Synthesis and Applications of Oil-Modified Polyesteramide Resins for Surface Coatings, *J. Sci. Ind. Res. 56*:159–163 (1997).

3. Ahmad, S., S.M. Ashraf, E. Sharmin, F. Zafar, and A. Hasnat, Studies on Ambient Cured Polyurethane Modified Epoxy Coatings Synthesized from a Sustainable Resource, *Prog. Cryst. Growth Charac. Mater. 45*:83–88 (2002).
4. John, J., M. Bhattacharya, and R.B. Turner, Characterization of Polyurethane Foams from Soybean Oil, *J. Appl. Polym. Sci. 86*:3097–3107 (2002).
5. Guo, A., Y.J. Cho, and Z.S. Petrovic, Structure and Properties of Halogenated and Nonhalogenated Soy-Based Polyols, *J. Polym. Sci., Part A: Polym. Chem. 38*:3900–3910 (2000).
6. Petrovic, Z.S., A. Guo, and W. Zhang, Structure and Properties of Polyurethanes Based on Halogenated and Nonhalogenated Soy-Polyols, *Ibid. 38*:4062–4069 (2000).
7. Petrovic, Z.S., W. Zhang, A. Zlatanic, C.C. Lava, and M. Ilavsky, Effect of OH/NCO Molar Ratio on Properties of Soy Based Polyurethane Networks, *J. Polym. Environ. 10*:5–12 (2002).
8. Javni, I., W. Zhang, and Z.S. Petrovic, Effect of Different Isocyanates on the Properties of Soy-Based Polyurethanes, *J. Appl. Polym. Sci. 88*:2912–2916 (2003).
9. Guo, A., D. Demydov, W. Zhang, and Z.S. Petrovic, Polyols and Polyurethanes from Hydroformylation of Soybean Oil, *J. Polym. Environ. 10*:49–52 (2002).
10. Javni, I., Z.S. Petrovic, A. Guo, and R. Fuller, Thermal Stability of Polyurethanes Based on Vegetable Oils, *J. Appl. Polym. Sci. 77*:1723–1734 (2000).
11. Gerbase, A.E., J.R. Gregório, M. Martinelli, M.C. Brasil, and A.N.F. Mendes, On the Epoxidation of Soybean Oil by the Methyltrioxorhenium-CH_2Cl_2/H_2O_2 Catalytic Biphasic System, *J. Am. Oil Chem. Soc. 79*:179–181 (2002).
12. Gerbase, A.E., J.R. Gregório, M. Martinelli, M.C. Brasil, and A.N.F. Mendes, Reactivity of the Biphasic Trichloroacetonitrile-CH_2Cl_2/H_2O_2 System in the Epoxidation of Soybean Oil, *Grasas Aceites 53*:175–178 (2002).
13. ASTM International, D 5155-96 Standard Test Method for Polyurethane Raw Materials: Determination of the Isocyanate Content of Aromatic Isocyanates, ASTM International, West Conshohocken, PA, 2005.
14. AOCS, Hydroxyl Value of Epoxidized Oils, *Official Methods and Recommended Practices of the AOCS*, 5th edn., AOCS Press, Champaign, 1997, Official Method Tx 1a-66.
15. ASTM International, D 792-91 Standard Test Method for Density and Specific Gravity (relative density) of Plastics by Displacement, ASTM International, West Conshohocken, PA, 1991.
16. Ward, I.M., *Mechanical Properties of Solid Polymers*, John Wiley & Sons, London, 1971, pp. 77–107.
17. ASTM International, D 2240-97 Standard Test Method for Rubber Property—Durometer Hardness, ASTM International, West Conshohocken, PA, 1997.
18. Hwang, H.-S., and S.Z. Erhan, Modification of Epoxidized Soybean Oil for Lubricant Formulations with Improved Oxidative Stability and Lower Pour Point, *J. Am. Oil Chem. Soc. 78*:1179–1184 (2001).
19. Nielsen, L.E., and R.F. Landel, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1994, pp. 131–217.
20. Zlatanic, A., Z.S. Petrovic, and K. Dusek, Structure and Properties of Triolein-Based Polyurethane Networks, *Biomacromolecules 3*:1048–1056 (2002).

[Received September 30, 2004; accepted April 25, 2005]