Characterization and Comparison of Polyurethane Networks Prepared Using Soybean-Based Polyols with Varying Hydroxyl Content and Their Blends with Petroleum-Based Polyols

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ABSTRACT: Polyurethane Networks (PUNs) were synthesized using polyols derived from soybean oil, petroleum, or a blend of the two in conjunction with diisocyanate. The soybean-based polyols (SBPs) were prepared using air oxidation, or by hydroxylating epoxidized soybean oil. Some of the networks were subjected to several solvents to determine their respective swelling behavior and solubility parameters. Sol-fractions were also determined, and DMA experiments were utilized to monitor the changes in storage modulus and tan δ with temperature for networks with sol and with the sol extracted. A linear relationship was noted between the hydroxyl number of a SBP and the glass transition temperature of its corresponding unextracted PU network within the range of hydroxyl numbers (i.e., 55–237 mg KOH/g) and glass transition temperatures (i.e., −21–+83°C) encountered in this work. This same linear relationship was realized between the weighted hydroxyl number of soy and petroleum-based polyol blends and the glass transition temperature of the resulting unextracted and extracted network PUs within the ranges utilized in this study (i.e., 44–57 mg KOH/g, −54–19°C). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1432–1443, 2006

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INTRODUCTION

Polyurethanes (PUs) are a class of polymers that have found many important applications such as thermoset and thermoplastic elastomers, adhesives, coatings, and both flexible as well as rigid foams. The general route to synthesize a thermoset network form of these polymers is to react a diisocyanate or one of higher functionality with a polyol that possesses an average functionality greater than 2. Conventionally, this polyol is petroleum-based, but due to uncertainty about the cost of petroleum in the future, as well as desires to move towards more environmentally friendly feed stocks, many recent efforts have focused on replacing all or a portion of the conventional petroleum-based polyols with those made from renewable resources such as vegetable oil.[1–3]

Soybean oil is one of many vegetable oils that can be converted into a polyol. This oil is comprised of triglycerides, which possess both saturated and unsaturated fatty acid residues. The two most common fatty acids in soybean oil are linoleic acid (53%) and oleic acid (23%), and some saturated fatty acids are present (16%) though the actual composition of soybean oil can vary depending on factors such as soil type.[4] These fatty acids can vary from 14 to 22 carbons in length, and may have from 0 to 3 double bonds per fatty acid. The average number of double bonds per molecule is 4.6, and the molecular weight of soy oil is typically near 900 g/mol.[5] Soybean oil triglycerides contain several reactive functional groups such as double bonds, allylic carbons, esters and their corresponding α-carbons. These groups can be used to chemically tailor the soybean oil structure, such that it contains specific functional groups, particularly hydroxyl groups to make soybean oil-based polyols.[6]

Addressing prior research efforts using SBPs for urethane applications, there has been a considerable research effort focused on producing PU foams, a cellular PU network, using soy-based polyols. Guo et al. used soy-based polyols, which were prepared via the oxirane ring-opening reaction of epoxidized soyean oil with methanol to make blown rigid PU foams.[7] These soy-based foams were shown to have

comparable compressive strengths and insulating properties, and better thermal stabilities than those of foams of petrochemical origin. John et al. characterized flexible slabstock PU foams that were prepared using commercial soybean-based polyols and diisocyanates with a constant isocyanate index of 110.[8] The focus of their study was to determine the effects of water content and the type of diisocyanate on the final foam structure. They found that as the amount of water increased from 2 to 6% of the mass of the polyol, the cell size within the foam increased. The authors also noted that choosing methylene diphenyl diisocyanate (MDI) as the isocyanate in the synthesis lead to more rigid foams than choosing toluene diisocyanate (TDI); this is not surprising in view of the fact that the molecular weight of MDI is about twice than that of TDI, thus increasing the percent of hard segments in the foam, thereby making the MDI foam more rigid.

Efforts have also been made to understand the effects of structure on the properties of soy-based polyurethanes (SPUs). Petrovic et al. studied the effect of crosslink density on the properties of SPU networks synthesized using soybased polyols prepared from epoxidized soybean oil and diphenyl methane diisocyanate.[9,10] Their work involved varying the isocyanate index from 0.4 to 1.05 while working with a constant hydroxyl number (i.e., 203 mg KOH/g) to synthesize SPU networks with different levels of crosslinking. As expected, they observed that the swelling of networks increased as the isocyanate index was lowered from 1.05 to 0.4, and the swelling results were used to calculate the molecular weight between crosslinks (M_c) for each network. Their calculations stated that the M_c ranged from 404 for the SPU with an isocyanate index of 1.05–7118 for the SPU with an isocyanate index of 0.4. The authors also noted that at room temperature these networks were glassy if the indices were between 1.05 and 0.8, and rubbery if the indices were equal to or less than 0.7. As the index was lowered from 1.05 to 0.4 the glass transition temperature (T_g) decreased from 64 to $-7°C$, and the tensile strength of the SPUs decreased from 47.3 to 0.3 MPa, while the elongation increased from 7 to 232%.

Javni et al. investigated the effect of using different isocyanates on the properties of SPU networks.[11] Using several aromatic and aliphatic diisocyantates and triisocyanates they chose for the study and the same soy polyol that possessed a hydroxyl number (OH#) of 206 mg KOH/g for each synthesis (the isocyanate index was not reported), several SPU networks were synthesized. They observed that the T_g of a SPU was highest (91°C) for those that were prepared using isocyanates with a functionality of 3 such as aromatic triisocyanates (e.g., tris(p-isocyanato-phenyl)-thiophosphate), followed by those prepared using isocyanates with a functionality equal to 2 such as an aromatic (e.g., MDI) or cycloaliphatic diisocyanate (e.g.,

hydrogenated MDI) ($-54°C$), and lowest (15°C) if it were prepared using a linear aliphatic triisocyanate or diisocyanate (e.g., hexamethyl diisocyanate). They also noted that their SPUs made using the aromatic triisocyanates had the highest resistance to swelling in toluene, while those made using the aromatic and cycloaliphatic diisocyanate had better impact resistance, but lower strength. The PUs prepared using the linear aliphatic diisocyanates offered the lowest strength (~4 MPa) and swelling resistance, but provided the highest flexibility and impact resistance.

A promising feature of SPUs is that they can also be synthesized without the use of isocyanates that are associated with health risks. From our laboratory, Tamami et al. successfully developed soy-based PU networks without the aid of diisocyanates.[12] The authors were able to convert epoxidized soybean oil into carbonated soybean oil containing five-membered cyclic carbonates via a reaction with CO_2 and a catalyst (i.e., tetrabutylammonium bromide). The carbonated soybean oil was able to react with amine-functionalized monomers to produce PUs. In addition to introducing a urethane linkage into the polymer, this reaction also resulted in a primary hydroxyl group adjacent to each urethane linkage.

In this paper, two commercially available polyols derived from soybean oil (i.e., SoyOylTM P38N and SoyolTM R2–052 Urethane Soy Systems Co., Inc., Volga, SD) are used to synthesize PU networks. SoyolTM R2-052, which is designationed in this report as R2052, is a more recent polyol supplied by Urethane Soy Systems Company than its counterpart SoyOylTM P38N (P38N). In addition, network PUs are prepared using SBPs synthesized in our laboratory via an air oxidation process that provided SPBs with relatively low OH#s, and by hydroxylating epoxidized soybean oil, which provided SBPs with a relatively high OH#. This allowed an investigation of the effects of the hydroxyl number of the polyol on the properties of PU. The characterization results of network polyurethanes made using these polyols are compared to each other in order to determine if there were any differences among them, and if these differences could be related to the properties of polyols. In addition, these results are compared to those of polyurethane networks that were prepared using either a petroleum-based polyol, or a blend of soy and petroleum-based polyols.

EXPERIMENTAL

Materials

Urethane Soy Systems Company (USSC) of Volga, SD generously donated two different soy-based polyols, P38N and R2052. Both polyols were stated to possess a hydroxyl number of 54 mg KOH/g, an average

functionality near 2, and were produced by South Dakota Soybean Processors (Volga, SD). These two polyols were prepared via an air oxidation process, the details of which are proprietary and were not released to the authors. USSC also donated raw soybean oil (RSBO).

An epoxidized soybean oil (ESBO), Paraplex G-62, was provided through the courtesy of C.P. Hall Company (Memphis, TN) and used as received.

Dow Chemical Company (Midland, MI) generously supplied a petroleum-based propylene oxide extended polyether polyol, Voranol 4701 ($M_n \sim 5000$ g/mol, average functionality ~ 2.5, ~74% ethylene oxide end-capped), and ISONATE 143L® (a polycarbodiimide-modified diphenylmethane diisocyanate) having an isocyanate equivalent weight of 144.5. These materials were used as received.

An organometallic catalyst, DABCO T-12®, was provided through the courtesy of Air Products (Allentown, PA) and used as received.

Solvents used for the swelling experiments were methanol, dimethyl formamide, dimethylacetamide (DMAC), acetone, methyl ethyl ketone, ethyl acetate, toluene, and n-heptane. These were purchased from Sigma Aldrich (St. Louis, MO) used as received. DMAC was also used for sol-extraction in the determination of the Sol-fraction of the PU networks.

Hydroxylation of raw soybean oil via air oxidation

RSBO (200 g. $M_n = 1120$ g/mol, PDI = 1.02) was placed into a 1000 mL, 3-neck round bottom flask. Air was dispersed into the RSBO with the aid of a single or double dispersion tube at a flow rate of 20–35 mL/min. The flask was held at a constant temperature of 110°C for a few days. Two types of SBPs with different OH#s due to different reaction times, AHSBO1 (4 days) and AHSBO2 (5 days), were prepared using this method. AHSBO1 possessed an OH# of 73 mg KOH/g, a M_n of 2400 g/mol, and PDI of 3.00, while AHSBO2 possessed an OH# of 88 mg KOH/g, a M_n of 2600 g/mol, and PDI of 3.06.

Hydroxylation of esbo

ESBO (200 g) was slowly added to a stirred mixture of methanol (200 mL), water (20 mL), isopropanol (500 mL.), and 8 g of 48% HBF_4(aq). The OH# was controlled by adjusting the amount of tetrafluoroboric acid added to the reaction. After reaching a temperature of 50°C for 1 h, ammonia (30% in water) was added drop-wise to quench the reaction. Ammonia was no longer added once the mixture attained a neutral pH. The mixture was then placed under vacuum to remove the solvents. This left a viscous yellow liquid with a mass of 150 g. This procedure produced ESBO with OH#s of 179 and 237 mg KOH/g.

Determination of hydroxyl number

The hydroxyl number for each soybean-based polyol synthesized in this study was determined using the AOCS official method Cd 13–60.

The hydroxyl numbers of Voranol 4701, P38N and R2052 were provided by the suppliers.

Polyurethane synthesis

Polyurethane (PU) networks were synthesized as follows. Equivalent weights (EWs) were determined for each polyol using the hydroxyl numbers provided by the supplier. Calculations for the required masses of the reactants were determined on a 30 g polyol-basis and at an isocyanate index of 105. Equation 1 shown below was used to determine the mass of ISONATE 143L needed for the synthesis:

$$\frac{M_{143L}}{EW_{143L}} = \sum_{i=1}^{n} \left(\frac{M_{polyol_i}}{EW_{polyol_i}} \right) \cdot 1.05 \qquad (1)$$

In this equation M is the mass of a reactant. EW is its equivalent weight, and n is the total number of blend components used in the synthesis. Networks were made using 100 wt %, 75 wt %, and 50 wt % soybean-based polyol with the balance being 4701. Catalyst (DABCO T-12) was added at a weight equal to 0.1% of the mass of the polyol used in the synthesis of a series of PUs prepared using only Voranol 4701, P38N, or R2052 as the polyol. However, the use of a catalyst results in several bubbles being trapped within the network during the synthesis, which in turn become voids within the network and make the PUs unacceptable for mechanical testing of ultimate properties such as tensile strength. This entrapment of bubbles was due to the more rapid gelation time, which limited the time for entrapped gas to escape. As a result, to decrease the reaction rate a second series of network PUs were synthesized using only SBP and no catalyst.

The determined masses of reactants were mixed together and carefully stirred to minimize the presence of air bubbles in the mixture. The mixture was cast onto glass petri dishes, placed in a hood, and allowed to sit for 1 h to let any air bubbles escape from the cast film. The samples were then placed into a forced convection curing oven and heated to 70°C for 12 h, 100°C for 2 h, and 125°C for 1 h, before being cooled to 35°C at a rate of 2°C/min.

Characterization

Swelling experiments

Multiple thin samples (thickness less than 200 μm) were cut from three PU networks that were synthe-

sized using only P38N, only 4701, and a 60/40 wt % blend of P38N and 4701, respectively. The samples had their initial dimensions recorded and were immersed in a solvent for 72 h at a constant temperature of 23°C. Samples had their swollen dimensions recorded at specific time intervals to determine when equilibrium swelling was attained. It was found that 24 h was a sufficient time period to reach equilibrium.

After 72 h exposure to DMAC, each swollen sample's dimensions were measured, and its percent change in volume was calculated and reported as the percent change in volume for the sample. The percent changes in volume were plotted against the solubility parameters of the solvents and curve fitted. The maximum of the fitted curve was taken as the solubility parameter of the PU network.

Sol-fraction measurements

Thin samples (thickness $\sim$ 200 μm) were cut from each PU used in this study and weighed, then immersed in an excess of DMAC for 24 h at 50°C. After 24 h, the samples were removed from the solvent. The samples were dried under vacuum at 100°C for at least 12 h. The dried samples were then weighed, and the sol-fraction was taken as the difference between the mass of the sample before immersion in DMAC and the mass after drying under vacuum, normalized to the mass before immersion in DMAC.

Dynamic mechanical analysis tests

Dynamic mechanical analysis was carried out in tensile mode using a Seiko DMA 210 model over a temperature range of 110–150°C. A heating rate of 2°C/min, a frequency of 1 Hz, and a grip-to-grip distance of 10 mm were used for all tests. The principle peak in tan δ was assigned as the glass transition temperature for each sample.

Small angle X-ray scattering (SAXS)

Pin-hole collimated SAXS profiles were collected at ambient temperature using a Rigaku Ultrax l8 rotating anode X-ray generator operated at 40 kV and 60 mA. A pyrolytic graphite monochromator was used to filter out all radiation except the Cu Kα doublet, with an average wavelength of λ = 1.5418 Å. The camera used 200, 100, and 300 μm pinholes for X-ray collimation. Two-dimensional data sets were collected using a Molecular Metrology 2D multiwire area detector, located approximately 65 cm from the sample. After azimuthal averaging, the raw data were corrected for detector noise, sample absorption, and background noise. The data were then placed on an absolute scale using a type 2 glassy carbon sample 1.07 mm thick, previously calibrated at the Advanced Photon Source

at the Argonne National Laboratory, as a secondary standard. All the SAXS profiles presented have been masked in the low scattering vector region where the beam stop influenced the profiles. The absolute intensity data are presented as a function of the magnitude of the scattering vector, s, where $s = 2 \sin\theta/\lambda$, and 2θ is the radial scattering angle.

RESULTS AND DISCUSSION

Hydroxylated soybean oil was prepared within our lab using one of several methods discussed previously and used to synthesize PU networks as outlined in the Experimental section. The functionalization of the soybean oil using the air oxidation process, and the urethane synthesis are shown in Figure 1. It should be noted that USSC prepares P38N and R2052 using an air oxidation process, the details of which are proprietary and were not shared with the authors.

Epoxidized soybean oil was hydroxylated using the protocol listed in the Experimental section. An illustration of the reaction scheme is shown in Figure 2. Two SBPs were synthesized using this procedure, EHSBO1 and EHSBO2, which had OH#s of 179 and 237 mg KOH/g, respectively.

To provide a trend of the solubility parameter as a function of soybean-based polyol content, the experiment was performed for PUs synthesized using only P38N, only 4701, and a blend of 60/40 wt % P38N to 4701, respectively. The changes in the length of a sample upon immersion in DMAC were observed to reach a maximum near 24 h as shown in Figure 3. The results of the experiments are shown in Figure 4. A trend of increasing swelling with decreasing soybean-based polyol content was observed. Networks made using only the 4701 polyol swelled to 370%, while those made using only the P38N polyol swelled less than 100%. We distinctly believe that this is associated with the fact that the hydroxyl number of P38N is almost twice as large as that of 4701 (i.e., 54 mg KOH/g vs. 34 mg KOH/g). In addition, this may be also influenced by the location of the —OH groups on each polyol. The —OH groups of the soybean-based polyol are more located in the inner regions of the backbone and not at the terminal points of the triarm molecule, whereas those of the 4701 polyol are located at the terminal points of the triol. This would provide a lower molecular weight between crosslinks for PU P38N relative to PU 4701, and thus increase PU P38N's resistance to swelling. Finally, the propylene oxide backbone of 4701 is certainly somewhat chemically different than that of the triglyceride backbone, and thus when placed in DMAC, some difference in the degree of swelling may occur.

The largest change in percent swelling of each PU network occurred when swollen with DMAC. As a result, this solvent was then selected as the swelling
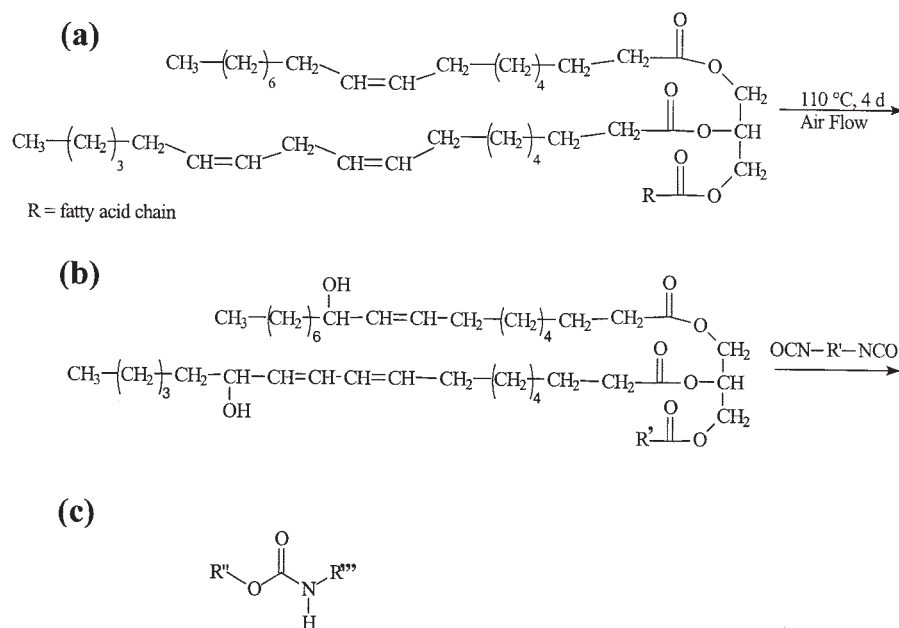
(a)

R = fatty acid chain

(b)

(c)

Figure 1 Synthesis of a polyurethane using soybean oil (a) that undergoes an air oxidation process to yield a soybean oil-based polyol (b), which can react with a diisocyanate to form a polyurethane (c). In this figure, R′ is a saturated fatty acid chain that may or may not become functionalized with hydroxyl or other groups (e.g. aldehydes, ketones, epoxides, acids, etc) while R′ and R‴ represent arms of triglycerides that have reacted to form a urethane linkage.

solvent for all later sol-fraction experiments. Using the maxima of the curves in Figure 2, the solubility parameters of the polymers were estimated to be ~10.8 $[(cal/cm^3)]^{1/2}$ for PUs containing only soy-polyols, and ~11.3 $[(cal/cm^3)]^{1/2}$ for the PU synthesized using only the 4701 polyol. The solubility coefficient of
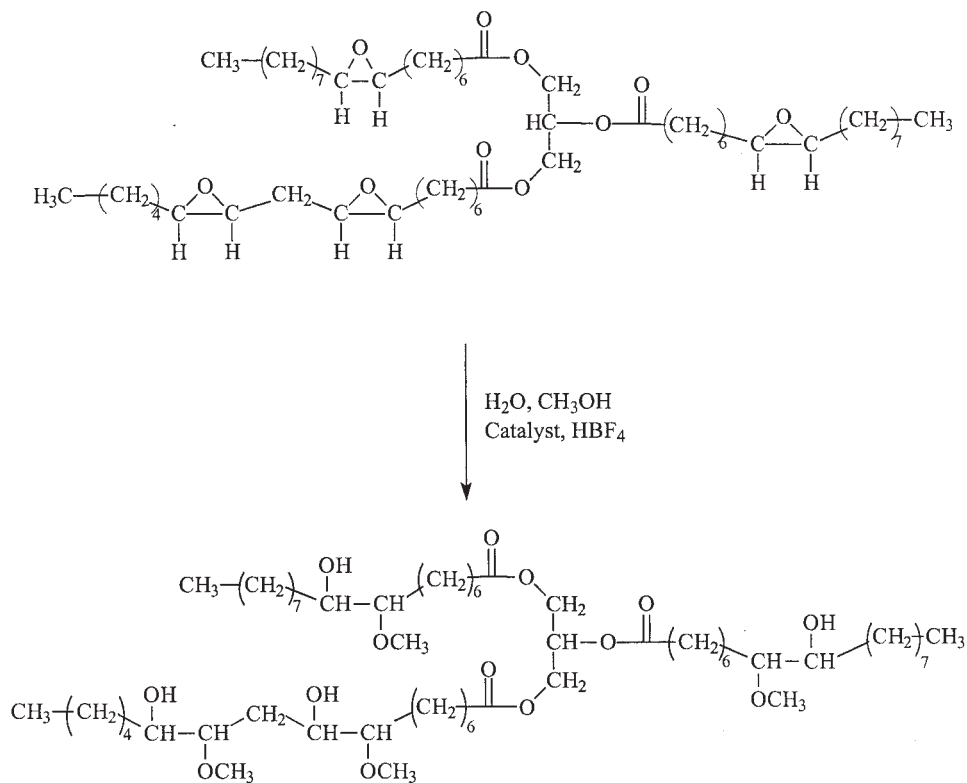
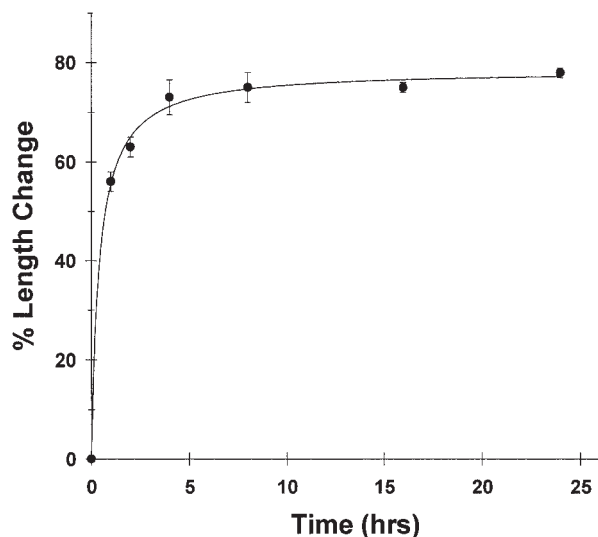**Figure 2** Route used in this study to hydroxylize epoxidized soybean oil.

Figure 3 Change in length of a PUN upon immersion in DMAC for different time intervals.

DMAC is 10.8 $[(cal/cm^3)]^{1/2}$.[13] The shift in the solubility parameter to a higher value when only 4701 is used in the synthesis may be attributed to the variation in chemical structure of this polyol compared with that of P38N as mentioned above. The backbone structure of 4701 is propylene oxide-based with a por-

tion of its tips (20% or less) being ethylene oxide-based. Because of this, it is expected that 4701 should be somewhat more polar than the modified soybean oil backbone structure of P38N. This would lead to a slightly higher network solubility parameter as 4701 becomes the dominant polyol used in the synthesis.

The sol-fraction results for all PUs are shown in Figure 5. A trend of increasing sol-fraction with increasing soybean-based polyol content was observed regardless of which polyol was chosen to prepare the network. The PUs synthesized using R2052 and P38N possessed the highest levels of sol. This may be a result of their relatively low OH# compared with the other SBPs. The R2052 polyol possessed larger sol-fractions than their P38N counterparts, however, as expected, the differences in sol-fractions between PUs synthesized using these two polyols decreased as more 4701 polyol was blended with either of them in the synthesis. At a 50/50 wt % mixture of soy and petroleum-based polyol, the two types of PUs displayed almost the same sol fraction. The origin of the differences in sol-fractions may be due to the different molecular weights of the SBPs. Viscosity measurements gathered on both pure R2052 and P38N revealed that P38N has a higher viscosity than R2052 (i.e., 3600 vs. 2200 cp. respectively). Viscosity is known to increase with M_w indicating that R2052 is a lower
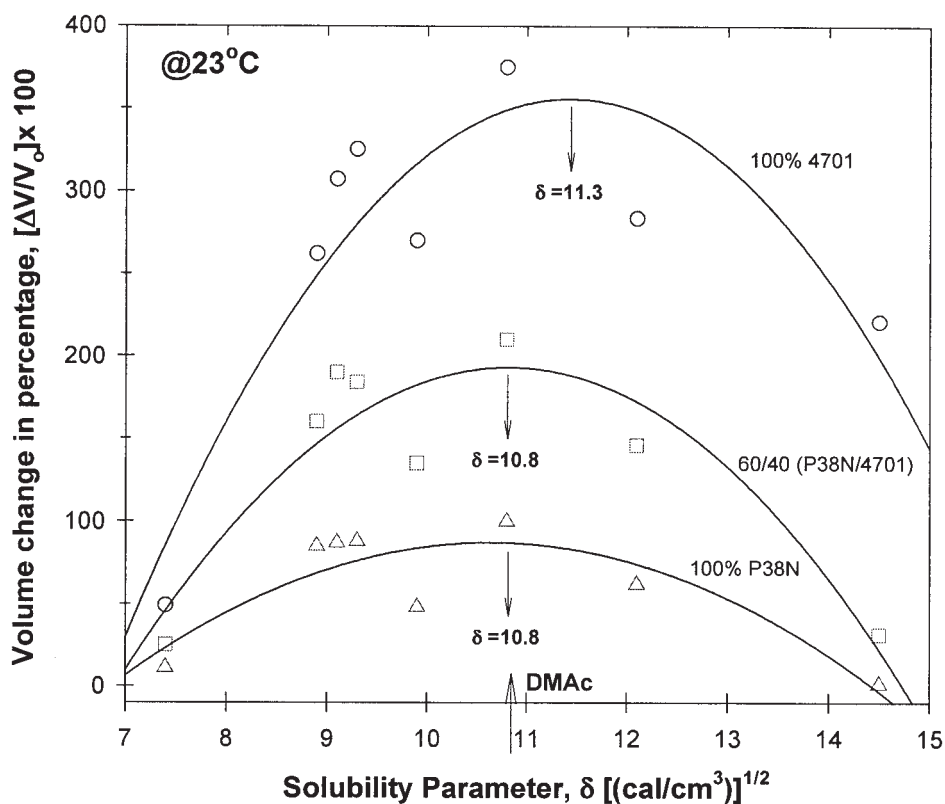

Figure 4 Percent volume change of PU networks synthesized with varying soy-polyol content as a function of the solubility parameter of eight different swelling solvents.
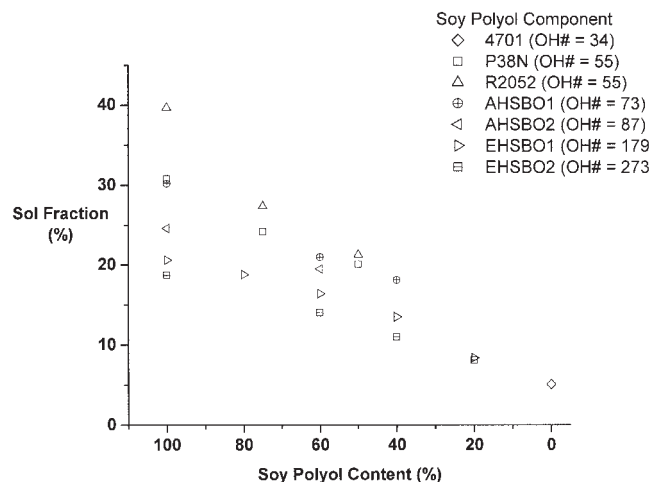
Figure 5 Sol-fraction of PU networks as they relate to each networks' soybean-based polyol content. A standard deviation near 1% or less was typical for each data point.

molecular weight polyol than P38N. The reader will recall that P38N and R2052 have very similar OH#s (54.5 vs. 56, respectively). This means for equal masses of polyol, there is essentially the same number of —OH groups, however these —OH groups are spread out over somewhat more triglycerides in the R2052 polyol as it has a lower molecular weight per polyol. Succinctly stated, this data indicates the slightly lower functionality for R2052 compared with P38N would be expected to lead to a poorer network, and thus a higher sol-fraction.

When the catalyst (i.e., DABCO T–12) was added to the preparation of either R2O52 PU or P38N PU, a lower sol-fraction was observed as expected. The sol-fraction of these networks was determined to be 33 ± 2% and 26 ± 2%, respectively. This represents almost a 20% decrease in sol-fraction for the R2052 PU, and a roughly 17% decrease in sol-fraction for the P38N PU.

The SPUs prepared in our laboratories via air oxidation (i.e., AHSBO1, AHSBO2) displayed sol-fractions that were similar to that of P38N. AHSBO1 sol-fraction was near 30% while that of AHSBO2 was near 25%. The AHSBO2 polyol has a higher OH# than AHSBO1, which would favor an increase in the amount of polyol included in the network, and thus reduce the sol-fraction. As was seen with R2052 and P38N, when AHSBO2 and AHSBO1 were blended with the petroleum-based polyol 4701 in a 60/40 wt % ratio, respectively, the resulting PUs displayed very similar sol-fractions (i.e., 20 and 21%).

The polyols synthesized from ESBO were prepared to achieve higher OH#s than those of the other SBPs, which in turn, should lead to lower sol-fractions and higher T_gs than what is provided by other SBPs. SPU prepared from this type of SBP offered the lowest

sol-fractions of any of the SPUs of comparable soy content, likely because these SBPs should be approaching the upper limit of the OH# achievable using RSBO. In the absence of 4701, the PUs prepared using EHSBO1 possessed a 21% sol-fraction, while that of EHSBO2 was 19%; standard deviations were typically less than ±2%. Their corresponding PUs offered statistically equivalent sol-fractions when a blend of 20 wt % EHSBO1 or EHSBO2 and 80 wt % 4701 was used in the synthesis. The lower sol-fractions of these two polyols when compared with the other SBPs are a result of their higher OH#. Their enhanced OH# would increase the likelihood that nearly all of the hydroxylated triglycerides would be included in the network. It also would lead to a tighter network, as the molecular weight between crosslinks would be due to the more prevalent —OH groups along the backbone that could react with the diisocyanate crosslinker to form a urethane linkage.

The PU made using only 4701 as the polyol offered much lower sol-fractions than any of the SPUs, and this is believed to be clearly due to 4701's higher functionality than the soy-based polyols. The average sol-fraction of the PUs made using only the petroleum-based polyol (4701) was 5%. The higher functionality allows more of the monomers to react and become part of the network, thereby leaving less "unattached" or sol species.

Dynamic mechanical analysis (DMA) was employed to determine the storage modulus (E') and the thermal transitional behavior of each network PU. The storage modulus for PUs synthesized using these polyols, and their blends are shown in Figure 6(a). Network PUs made using only the 4701 polyol experienced a sharp drop in E' associated with the T_g over a relatively small temperature range (~25°C) that occurs between −75 and −50°C. As soybean-based polyols are included in the fabrication of these materials, the drop in storage modulus becomes more gradual, and the temperature range over which this drop occurs becomes larger. This trend of a more gradual drop in E' with temperature is proportional to the amount of soy-polyol used in the synthesis. For example, both the R2052-based PU and the P38N-based PU show a large drop in modulus between −75 and 10°C. It should be noted that in no case was there a large difference in E' between a PU network made using P38N and its R2052 counterpart when no measures were taken to extract the sol.

In addition to recording the changes in E' with temperature, the DMA data of the network PUs containing their sol offered trends in tan δ, which have been plotted in Figure 6(b). The breadth of the tan δ peaks was the smallest for the purely petroleum-based PU, ranging from roughly −75 to −35°C. As more soy-polyol was included in the fabrication of the PU, the tan δ peak moved to a higher temperature, and its
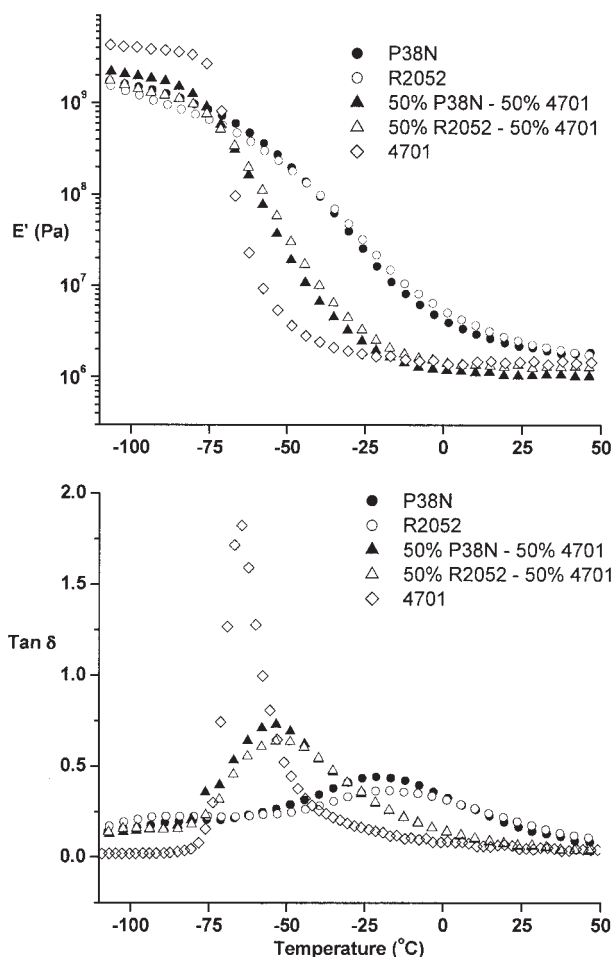
Figure 6 Storage modulus (E') as a function of temperature (a) for PU networks synthesized using pure R2052, pure P38N, pure 4701, or blends thereof. The reader will note that the glass transition region becomes larger as the soy-content of the network is increased. Tan δ as a function of temperature (b) for PUs synthesized using pure R2052, pure P38N, pure 4701, or blends thereof. The reader may note the presence of an secondary peak for all networks synthesized using a soybased-polyol.

breadth increased. For example, when R2052 was the only polyol used in the synthesis, the breadth of tan δ spanned from roughly −100 to 25°C. In addition, the magnitude of tan δ diminished as more soy-polyol was used, ranging from ~1.85 for the purely petroleum-based PU to ~0.45 for PUs prepared using only R2052 or P38N. The reader may recognize that the SPU networks displayed a secondary tan δ peak beginning near −100°C and ultimately merging with the primary tan δ peak. The magnitude of tan δ for this secondary peak was also proportional to the amount of SBP used in the synthesis. It is not yet known if this can be attributed to motion of the networks' dangling ends, or a localized motion of some small group within the networks backbone. It should be noted that although not shown in the graph, the 75–25 wt % blends of soy and petroleum polyol show the same

behavior, and fit the trends of the other PUs included in Figures 6(a) and 6(b).

When catalyst was added to the synthesis of the R2052 PU and the P38N PU, an increase in T_g was observed for both networks as was one might expect. The catalyst would enhance the reaction rate, and thus favor a smaller sol-fraction that increases the T_g of the network. The R2052 PU's T_g increased 10°C, and the P38N PU's T_g increased 4°C upon the use of a catalyst. The samples also possessed a slightly increased rubbery plateau modulus relative to their counterparts, which were not synthesized with the aid of a catalyst thereby supporting that the catalyst did promote further network development.

As stated earlier, the peak in tan δ for each PU was reported as its T_g and a plot of T_g as a function of soy-content for these PUs is given in Figure 7. The tan δ peak of the 4701 PU is much sharper than that of any of the soy-based PUs. It is also evident from Figure 7 that as the soy-content was increased, the T_g of the PUs increased. Furthermore, there were no large differences in the T_gs of PUs that were synthesized using either P38N or R2052, regardless if they were blended with 4701. This was somewhat surprising as the sol-fraction of the SPU synthesized using only the R2052 polyol was much higher than its P38N SPU counterpart (i.e., 40 and 31%, respectively). The largest difference was observed for the 50/50 wt % blends of soy-based and petroleum-based polyols. The 50/50 wt % blend using P38N displayed a T_g of −55°C, while the corresponding blend using R2052 was −52°C.

The changes in E' associated with temperature clearly indicate that the soy-based PUs have a wider glass transition region over which their mechanical properties will vary as compared to the petroleum-based 4701 PUs. This could be viewed as a benefit or
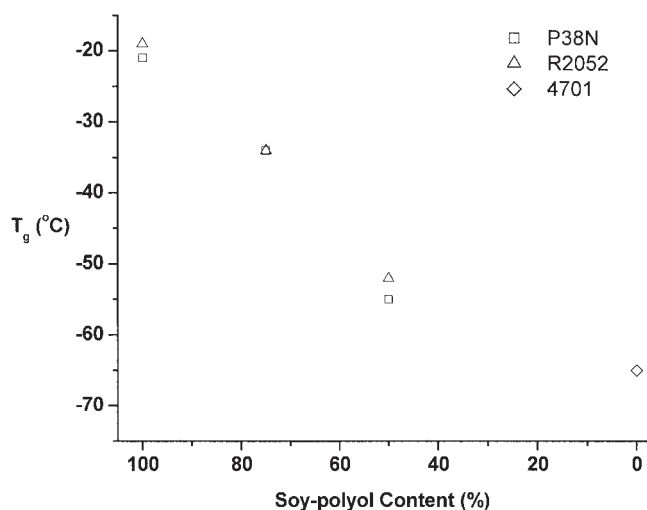

Figure 7 Glass transition temperature of PU networks synthesized using either P38N or R2052 and varying amounts of 4701 polyol.

a hindrance by the end-user depending on the application and environment in which these PUNs would be expected to operate.

The trend of T_gs for the PUs, as well as the breadth of the tan δ peaks can be potentially explained by consideration of the crosslink density of the PUs, as well as the functionality of the reactants if one assumes that the molecular weight of the hydroxyl-functionalized soy-based polyols is ~1000 g/mol (It might be noted that excess oxidation of soy bean oil can lead to higher molecular weight through branching reactions.). This is much lower than that of 4701, which has a M_n near 5000 g/mol. If an average functionality of 2.5 were assumed for both polyols, the soy-based polyols would, on average, be less than 500 g/mol between each reactive —OH group. This is much smaller than the average ~1700 g/mol between each reactive —OH group for 4701. With shorter chains between each network junction (i.e., urethane linkage), the soy-based PUs would form a tighter network. This in turn, restricts chain movement, and raises the T_g of the soy-based PUs to a higher temperature. It should be emphasized that for the sake of simplicity that the above analysis did not consider the triglyceride structure of the SBPs or the glycerin extended structure of 4701, which essentially behaves as another crosslink and further reduces the M_c of the SPU networks. Finally. the principally propylene oxide backbone of 4701 is expected to be somewhat more flexible than the triglyceride backbone of the SPU networks, which may possess a few carbon–carbon double bonds if left unaltered during the hydroxylation.

The increasing breadth of the tan δ peaks with soy-polyol content can be explained by considering the functionality of the polyols. The functionality of the 4701 polyol is near 2.5, while the average functionality of P38N and R2052 is anticipated to be distinctly less than this. In addition, and as stated earlier in this report, the —OH groups of 4701 are terminal, while those of P38N and R2052 are likely not at the termini of the triglyceride arms. This implies that there will be less dangling ends for 4701, and thus results in a more uniform polymer network. In contrast, the soy-polyol based PUs will have more dangling ends or branches, which can act somewhat as a plasticizer, and also result in less of a uniform network, thus contributing to the wider tan δ peak. Similar work by Zlatanic et al. showed that dangling triglyceride arms depressed the T_g of triolein-based PU networks by 6°C relative to those without dangling ends.[15] The reader is reminded that soybean oil triglycerides possess about 16% saturated acid residues, which will be less likely to undergo hydroxylation during oxidation. Furthermore, there is expected to be a wider distribution in the functionality of the soybean polyols within a given polyol. This would contribute to a less uniform network as well, and further widen the tan δ peak.
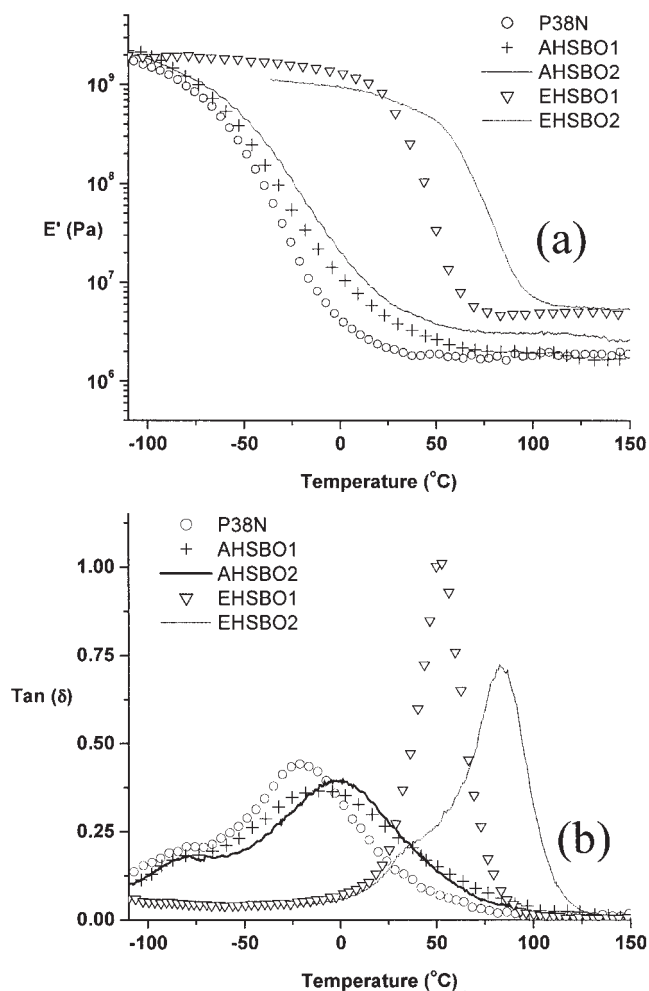

Figure 8 Storage modulus (E') as a function of temperature (a) for PUs synthesized using AHSBO1, AHSBO2, EHSBO1, or EHSBO2. The reader may note the general trend of increasing E' with increasing OH# in the rubbery region. Tan δ as a function of temperature (b) for PUs synthesized using AHSBO1, AHSBO2, EHSBO1, or EHSBO2. The E' and tan δ curves of P38N were included as a reference for the PUs discussed earlier.

DMA profiles were also gathered for SPUs synthesized using AHSBO1, AHSBO2, EHSBO1, and EHSBO2 polyols to observe any trends associated with the hydroxyl number of the soybased-polyol. The changes in E' with temperature for these SPU networks are shown in Figure 8(a). The air-oxidized polyols (i.e., AHSBO1 and AHSB02) provided SPUs with similar modulus behavior to that of P38N and R2052, which were also prepared via air oxidation. The PUs synthesized from EHSBO1 and EHSBO2, however, have a much sharper drop occurring over an approximately 50°C range. Furthermore, these drops in E' begin at a much higher temperature (i.e., ~50°C) than those of the other PUs. This is clearly attributed to the higher OH# of the EHSBO polyols, which are capable of forming a tighter network and thus raising the T_g of
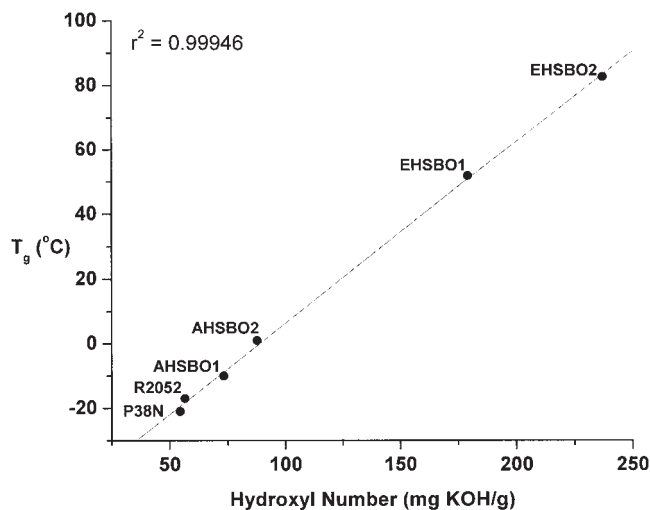
Figure 9 Relationship between the glass transition temperature of a PU containing its sol, and the hydroxyl number of the polyol from which it was synthesized.

the polymer. It should be noted that the drop in E' begins at a higher temperature for the PU prepared using the EHSBO2 polyol (i.e., ~83°C) than its EHSBO1 counterpart (i.e., ~50°C). This too is undoubtedly a consequence of the EHSBO2's higher OH# relative to that of EHSB01 (i.e., 237 vs. 179 mg KOH/g). The reader may also note a general trend of increasing E' with increasing SBP OH# in the rubbery plateau region. This would be expected, as the higher OH# polyols are capable of reacting to form tighter networks than their lower OH# counterparts.

The tan δ curves associated with the E' behavior for the samples given in Figure 8(a) are shown in Figure 8(b) from which the T_gs can be determined. Much like the changes in E' with temperature, the changes in tan δ with temperature of the PUs prepared from the air-oxidized polyols occur at lower temperatures and over a broader temperature range than those of the PUs prepared from the epoxidized soybean oil. The broader tan δ profiles may be a result of more dangling ends in the air oxidized soybased-polyol networks. The polyols associated with these relatively broad profiles have lower OH#s than those of the epoxidized polyols, and thus should have more dangling ends, and a higher M_c both of which may broaden the tan δ peak, and cause it to occur at a lower temperature. In addition, the air oxidation process broadens the molar mass distribution of the SBPs relative to RSBO due to coupling of the triglycerides, as was noted in the Experimental section. This broader molar mass distribution would also contribute to the broadening of the tan δ peak.

In light of how the T_g of a SPU network without its sol extracted depends on the OH# of a given polyol, a plot of the T_g versus the OH# is shown in Figure 9. This plot indicates that at least for the range of soy polyols stud-

ied, the T_g of the SPU is linearly related to the OH# of the polyol with an impressive r^2 value of 0.999!

To determine the effects of the sol-content on T_g and E', samples with the sol extracted, and which were thoroughly dried, were subjected to an identical DMA test as those with sol (i.e., unextracted samples). As expected, in each case the SPUs without their sol extracted displayed a higher T_g relative to their sol-containing counterpart, and these shifts were proportional to the initial soy-polyol content. As an example, the shifts for both tan δ and E' upon extraction of the sol for PU networks prepared using only the R2052 polyol are shown in Figure 10. This SPU experienced the largest shift in T_g (i.e., 36°C) of any of the SPUs synthesized using blends of R2052 and 4701 and blends of P38N and 4701. As would be anticipated, the extraction of the sol increased E' in the rubbery plateau region as well. The shift in T_g for each SPU network has been plotted in Figure 11. When the T_g's
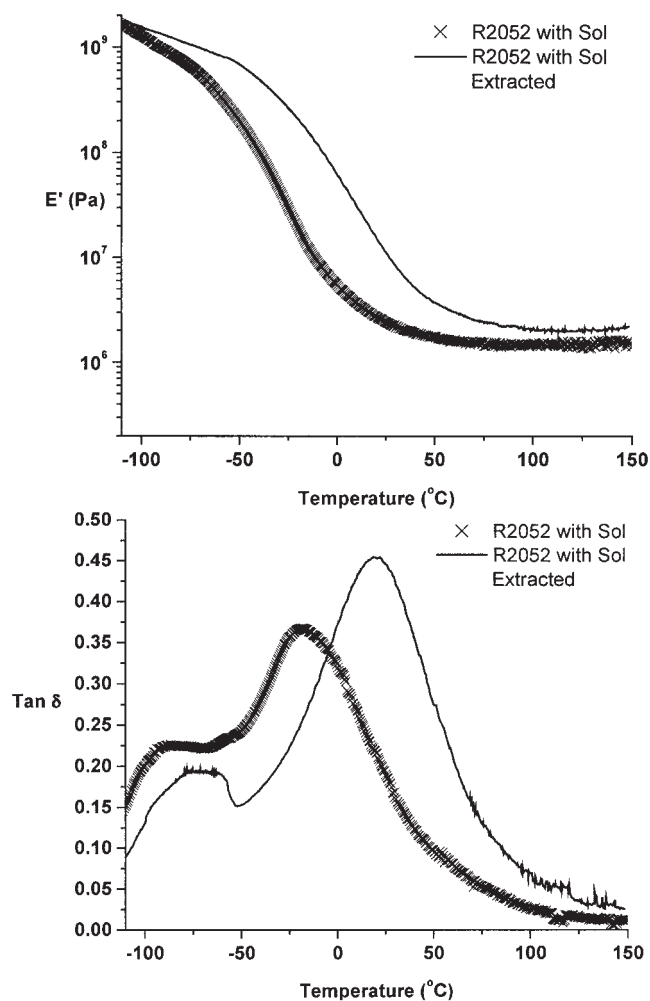

Figure 10 Storage modulus E' (top) and tan δ (bottom) versus temperature for a SPU network both with sol (dashed line) and with the sol extracted (solid line). The network was synthesized using only R2052 polyol and possessed a sol fraction of 39%.
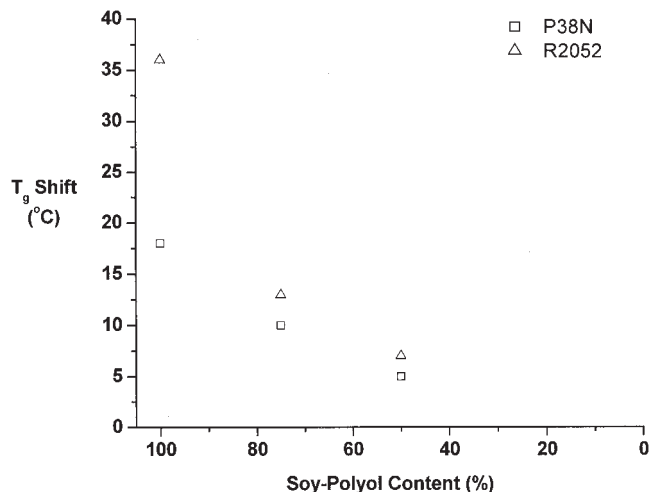
Figure 11 Magnitude of the shift in T_g upon removal of the sol-fraction from the soy-based PU films. In each case, extraction of the sol resulted in a shift to a higher T_g.

Figure 13 SAXS profiles for three network PUs listed by the polyol content from which they were synthesized.

of these materials, both extracted and unextracted, are plotted as a function of the OH# (for a pure polyol PUN) or weighted OH# (for a blended polyol PUN), a linear relationship is once again realized as seen in Figure 12. Although the r-values (0.986 for extracted, and 0.977 for unextracted) are not as high as that of the pure SBP networks in Figure 9, they are still very respectable. While a bit of an aside, it might be pointed out that in the event these nonextracted materials were in contact with a substrate that was compatible with the sol. then, with time, the sol fraction of a specific PU network would be expected to diffuse from the network and into the substrate. This removal
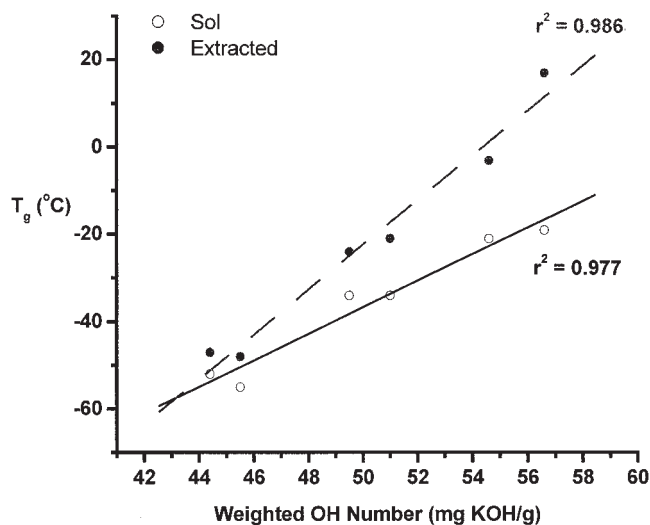

Figure 12 Relationship between the T_g of both the extracted and unextracted PUN and the weighted OH# of the polyols used in the synthesis of the network. The weight-percent of SBPs (R2052 and P38N) decreased right to left from 100 to 75% to 50%.
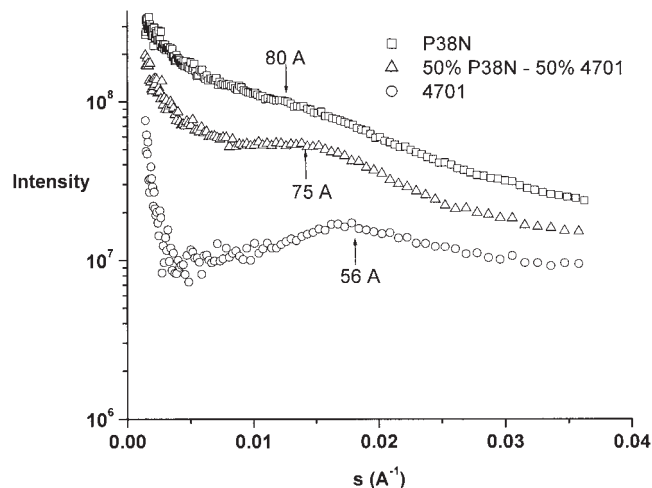
of the sol from the PU would in turn increase the stiffness and also raise the T_g as noted in Figures 10(a) and 10(b), respectively.

It is well established that in the case of elastomeric linear segmented PUs which are comprised of both soft and hard segments, due to the incompatibility of these two segment types, this typically promotes their microphase separation into a domain texture.[16] In general the interdomain distance or correlation length is on the order of 100 Å. One might expect that in the elastomeric urethane networks of the type discussed in this report that there would not be a sign of a correlation length within the final network. However, as Figure 13 illustrates a relatively weak first order interference peak is noted. Only the SAXS profiles of three of the networks discussed earlier are provided to confirm this result. It is clear that this interference peak, which provides an estimation of the correlation length via use of Bragg's law, is particularly evident for the pure 4701 (PPO) network and for the 50/50 wt % 4701/P38N network although there is also a very weak shoulder in the pure P38N SAXS profile as well. These first order interference shoulders provides correlation length values of *ca.* 56 Å, 75 Å and 80 Å, respectively. To account for this structural correlation, it is suggested that this is not a result of a correlation hole effect[17] but rather, we believe, is caused by the average distance between the isocyanate crosslinking connectors, which possess higher electron density relative to the polyol components of the network. If it were due to the common triglyceride moieties within all of the polyols utilized in our networks, it would be expected that the correlation distances would be smaller for the soy based networks since the overall molecular weight of these polyols are always less than that of the PPO based 4701 polyol. The fact that the latter system would be expected to have the highest regularity in molecular structure also helps support our argument

why it is the 4701 network that has the most pronounced interference shoulder of the three systems. In addition, since the location of the hydroxyl groups is more randomly arranged in the soy based polyol moieties in contrast to the terminal points of the 4701 material, this would promote a more random placement of the higher electron density crosslinking units in the network containing soy polyols. This, in turn, would also cause a broadening and less intense interference shoulder that indeed occurs in the two networks that incorporate soy based polyols in Figure 13 (P38N and the 50/50 wt % P38N/4701 networks). Future efforts will be made to test our supposition of the origin of these interesting SAXS results by making comparable networks that utilize other diisocyanates whose electron density characteristics are different from that of ISONATE 143L and the results of these future investigations and their implication regarding structure-property behavior will be addressed in more detail at that time.

CONCLUSIONS

Several polyols with varying hydroxyl number that were derived from soybean oil were mixed with a modified MDI to synthesize PU networks. PU networks made using a petroleum-based propylene oxide polyether polyol with some ethylene oxide capping, 4701, and ISONATE 143L were used as a benchmark to gauge the performance of the soy-based materials. Additionally, blends of soybean-based and petroleum based polyols were used to prepare PU networks.

Swelling experiments revealed that the percent change in volume of swollen networks decreased as the amount of soy-polyol used in the synthesis increased. Solubility parameters of the networks were determined to be ~10.8 $[(cal/cm^3)]^{1/2}$ for PUs prepared using P38N and a 60/40 wt % blend of P38N and 4701, and ~11.3 $[(cal/cm^3)]^{1/2}$ for the PU synthesized using only the 4701 polyol. The sol-fractions were shown to be highest for the PU networks that were synthesized from SBPs prepared via air oxidation, followed by those prepared using epoxidized SBPs, and lowest for those prepared using only the petroleum-based polyol. The sol-fraction of the SPUs was shown, in general, to be inversely related to the hydroxyl number of the soybased-polyol employed in the synthesis, and in the case of blends, inversely related to the wt % of 4701.

The storage modulus and tan δ of each PU was determined as a function of temperature. The drop in E' associated with the glass transition region of the PUs became more gradual as the amount of soy-content in the polymer was increased. This trend was reflected in the tan δ peaks as they displayed a smaller magnitude and became broader with increasing soy-content. The T_gs of the films increased with the amount of soy-polyol

used in the synthesis, as well as the OH# of the polyol. It was also shown that for the soy-based polyols prepared in this paper, there is a linear relationship between the OH# of the polyol used in the synthesis, and the T_g of the unextracted PU network.

PU networks were prepared using either pure R2052 or pure P38N with ISONATE 143I and the aide of a catalyst. As one might expect, these networks possessed somewhat lower sol-fractions and higher rubbery plateau moduli than their counterparts synthesized without the use of catalyst.

When the sol was extracted from both R2052 and P38N PU networks, the T_g and corresponding drop in E' occurred at a higher temperature than their respective unextracted network. The magnitude of the shift in T_g scaled with amount of soy-polyol used in the synthesis.

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