Polyurethane Foams from Soyoil-Based Polyols

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ABSTRACT: The focus of this work was to synthesize bio-based polyurethane (PU) foams from soybean oil (SO). Different polyols from SO were produced as follows: soybean oil monoglyceride (SOMG), hydroxylated soybean oil (HSO), and soybean oil methanol polyol (SOMP). The SOMG was a mixture of 90.1% of monoglyceride, 1.3% of diglyceride, and 8.6% of glycerol. The effect of various variables (polyol reactivity, water content curing temperature, type of catalyst, isocyanate, and surfactant) on the foam structure and properties were analyzed. SOMG had the highest reactivity because it was the only polyol-containing primary hydroxyl ($-$OH) groups in addition to a secondary $-$OH group. PU foams made with SOMG and synthetic polyol contained small uniform cells, whereas the other SO polyols produced foams with a mixture of larger and less uniform cells. The type of isocyanate also had an influence on the morphology, especially on the type of cells produced. The foam structure was found to be affected by the water and catalyst content, which controlled the foam density and the cure rate of the PU polymer. We observed that the glass transition (T_g) increased with the OH value and the type of diisocyanate. Also, we found that the degree of solvent swelling (DS) decreased as T_g increased with crosslink density. These results are consistent with the Twinkling Fractal Theory of T_g. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2567–2578, 2009

Key words: polyurethane; foam; polyol; soybean oil; biobased polymer

INTRODUCTION

Polyurethanes (PUs) play an important role as thermal and sound insulators in many industries such as shipbuilding, footwear, construction, cars, electronics, sporting goods, and many others. PU is prepared by the reaction of diisocyanates or polyisocyanates with polyols (Scheme 1). The reaction between the isocyanate and water (H_2O) produces both a substituted urea and the carbon dioxide blowing agent, which creates the PU foam.[1,2] Therefore, the foam structure depends on the relative rates of these two reactions.
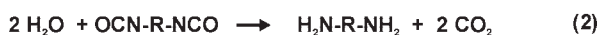
The polyol can be synthesized from vegetable oils (VO) such as soybean, palm, castor, sunflower, canola, and linseed. Soybean oil (SO) is a commodity material and has been used in diverse applications such as coatings, paint formulations, and foams.[3–18]

There have been several studies on rigid foams based on SO polyols. Petrovic's group made numerous contributions to the production of rigid foams from SO-based polyols (SOP), and most of their research was dedicated to polyols containing secondary OH groups.[4–8] The unsaturated C=C bonds were converted to epoxy groups, followed by oxirane ring opening to produce the polyol secondary OH groups. Recently, they developed polyols with primary OH groups.[5,8,9] This synthesis involves the hydroformylation of the double bonds followed by the hydrogenation of the carboxylic groups. In this process, the oil was reacted with carbon monoxide in the presence of a Group-VIII metal catalyst (e.g., rhodium or cobalt) to form a hydroformylated vegetable oil. This product is then hydrogenated to form the modified natural oil-based polyol in the presence of a catalyst (e.g., raney nickel). Such PU foams have properties comparable with those derived from petroleum-based materials; but have the disadvantage of containing many reaction steps, making the final product expensive. Pechar et al. compared different soy-based polyols by changing their hydroxyl content and their blends with petroleum-based polyols.[13,14] They also used a hydroxylated soybean polyol (HSO) to study the effect of different parameters, such as functionality of the polyol and type of isocyanate, in the PU networks. They observed a linear increase in the glass transition temperature T_g with $-$OH content, similar to that observed by La Scala and Wool for acrylated triglycerides.[19] Pechar et al. also found that for a given soy-based polyol, the HDI-based network displayed the lowest T_g,

$$HO\text{-}R'\text{-}OH + OCN\text{-}R\text{-}NCO \longrightarrow \left[\underset{\underset{O}{\parallel}\ \underset{H}{|}}{C}\text{-}N\text{-}R\text{-}\underset{\underset{H}{|}\ \underset{O}{\parallel}}{N\text{-}C}\text{-}O\text{-}R'\text{-}O \right]_n \quad (1)$$

$$2\,H_2O + OCN\text{-}R\text{-}NCO \longrightarrow H_2N\text{-}R\text{-}NH_2 + 2\,CO_2 \quad (2)$$

**Scheme 1** Chemical pathways leading to triglyceride polyols.

followed by toluene diisocyanate (TDI) and then methane diphenyl diisocyanate (MDI), whereas the PASI 27 system offered the highest T_gs.[13,14] Lligadas et al. developed a polyether polyol with fatty acids (FA) prepared through an acid-catalyzed ring-opening polymerization of epoxidized methyl ester. Partial reduction of the ester groups gave primary alcohols that were shown to produce hard PU.[16] Tu et al. also prepared several vegetable oil-based polyols that gave rigid PU when compared with petroleum-based polyols.[3]

In this article, we are interested in bio-based flexible and rigid PU foams. Flexible PU foams have the highest volume applications, especially in the manufacture of mattresses. John et al.[17] synthesized flexible PU foams from a modified soy-based polyol. They found that the properties could be changed by controlling the water content, isocyanate index, and

catalyst. By analyzing their results, it is apparent that improvements can be made, especially with the reactivity of the modified soy-based polyol and also with the surfactants. Recently, Zhang et al.[15] studied flexible foams by replacing up to 30% of petroleum-derived polyether polyol with three substituent polyols: styrene acrylonitrile copolymer-filled, crosslinker, and soybean oil-derived polyol. They studied the effects of substituent polyols on the cellular structure and the polymer phase morphology. They found that SOP had an important influence on all the properties studied.

All these polyols are made by chemically modifying the triglyceride. The use of plant and animal oils has economic and environmental advantages that make them attractive alternatives to petroleum-based materials. The cost advantage is subject to market competition between food and energy utilization of plant oils. As shown in Scheme 2, triglycerides contain active sites (such as double bonds, allylic carbons, esters groups, and carbons alpha to the ester group) that can be used to introduce hydroxide groups to generate polyols.[4–9,19–22]

The objective of this work was to synthesize biorenewable flexible PU foams from SO-based polyols and study the effect on the foam morphology of
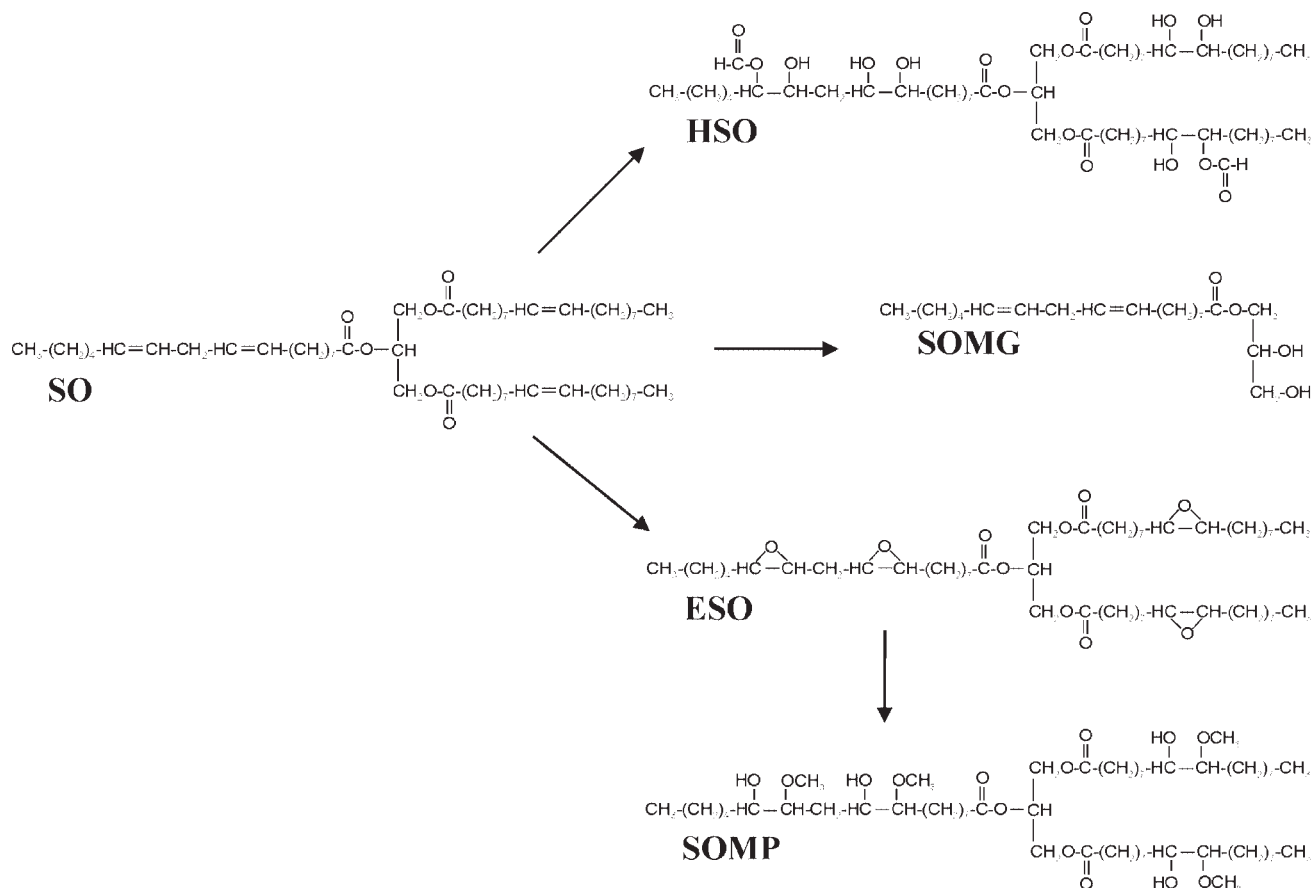
Scheme 2 General polyurethane foam reaction.

various variables such as polyol reactivity, water content, temperature, type of isocyanate, catalyst, and surfactant. For this purpose, different polyol monomers from SO were produced, as shown in Scheme 2: soybean oil monoglyceride (SOMG), HSO, and soybean oil methanol polyol (SOMP). The SOMG had both primary and secondary OH groups, whereas the SOMP and HSO had only secondary OH groups, which will affect the rates of reaction, as shown in Scheme 1.

EXPERIMENTAL

Materials

Formic acid (acs, 99.8% v/v), glycerol, hydrogen peroxide (30 wt %), ethylene glycol (acs), methanol (acs), soap (Deacon Bacdown), and fluoroboric acid (48 wt %) were purchased from Fisher Scientific (Pittsburg, PA). Refined SO, glycerol (acs), calcium hydroxide (acs), N,N-dimethylbenzylamine, and chloroform-D with 0.03% v/v of trimethylsilane (TMS) were purchased from Sigma-Aldrich (St. Louis, MO). BF 2470 was used as a surfactant (Evonik Goldschmidt, Hopewell, VA). The synthetic polyol, glycerol propoxylate had a molecular weight of 400 g/mol and a functionality of 3 (Sigma-Aldrich). We used three different isocyanates: (1) modified MDI (mod MDI; NCO content = 32.8; functionality = 2.22; Huntsman, The Woodlands, TX); (2) methane diphenyl diisocyanate (MDI; NCO = 33.4; functionality = 2; Sigma-Aldrich), and (3) TDI (NCO = 48; functionality = 2; Sigma-Aldrich). TDI is an 80/20 mixture of the 2,4 and 2,6 TDI isomers systems, respectively.

Synthesis of soybean oil monoglyceride

The glycerolysis reaction was done by heating the SO in the presence of glycerol and catalyst (Scheme 2), as described by Can et al.[22] The only difference in our synthesis is that we did not separate the remaining glycerol at the end of the reaction. The glycerol was placed with the $Ca(OH)_2$ (catalyst; in the amount of 0.65 wt % of the total oil amount) in a four-necked round-bottom flask equipped with a N_2 gas inlet, a mechanical stirrer, thermometer, and a calcium drier, and then heated at 230°C for 2 h under N_2 atmosphere to distill any water present. Then, SO was added in five portions to the glycerol, with each portion added at 1-h intervals. With the first portion, a commercial soap was added in the amount of 1 wt % of the total oil amount to act as an emulsifier. The solution was heated at 230°C under N_2, while being stirred for 5.5 h. The mass ratio of SO reacted with glycerol was 4 g of SO to 1 g of glycerol, corresponding to a molar ratio of 4.75 mol of glycerol to 1 mol of triglyceride.

Synthesis of epoxidized soybean oil

SO was epoxidized (see Scheme 2) at low temperature, with performic acid generated *in situ*, using benzene as a diluent for the organic phase, to minimize oxirane ring opening. The molar ratio of hydrogen peroxide (H_2O_2)/formic acid (FA)/SO unsaturation (double bonds) was 10/2/1. First, SO, benzene, and FA were placed together into a well-stirred, round-bottom glass reactor kept at room temperature. Then, dilute hydrogen peroxide (30 wt %) was added dropwise, after which the reactor temperature was slowly raised to 40°C, to complete the reaction. This procedure requires 22 h to complete the reaction. Formic acid and H_2O_2 were removed by washing the resin multiple times with water and then with saturated (aq.) sodium bicarbonate until a neutral pH was attained. The contents were allowed to phase-separate, and the aqueous layer was discarded. Then, the solution was washed with aqueous sodium chloride and dried over sodium sulfate. Finally, the benzene was removed by evaporation under vacuum.

Synthesis of hydroxylated soybean oil

HSO was synthesized directly from SO (Scheme 2).[21] The mass relation of SO/H_2O_2 (30 wt %)/FA was 1/1.25/1.25. SO and FA were placed in a 3-bore thermostated round-bottom flask, furnished with a reflux condenser and a mechanical stirrer. The reaction temperature was kept at room temperature and stirred vigorously for 14 h. Then, the organic phase was dissolved in ethyl ether. The acid was removed by washing multiple times with water and then with saturated (aq.) sodium bicarbonate until reaching a neutral pH. The solution was washed with saturated (aq.) sodium chloride and then dried over sodium sulfate. Finally, the ethyl ether was removed by evaporation under vacuum.

Synthesis of soybean oil methanol polyol

SOMP was prepared via oxirane ring-opening reaction of epoxidized soybean oil (ESO) with methanol (Scheme 2).[4–7] The molar ratio of MeOH/ESO was 20/1, and then 10 wt % of water and 0.4 wt % of HBF_4 were added with respect to the reaction mixture. ESO was placed in a 3-bore thermostated round-bottom flask furnished with a reflux condenser and a mechanical stirrer and preheated to 50°C. Then, the reaction mixture (containing the fluoroboric acid, water, and methanol), which was pre-equilibrated at the same temperature, was added. The reaction continued for 1 h at 50°C. The organic phase was dissolved in chloroform and then was washed with 200 mL of distilled deionized water

TABLE I
Reaction Conditions to Synthesize Polyurethane Foams from Soybean Oil Polyols

Sample no.	SOP[a] type	SOP (wt %)	SYNP[b] (wt %)	Iso[c] type	Iso[c] (wt %)	H$_2$O (wt %)	Cat.[d] (wt %)	Surf.[e] (wt %)	Ratio SYNP/SOP	NCO index	Curing Temp. (°C)	Foam density (g/cm^3)
1	SOMG	33.4	33.5	Mod MDI	32.3	0.36	0.46	0.31	1.00	92.9	23	0.34 ± 0.05
2	SOMG	33.4	33.5	Mod MDI	32.3	0.36	0.20	0.31	1.00	92.9	23	0.15 ± 0.02
3	SOMG	33.4	33.5	Mod MDI	32.3	0.36	0.36	0.31	1.00	92.9	23	0.25 ± 0.04
4	SOMP	33.4	33.6	Mod MDI	52.1	0.34	0.35	0.32	1.01	92.7	23	0.21 ± 0.01
5	HSO	33.6	33.5	Mod MDI	38.5	0.33	0.37	0.33	1.00	92.5	23	0.19 ± 0.04
6	SOMG	31.0	35.7	Mod MDI	32.4	0.36	0.36	0.34	1.15	93.2	23	0.16 ± 0.02
7	SOMG	37.8	29.1	Mod MDI	32.3	0.35	0.37	0.32	0.77	92.9	23	0.28 ± 0.03
8	SOMG	32.8	34.1	TDI	32.3	0.35	0.35	0.31	1.04	114.3	23	0.23 ± 0.04
9	–	–	66.4	Mod MDI	32.7	0.35	0.36	0.34	–	94.0	23	0.20 ± 0.02
10	–	–	67.0	MDI	32.2	0.35	0.35	0.31	–	93.5	23	0.23 ± 0.01
11	SOMG	33.4	33.5	Mod MDI	32.1	0.40	0.39	0.32	1.00	92.3	23	0.24 ± 0.01
12	SOMG	33.5	33.6	Mod MDI	31.9	0.50	0.36	0.33	1.00	91.7	23	0.18 ± 0.05
13	SOMG	33.1	33.5	Mod MDI	32.3	0.36	0.36	–	1.00	92.9	23	0.29 ± 0.01
14	SOMG	32.2	34.8	MDI	32.1	0.34	0.36	0.31	1.00	93.2	23	0.22 ± 0.03

[a] Soy polyol.
[b] Synthetic polyol.
[c] Diisocynate.
[d] Catalyst: *N,N*-dimethylbenzylamine.
[e] Surfactant.

two times and with 200 mL of a NH$_3$ solution for two times (5 wt %). The contents were allowed to phase-separate, and the aqueous layer was discarded. Then, the solution was washed with aqueous sodium chloride and dried over sodium sulfate. Finally, the methanol, the ethanol, and the chloroform were removed by evaporation under vacuum.

Synthesis of polyurethanes

PU foams were synthesized using polyols, catalyst, surfactant, water, and diisocyanate. The experimental matrix of reactants (Table I) included different types of SO polyols (SOMG, HSO, and SOMP), isocyanates (MDI, TDI, modified MDI, and modified ISO), synthetic polyol, blowing agent (water), and catalyst. The PU foams were prepared by adding the polyols, surfactant, catalysts, and water into a plastic beaker (diameter 9 cm and height 12 cm). Then, the diisocyanate was added, and the mixture was stirred vigorously for 20 s at 1000 rpm employing a mechanical stirrer with a crossed-blade impeller. All the reactants were preheated to 50°C. Afterward, the content of the cup was allowed to foam and settle for a week prior to analysis.

Analysis

[1]H-nuclear magnetic resonance was used to monitor ESO and the different polyols.[20–25] The samples were prepared by dissolving 60 mg of the sample in 0.6 mL of CDCl$_3$. A Brunker AV400 Spectrometer (Brunker, Germany) was used to analyze the sam-

ples with a pulse width of 90° in all cases. The samples were analyzed at 293 K and 16 scans of each sample were taken. The hydroxyl value of the polyol was determined by ASTM D 1957-86. Also, the rheology of the chemically modified SO was measured using a TA Instrument AR-G2 Rheometer (New Castle, DE). A conic-plate geometry with 40-mm plates was used for all the samples. The shear rate was increased from 1 to 1200 s^{-1} and then reduced back to 1 s^{-1}. The effect of the temperature was also evaluated. A repeat run was performed for all the samples.

The PU foams were characterized by density, tensile, and swelling tests. The structural properties were investigated using scanning electron microscopy (SEM) and the thermal properties with a differential scanning calorimetry (DSC). The apparent density was measured according to ASTM D 1622-93. The tensile tests were conducted on the Instron 4201 testing machine at a constant crosshead speed of 2 mm/min (four specimens with $60 \times 20 \times 8$ mm^3 of each PU were tested). DSC experiments were performed on the foams to determine the glass transition temperature (T_g) using a TA Q100 DSC, where 15 mg of the sample was weighed in a hermetically sealed aluminum pan and a heating rate of 10°C/min was used; the samples were dried at 60°C under vacuum to a constant weight before performing the DSC experiments. The cellular morphology of the foam was examined with a JSM-7400F field emission SEM. A small portion of an uncrushed foam was cut from the foam block and frozen in N$_2$ liquid, and then a thin piece of foam was carefully

TABLE II
Properties of the Soybean Oil Polyols (SOP)

SOP	SOMG	SOMP	HSO
OH value (mg KOH/g)	90	184	120
Equivalent weight	623.3	304.9	467.5
Molecular weight (g/mol)	354	990	995
Type of OH group	Primary and secondary	Secondary	Secondary

sliced with a sharp blade and stuck to aluminum stubs. The samples were then sputter-coated with a total of 15 nm of gold and observed under the microscope employing an accelerating voltage of 5 kV. For the PU foam swelling measurement, about 0.3 g of sample was dried at 60°C under vacuum to a constant weight and then immersed in an excess of toluene (20 mL) at room temperature for 48 h until equilibrium swelling occurred. The swollen samples were dried with a filter paper and weighed.[18,26–28]

RESULTS AND DISCUSSION

Polyol NMR analysis

Scheme 2 shows the synthetic pathways employed in this work to produce polyols from triglycerides, and Table II gives the OH values, the estimated molecular weight, and the type of OH group. The first route in Scheme 2 consisted in transforming the unsaturated sites of SO into epoxy groups (by performic acid generated *in situ*) and then producing the polyol (SOMP) via oxirane ring opening with an alcohol and a homogeneous acid catalyst.[4–7] ^{1}H-NMR was used to monitor the reaction. Table III contains a list of the δ-values corresponding to the different protons of SO and ESO molecules and the ^{1}H-NMR spectrum of all the compounds synthesized in this work (Fig. 1). SOMP retains most of the characteristic peaks of ESO except those at δ = 2.8–3.2 ppm and δ = 1.4–1.55 ppm, which are the regions corresponding to the Hs attached to the epoxy groups and methylene groups adjacent to the epoxy groups, respectively. New peaks appear at δ = 3.2–3.9 ppm (Fig. 1) corresponding to the —CH—OH and —CH—OCH$_3$ groups, respectively. From the ^{1}H-NMR spectra, the number of initial unsaturated sites per triglyceride ($U = 4.4$) and the number of epoxide groups per TGD after the reaction ($E = 4.14$) were calculated and used to determine the extent of epoxidation, which was 0.94. The extent of reaction for the production of SOMP based on epoxides was 0.98. The equations used to obtain the extent of reaction can be found in La Scala's work.[23]

The second path (Scheme 2) was to directly convert the double bonds into diols by hydroxylation. The HSO retains most of the characteristic peaks of SO except the ones related to the double bonds. New peaks corresponding to —CH—OH appear at δ = 3.2–3.9 ppm and also δ = 7.8–8.2 ppm corresponding to —CH—OCOCH$_3$ (Fig. 1). The extent of hydroxylation was 0.71.

The last method was to generate monoglycerides from the reaction of triglycerides with glycerol. SOMG was monitored by the disappearances of the —CH$_2$—CH—CH$_2$— backbone proton at δ = 5.1–5.3 ppm, the methylene proton of —CH$_2$—CH—CH$_2$— backbone at δ = 4.0–4.4 ppm, and by the methyl esters of the methyl FA that appears at δ = 3.6 ppm (Fig. 1).[20–23] The resulting product contained 90.1% of monoglyceride, 1.3% of diglyceride, and 8.6% of glycerol.

Polyol rheology

Rheological measurements were performed on the ESO and the polyols using a TA Instrument AR-G2 Rheometer. Figure 2(A) shows the change of viscosity with temperature. As expected, the viscosity of all samples decreased exponentially with temperature. SOMG has the advantage of having the lowest viscosity when compared with any other SO-based polyols produced, which is important for resin transfer molding and other processing methods requiring low resin viscosity. Figure 2(B) shows the shear stress versus the shear rate for the four monomers. Most show a linear Newtonian fluid response below shear rates of about 400 s^{-1} and exhibit shear thinning at higher shear rates. Based on the overlap ability of the up and down shear rates, the ESO shows the most Newtonian behavior while the SOMP does

TABLE III
^{1}H-Nuclear Magnetic Resonance of SO and ESO: List of the δ-Values of the Different Protons

| Peak	Proton type	δ (ppm)
1	—CH$_2$—CH—CH$_2$— backbone	4.0–4.4
2	—CH$_2$—CH—CH$_2$— backbone	5.1–5.3
3	α-CH$_2$ adjacent to >C=O	2.2–2.4
4	β-CH$_2$ adjacent to >C=O	1.7–1.9
5	—(CH$_2$)$_n$—	1.1–1.4
6	terminal —CH$_3$	0.8–1.0
7	—CH— protons of the double bonds	5.3–5.4
8	—CH$_2$ protons adjacent to two double bonds	2.8
9	β-CH$_2$ adjacent to the double bond	2.01–2.06
10	—CH— protons of the epoxy ring	2.8–3.3
11	—CH$_2$ protons adjacent to two epoxy groups	1.8–2.0
12	β-CH$_2$ adjacent to epoxy group	1.4–1.55
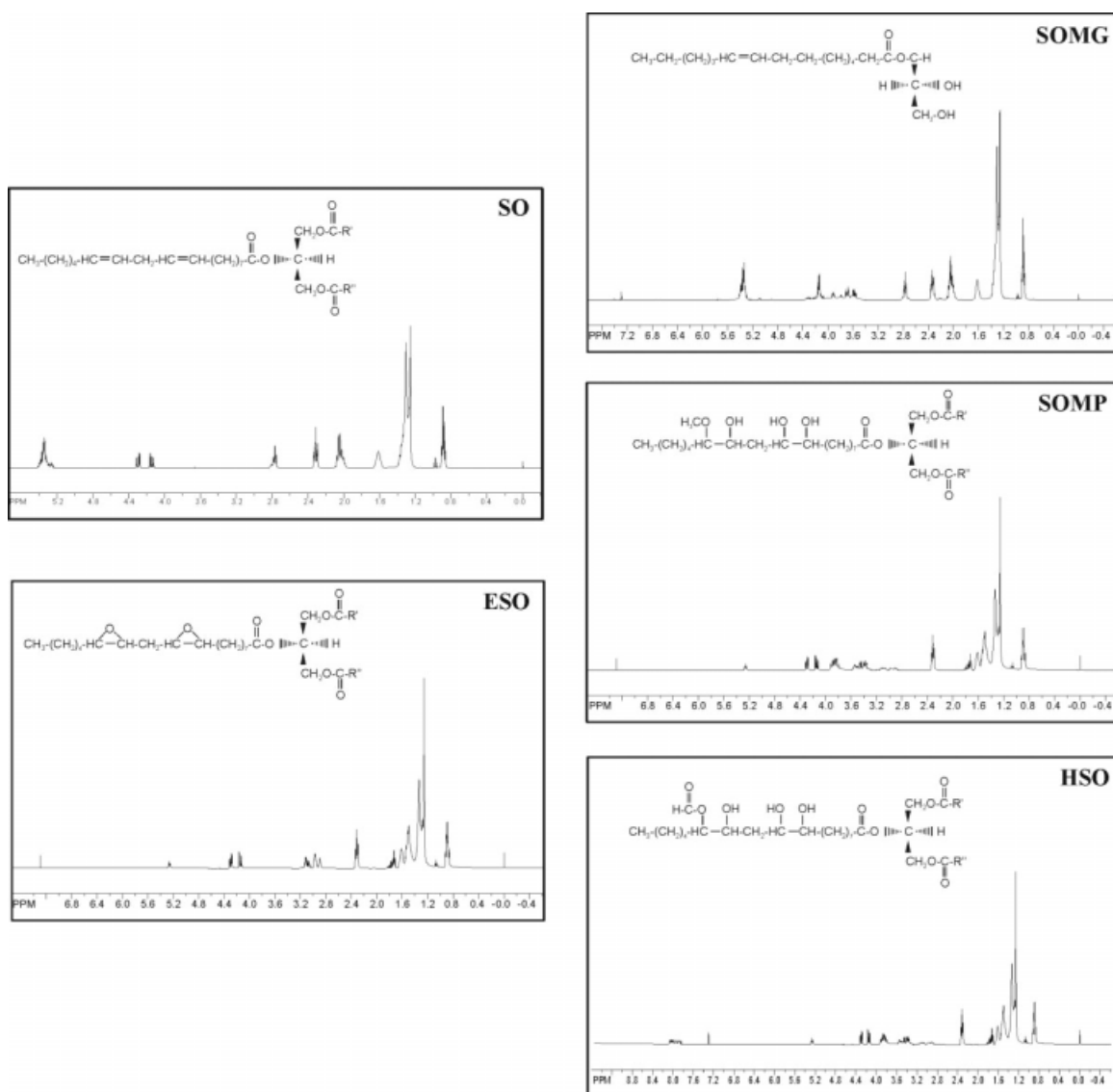
Figure 1 ^{1}H-nuclear magnetic resonance spectrum of soybean oil (SO), epoxidized soybean oil (ESO), and soybean oil polyols, SOMG, SOMP, and HSO.

not follow the same path during the cyclic reversal of shear rate. When the shear rate is lowered, the stress path lags and forms a hysteresis loop, which then returns to a point lower than the initial stress. The stress–shear rate hysteresis is due to the structure formation during shear and its relaxation time. Thus, all the SOP examined in this work exhibit thixotropic behavior.

It is important to emphasize that SOMG when compared with the other SOP discussed herein has the advantage of a primary OH group at the terminal fatty acid location and a secondary OH group. Furthermore, SOMG can be synthesized in a one-pot process with small reaction times, which facilitates lower manufacturing costs. SOMG also utilizes glycerol as a feedstock, which has become a cheap byproduct of the biodiesel manufacturing process.

These factors combine to make SOMG a useful reactive and low-cost polyol for bio-based PU.

Polyurethane foams

The structure of the PU foam is highly dependent on the relative rates of the two reactions presented in Scheme 1, where the formation of the PU polymer (Reaction 1) competes for the utilization of isocyanate with the cellular foaming process (Reaction 2). If Reaction 1 is faster, the polymer may cure before the foam is fully expanded by the slower CO_2 reaction and the final foam would have a higher density with smaller cells. If Reaction 2 is faster, the foaming process occurs faster and may even begin deteriorating before the polymer solidifies via the slower Reaction 1. In the latter case, the cured foam will
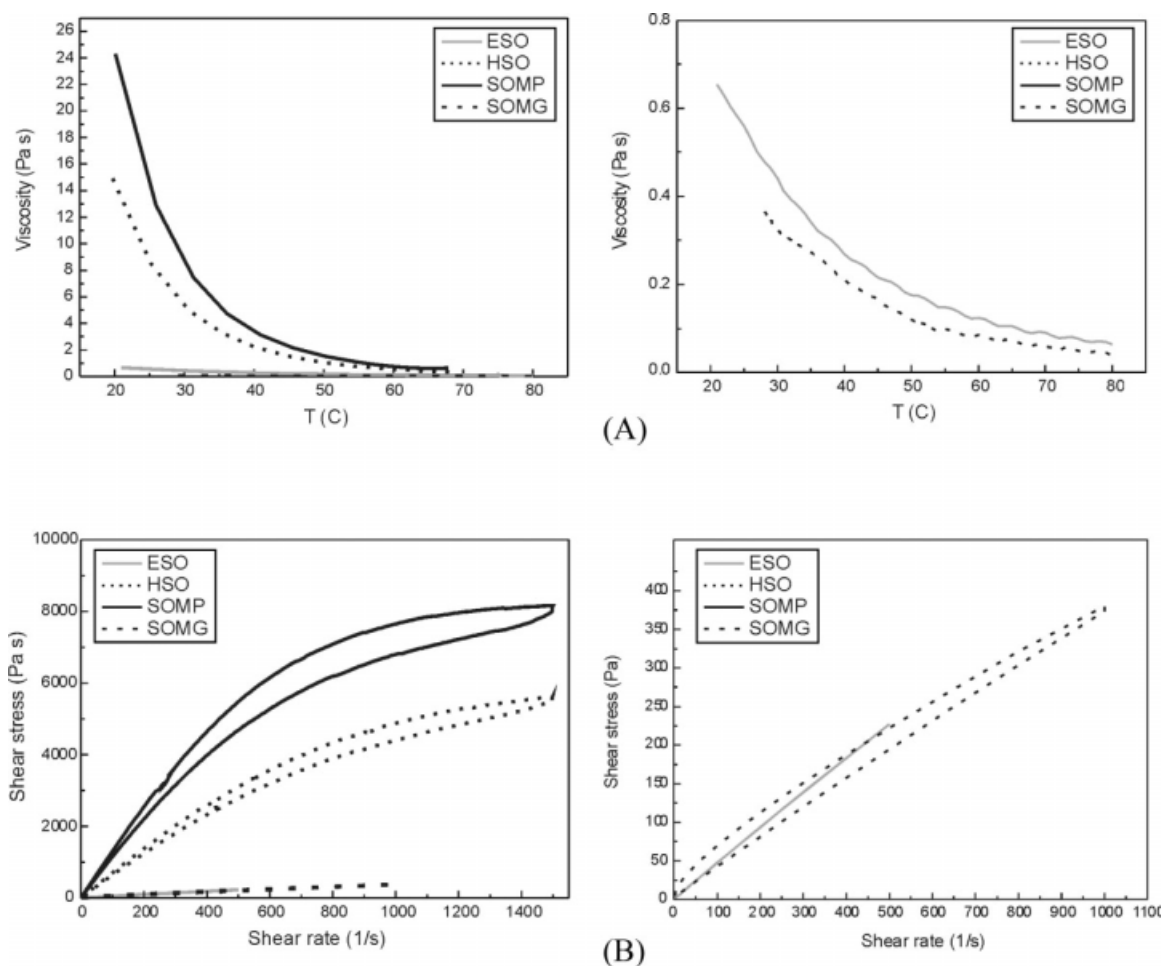
Figure 2 (A) Top: Viscosity as a function of temperature (left: SOMG and SOMP; right: HSO and ESO). (B) Bottom: Shear stress versus shear rate for epoxidized soybean oil (ESO) and the soybean oil polyols (SOMG, SOMP, and HSO).

have a lower density with a potentially irregular larger cell structure. In this section, we show the effects of different parameters on the foam structure, including the relative reactivity of the SO-based polyol and isocyanate, ratio of SOP to synthetic polyol (SYNP), amount of water, catalyst, and surfactant added to the mixture.

Catalyst effect on foam

The effects of the catalyst concentration on the cellular structure of the foam were examined. The production of PU foam from SOP/SYNP without the addition of any catalyst was first considered. In this case, the cure rate (Reaction 1) was much slower than the gas formation rate (Reaction 2). The foam completely collapsed before curing, and the resulting density was the highest obtained in this study. When 0.2 wt % of DMBA catalyst was added (Sample 2 from Table I), Reaction 2 still dominated the kinetics and the foam was optimally expanded. Thus, the cured foam had a lower density with a larger and more irregular cell structure. Using 0.36

wt % DMBA (Sample 3), the density was higher and the cells were smaller. With 0.46 wt % DMBA (Sample 1), the foam had higher density due to the faster cure of the polymer in comparison with the CO_2-producing reaction. The catalyst accelerates and balances the competing reactions that occur in the process, so we see that the foam structure sensitively depends on the amount of catalyst added.

Polyol effect on foam

The foam morphology was studied by considering the different types of SOP. Figure 3 shows SEM micrographs of the cellular structure from the core of the PU foams (Samples 3–5 in Table I). Higher concentration of (similar) OH groups causes more reactivity with the isocyanate, which results in foams with a smaller and more uniform cell structure. This is based on the type and amount of hydroxyl groups present on the polyol (Table II). As shown in Figure 3, smaller cells with more structural homogeneity are obtained with the polyols that contain primary OH groups. Thus, the reactivity of the SO polyols
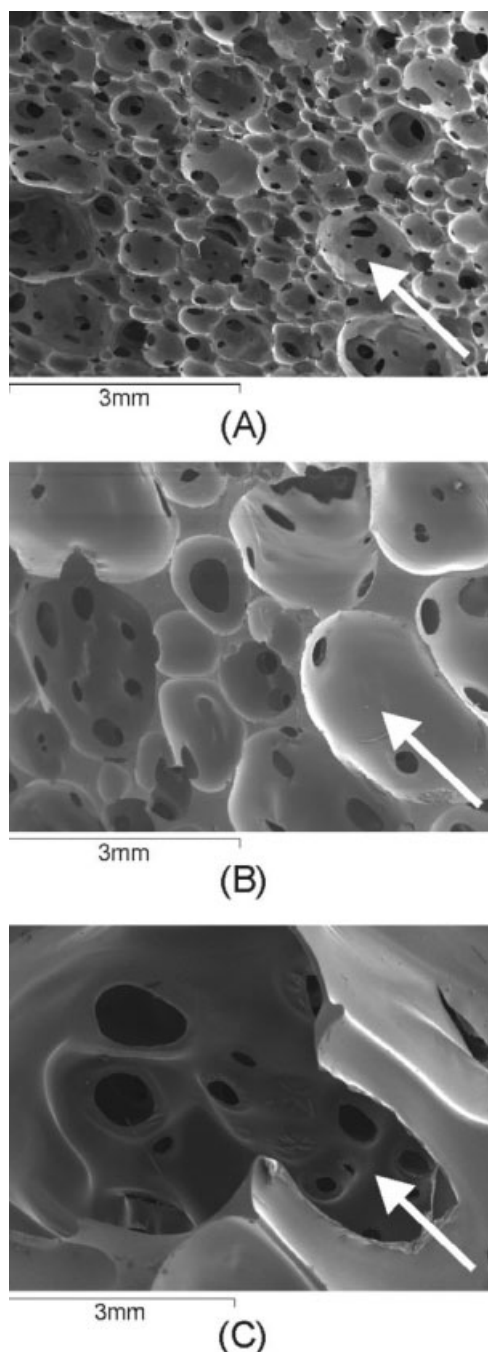
Figure 3 SEM images. Polyurethane foams made with (A) SOMG and Mod MDI, (B) SOMP and Mod MDI, and (C) HSO and Mod MDI (Samples 9, 10, and 11 from Table I, respectively). The arrow indicates the axis along the rise direction.

synthesized in this work was as follows: SOMG > SOMP > HSO. It was also shown by John et al.[17] that samples containing more synthetic polyol (with primary OH groups) had more well-organized cell shapes than the foam sample with SOP.

The effect of the SYNP/SOP mass ratio on the foam's structure was evaluated. Samples with a ratio of SYNP/SOMG 1.00, 1.15, and 0.77 were prepared

(Samples 3, 6, and 7 from Table I, respectively). As the proportion of SOMG increased, we observed an increase of the foam's average cell size due to the lower reactivity of the SOMG when compared with SYNP. As shown in Table I, the density decreased as the proportion of SOMG increased because Reaction 1 is slower than Reaction 2 in Scheme 1, and the foam begins to deteriorate before the polymer solidifies.

Isocyanate effect on foam

The influence of the isocyanate on the foam structure was evaluated. It affects the cellular structure, not only via the cell size and uniformity, as observed with the different types of polyol, but also via the open- or closed-cell type produced in the foam. As shown in Figure 4 (Table I, Samples 3 and 8–14), the foams produced with TDI gave closed cells, whereas both the MDI and modified MDI had open cells. Also, we evaluated the effect of the functionality on the foams structure, where a higher value (with the modified MDI) gave a smaller cell and more uniform foam structure. John et al.[17] studied PU foams prepared with SOP with different isocyanates and found that the foams produced with MDI were more rigid, and the reaction was slower when compared with that of TDI. This trend was also observed in our work and is described earlier (in the T_g section). They also observed that the foams with both MDI and TDI produced open and closed cells; this may be due to a difference between their SOP and ours.

Water effect on foam

Next, we considered the effect of the water content on the PU foam structure. The water is the reactive blowing agent and it is added for the production of CO_2. As shown in Table I (Samples 11 and 12), an increase in the water content produced more CO_2 during the foam formation resulting in a lower final density. Several groups have studied the effect of the water content in the foam structure.[3,7,17,29] They all found that an increase in the water content produced an expansion of the foam volume resulting in thinner foam cell walls and larger foam cells, changing the density of the foam and their morphology. All these formulations provide evidence that the cell structure becomes more uniform with lower water content.

Surfactant effect on foam

A surfactant was added to help the foam-forming process via stabilization of the growing cells. By comparing SEM micrographs in Figures 3(A) and
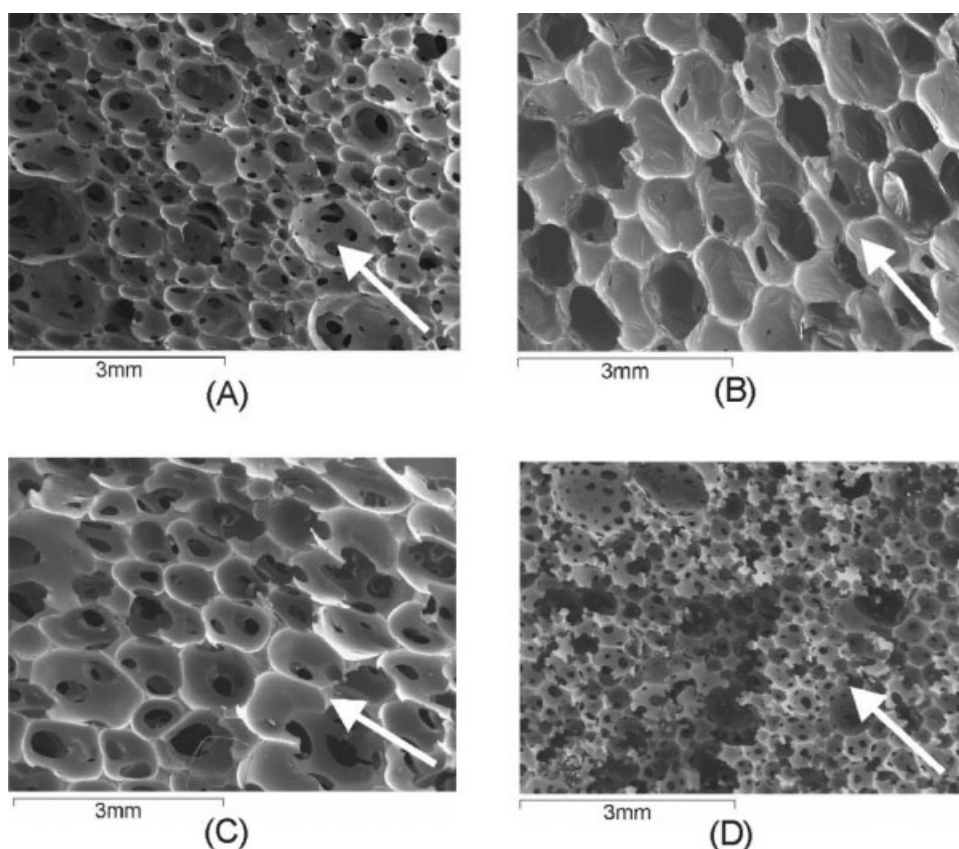
Figure 4 SEM images. Polyurethane foams made with (A) SOMG and Mod MDI, (B) SOMG and TDI, (C) synthetic polyol (SYNP) and Mod MDI, and (D) SYNP and MDI (Samples 9, 14, 15, and 16 from Table I, respectively). The arrow indicates the axis along the rise direction.

4(A) with respect to Figure 5, we can clearly see that the surfactant helps by controlling the size of the foam cell by stabilizing the gas bubbles formed during nucleation. During the manufacture of flexible foam, the surfactant allows the control of the degree of cell opening and the subsequent collapse of the foam.

Sol–Gel analysis of foam

Swelling experiments were performed in toluene at 30°C. The soluble fraction (W_s) for each sample was calculated by the following equation:

$$W_s = \frac{(w_1 - w_2)}{w_1} \qquad (1)$$

where w_1 is the dry weight before extraction and w_2 is the dry weight of the sample after extraction.

The volume fraction of the polymer in the swollen sample, φ_2, was calculated as follows:

$$\phi_2 = \frac{(w_2/\rho_2)}{[((W - w_2)/\rho) + (w_2/\rho_2)]} \qquad (2)$$

where ρ is the density of the solvent, ρ_2 is the density of the PU, and W is the weight of the solvent absorbed by the sample. The degree of swelling (DS) was then determined from the inverse of the
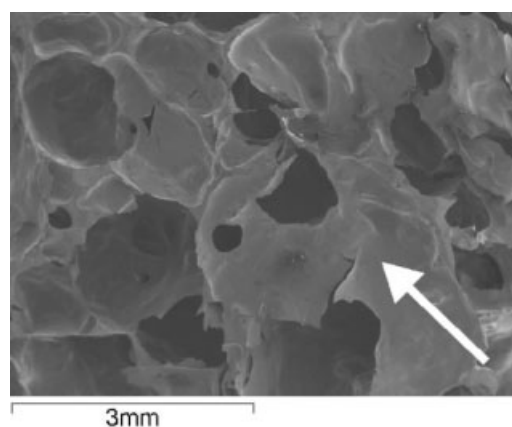

Figure 5 SEM image for a polyurethane foam made with SOMG and Mod MDI without the addition of surfactant (Sample 19 from Table I). The arrow indicates the axis along the rise direction.

<div align="center">

TABLE IV
Swelling, Thermal and Tensile Properties of Some of the Polyurethane from Soybean Oil Polyols

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Sample no.	W_s (%)	DS	T_g (°C)	Tensile strength (MPa)	Elongation at break (%)
3	13.6 ± 0.10	2.22 ± 0.14	−7 ± 0.53	1.7 ± 0.15	76
4	2.7 ± 0.24	1.26 ± 0.21	12 ± 0.41	2.5 ± 0.09	52
5	9.1 ± 0.18	1.97 ± 0.21	5 ± 1.71	2.3 ± 0.13	65
8	11.1 ± 0.54	2.01 ± 0.42	−10 ± 0.21	1.9 ± 0.08	74
14	17.1 ± 0.09	2.11 ± 0.08	−4 ± 0.29	1.9 ± 0.13	73

polymer volume fraction in the swollen sample as follows:

$$DS = \frac{1}{\phi_2} \quad (3)$$

We found that the sol fraction W_s (Table IV) increased with decreasing OH functionality as fewer crosslinks were formed, which was also noted by Montevaro et al.[18] The nature of the isocyanate also has an effect on W_s: when an isocyanate with a higher aromatic content was used, the solubility of toluene increased and a higher DS value was obtained.

Foam glass transition T_g

Table IV shows the values of T_g for different PUs. Foams prepared with MDI were slightly more rigid than those made with TDI, because of the presence of two aromatics rings compared to just one for the TDI (even if TDI had a higher NCO index when compared with the other PU). Pechar et al.[14] also found using a soy-based polyol that the TDI-based network displayed a lower T_g than MDI. Sample 3 from Table IV, made with modified MDI, was slightly softer than the PU foam made from MDI (Sample 14 from Table I), this is due to the observation that modified MDI reduces the hardness of the foam by interfering with the alignment of the polyurea hard segments and the effective degree of hard and soft segments segregation.[1] Pechar et al. also found that the nature of the isocyanate influences T_g.[14] We can also observe in Table IV that T_g increased with the OH functionality. This result agrees with other research, in that they also found a linear increase of T_g with the functionality of the polyol due to a higher degree of crosslinking.[6,7,12–14,18]

Comparing the DS values with T_g, we can observe that a decrease in the first one produces an increase in T_g. This was also observed with the PU foams from SO-based polyols produced by Montevaro et al.,[18] where they found that the DS values in toluene were consistent with the results obtained for the crosslinking density; PU networks with lower DS produced higher crosslinking density, and a higher T_g. The relation between T_g and crosslink density ν

is given by the Twinkling Fractal Theory (TFT) of T_g as follows[21,30]:

$$T_g(\nu) = T_g^0 + [T_g^0 M_{ox}/(1 - p_c)\rho]\nu \quad (4)$$

where ρ is the bulk density (≈ 1 g/cm^3), M_{ox} is the molecular weight per backbone atom of the crosslinking chain structure (≈ 14 g/mol for —CH$_2$—), p_c is the rigidity percolation threshold (≈ 0.4), and T_g^0 is the glass transition temperature of the linear polymer without crosslinks extrapolated to $\nu = 0$ (K). This relation is based on the intermolecular anharmonic potential interaction of atoms with a Boltzmann energy population creating dynamic fractal clusters in the liquid such that as T_g is approached, rigidity percolation of the connected fractal solid cluster occurs at the percolation threshold p_c. At T_g, the nonergodic solid fraction P_s is in dynamic equilibrium with the ergodic liquid fraction P_L creating spatiotemporal fluctuations with a vibrational density of states $g(w) \sim w^{4/3-1}$ and hence the name Twinkling Fractal.[31] The liquid fraction P_L behaves with temperature near T_g as $P_L = (1 - p_c)T/T_g^0$. The introduction of crosslinks reduces P_L by an amount [ν M_{ox} /ρ] such that at $T_g(\nu)$, we have $P_L = \{(1 - p_c)T_g(\nu)/T_g^0 - \nu M_{ox}/\rho\} = (1 - p_c)$ and solving for $T_g(\nu)$, we obtain eq. (4). For a model series of crosslinked triglycerides, La Scala and Wool found that $T_g^0 \approx 225$ K and the slope in eq. (4) is $[T_g^0 M_{ox}/p_c\rho] = 0.0055$ km^3/mol was also in good accord with the TFT theory.[19] Pechar et al. found that T_g increased linearly with the hydroxyl number [OH] of the PU from a value of about (−40°C) 233 K at [OH] = 0 to about (80°C) 353 K at [OH] = 250 [mg KOH/g].[14]

The T_gs of PU are influenced by chemical group polarity as well as crosslinking. According to the TFT, polarity affects T_g through the average intermolecular potential D_0 in the relation:[30]

$$T_g = \frac{2D_0}{9k} \quad (5)$$

where k is the Boltzmann's constant. The average intermolecular bond strength D_0 can be obtained from eq. (5) as follows:

$$D_0 \approx 9T_g[cal/mol.K] \quad (6)$$

For polyethylene, $T_g = 223$ K which gives the —CH$_2$— group interaction energy as $D_0 \approx 2$ kcal/mol, which is similar to the crystallization heat of fusion $\Delta H_f \approx 2$ kcal/mol. For chain sequences of mixed polarity, as with PU, we approximate D_0 in its simplest averaged form as follows:

$$D_0 = \sum \phi_i D_{0i} \qquad (7)$$

in which φ_i and D_{0i} are the mole fractions and bond strength, repsectively, for the various groups.

The interaction energy D_0 is expected to scale as $D_0 \sim \varphi_{OH}$, where φ_{OH} is the mole fraction of OH groups on the backbone of the crosslinked structure. Thus, the effect of polarity alone on T_g is given by the TFT as the normalized ratio:

$$T_g(\mathrm{OH})/T_g^0 = \phi_{OH} D_{OH}/D_{CH_2} + (1 - \phi_{OH}) \qquad (8)$$

in which D_{CH_2} represents the —CH$_2$— interaction energy and D_{OH} is the value for the polar interactions of the OH groups. Using polyvinyl alcohol (PVOH) as a model system with $\varphi_{OH} = 1/2$ and $\varphi_{CH2} = 1/2$, the PVOH/PE T_g ratio is $358/243 \approx 1.5$ such that eq. (8) gives $D_{OH} \approx 4$ kcal/mol. Thus, for 50 : 50 mixtures of SOP and isocyanate, eq. (8) predicts that the slope of the change in $T_g(\mathrm{OH})$ with φ_{OH} should be about $T_g(\mathrm{CH}_2) \approx 258$ K, as observed by Pechar et al.[14] The combined effect of polarity and crosslink density can be obtained by substituting eq. (8) for T_g^0 in eq. (4) to give $T_g[\nu, \varphi_{OH}]$. For PU systems, we thus expect to observe the linear relationship of T_g vs. φ_{OH} due to both polarity and crosslink density with a linear increase with OH content. Using the limited data for T_g vs. OH content in the mod MDI series in Table IV, we found that $T_g[\mathrm{OH}] = 252$ K $+ 0.183$ [OH] K mg/g (with $R = 0.94$), which is consistent with the TFT analysis.

Tensile properties of foam

The tensile properties of the flexible PU foams are shown in Figure 6. By analyzing the stress–strain curves, we can observe three regions. In the first part, with lower strain, the foam deforms in compression in a linear elastic manner. The slope of this portion is the Young's modulus, E. The E-values for PU samples 3, 4, 5, 8, and 14 were 0.18, 0.29, 0.23, 0.20, and 0.22 MPa, respectively. The second region of the curve exhibits a plateau of deformation at almost constant stress and occurs as a result of the unstable elastic bucking plastic yielding or brittle fracture of the cell wall struts. Finally in the third part of the curve, we observe a rising stress, this occurs when the opposing cell walls meet after they have completely collapsed upon compression and the interaction of the compacted struts forms a much denser foam system. Table IV shows the ten-
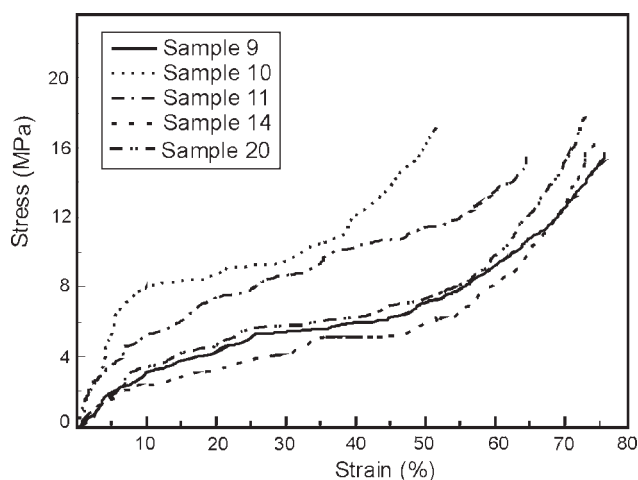

Figure 6 Stress–strain curves for some of the polyurethane foams made from soybean oil polyols (SOMG, SOMP, and HSO) with different types of diisocyanate (Mod MDI, MDI, and TDI) corresponding to Samples 9–11, 14, and 20 from Table I.

sile strength and the elongation at break of different PU foams. It can be observed in all cases that the type and functionality of the SO polyols has more influence on the tensile properties than the type of isocyanate. Petrović et al.[7,8] also found that the elongation at break decreased as the content of OH groups increased.

All the PU foams based on SOP prepared in this work can be used in many applications such as automotive interior trim, arm- and head-rests, and other interior items such as office furniture, footwear, toys, and bicycle and motorcycle seats. Customizing the foam's composition, e.g., by modifying the type and proportion of SOP and isocyanate used, and the amounts of water and catalyst added, allows one to make foams with specific average cell size and apparent foam density that can fit different applications.

CONCLUSIONS

Soybean oil polyols (SOMG, HSO, and SOMP) were used to synthesize flexible PU foams. The utilization of these polyols has the advantage of using less petroleum-based materials. We showed in this work that several factors affected the morphology of the foam: the type and functionality of the SO polyols, the type of isocyanate, the amount of water, and the amount of catalyst. SOMG was the most reactive SO polyol because it contained primary OH groups producing foams with smaller and more uniform cells. Also, the functionality of the polyol affected the foam's cell size (and therefore the foam expansion). Comparing the foams produced with secondary OH groups, SOMP had a higher functionality, which was more reactive and had smaller and more

uniform cells than HSO. The type of isocyanate used produced changes in the foam not only in the morphology and uniformity but also in the type of cell produced. The water content also affected the foam structure, i.e., as the water content increased, the cell size increased and the foam's density decreased. We observed that the higher OH functionality of the polyols increased the glass temperature (T_g) and decreased in the DS, which is consistent with the TFT. Also, the type of isocyanate affected the T_g.

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