

Characterization of Soy-Based Polyurethane Networks Prepared with Different Diisocyanates and Their Blends with Petroleum-Based Polyols

Todd W. Pechar,¹ Garth L. Wilkes,¹ Bing Zhou,² Ning Luo²

¹Macromolecules and Interfaces Institute, Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24060

²BioBased Technologies, 1315 North 13th Street, Rogers, Arkansas 72756

Received 23 August 2006; accepted 14 March 2007

DOI 10.1002/app.26569

Published online 26 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Raw soybean oil was hydroxylated with acetic acid and hydrogen peroxide to prepare soy-based polyols of various functionalities. These polyols were reacted with a modified diphenyl methane diisocyanate (Isonate 143L) to make polyurethane networks. The sol fractions decreased as the hydroxyl number of the polyol increased, and the glass-transition temperatures increased with the hydroxyl number, as did the rubbery plateau storage modulus and Young's modulus of the networks. When the glass-transition temperatures of each network were plotted as a function of the polyol's hydroxyl number, a linear relationship was observed over the range investigated. This trend closely matched that of our previous work with soy-based polyurethane networks. A second series of networks was prepared with the same polyols but

with different isocyanates. The nature of the crosslinker was shown to somewhat influence the sol fractions, glass-transition temperatures, and stress-strain behavior of the networks. A linear relationship was recorded between the storage modulus at 125°C of a network and the average functionality of the polyol from which it was synthesized. Finally, two separate polyurethane networks were prepared through the blending of two polyols: one based on petroleum and the other based on soy. These networks were also characterized, and the compatibility of each blend was addressed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2350–2362, 2007

Key words: networks; polyurethanes; renewable resources; soybean oil; polyol

INTRODUCTION

Polyurethanes (PUs) are a family of polymers that has sometimes been named a "Jack of all trades" as they have been successfully employed in many diverse applications such as elastomers, foams (flexible, semi-rigid, and rigid), coatings, adhesives, fibers, thermosets, and thermoplastics.^{1,2} It is commonplace to synthesize PUs through the mixing of a hydroxyl-functionalized monomer with a second monomer containing an isocyanate group, which will react to form a urethane linkage. If the functionality of both reactants is 2, then a linear PU will be produced. However, if one or both reactants have an average functionality greater than 2, then a polyurethane network (PUN) can be formed, provided that the stoichiometry is properly balanced and the extent of the reaction reaches the gel point of the system.

The content of the polyol can surpass 80 wt % in some PU or poly(urethane urea) elastomers. As such, the cost of the polyol strongly influences the final cost

of the PU product. To date, the polyol used in this reaction is typically of a petroleum origin; however, with increasing worldwide demand and a more limited supply of crude oil, the price of this primary feedstock for the PU industry has been escalating with no end in the foreseeable future. This trend along with mounting pressures to move toward inexpensive, domestic, renewable, and more environmentally friendly raw materials offers an excellent opportunity for polyols derived from soybean oil to enter into the PU market as a better and less expensive feedstock in comparison with the current petroleum-based feedstock.

Soybean oil contains triglycerides, which are three-arm structures in which the arms can be either saturated or unsaturated fatty acids. The arms can vary from 14 to 22 carbons in length and may have 0–3 double bonds per fatty acid. The average number of double bonds per molecules is 4.6, and the molecular weight of soy oil of American origin is about 900 g/mol.³ The most common fatty acid found among the arms is linoleic acid, which is composed of 18 carbons and contains two carbon-carbon double bonds. The next most common acid is oleic acid, which also contains 18 carbons but has only one C=C bond. Approximately 16% of all the arms are saturated fatty

Correspondence to: G. L. Wilkes (gwilkes@vt.edu).
Contract grant sponsor: United Soybean Board.

acids. Soybean oil triglycerides contain several reactive functional groups such as double bonds, allylic hydrogens, esters, and their corresponding α -carbons. These groups can be used to tailor the soybean oil structure so that it contains specific functional groups, particularly hydroxyl groups, to make soybean-oil-based polyols (SBPs).⁴

SBPs have already been used to synthesize PUs in the form of foams (e.g., flexible, rigid, and semirigid), composites, and elastomeric and rigid solids. The details of the work focused on foams has been discussed elsewhere.⁵⁻⁷ Likewise, the efforts toward developing soy-based composites have been outlined previously.^{4,8,9}

Several research efforts have been centered on fabricating elastomeric and rigid PU thermosets. Petrovic et al.^{10,11} studied the effect of the ratio of isocyanate groups to hydroxyl groups on the properties of soy-based polyurethane networks (SPUNs).^{10,11} In their study, the amount of diphenyl methane diisocyanate (MDI) available to crosslink with an SBP (functionality of 3.6 and hydroxyl number of 203 mg of KOH/g) was varied. The hydroxyl number is defined as the number of hydroxyl groups in 1 g of the polyol expressed as an equivalent weight in potassium hydroxide. It was found that the isocyanate index changed the crosslinking density of the PU as well as the amount of dangling ends within the network. Both of these were determined to be responsible for the observed trend of an increasing glass-transition temperature (T_g) with an increasing isocyanate index (which was 0.4–1.05 in this study). They observed that the swelling of the networks increased as the isocyanate index decreased and that these networks were rubbery if the index was equal to or less than 0.7 and glassy if the index was 0.8 or greater.

Javni et al.¹² were able to alter the properties of SPUNs by using different isocyanates. This group employed several diisocyanates and triisocyanates (both aromatic and aliphatic) for the study to react with an SBP that possessed a hydroxyl number of 206 mg of KOH/g. The T_g of a SPUN was highest when aromatic triisocyanates (91°C) were used in the synthesis, and the next highest T_g of a SPUN came from an aromatic diisocyanate, followed by those prepared with a cycloaliphatic diisocyanates; the lowest was achieved with a linear aliphatic triisocyanate or diisocyanate (12°C). The highest resistance to swelling in toluene came from the materials made with the aromatic triisocyanates, whereas those made with the aromatic and cycloaliphatic diisocyanates outperformed the aromatic triisocyanate networks in terms of impact resistance but suffered from lower strength under ambient conditions. The PUs prepared with the linear aliphatic diisocyanates provided the highest flexibility and impact resistance but offered the lowest tensile strength and swelling resistance of the systems.

Earlier work from our laboratory¹³ has shown that one can successfully synthesize SPUNs without the aide of diisocyanates. This provides a very appealing feature for SPUNs as this removes the need for diisocyanates, which are known to carry very serious health risks and thus require suitable ventilation and personal protection equipment. As demonstrated in that work,¹⁴ we were able to use CO₂ and tetrabutylammonium bromide (i.e., a catalyst) to prepare carbonated soybean oil containing five-membered cyclic carbonates from epoxidized soybean oil. Amine-functionalized monomers were reacted with the carbonated soybean oil to make PUs. This reaction introduced a urethane linkage into the polymer and also provided a secondary hydroxyl group adjacent to each urethane linkage. The resulting PUNs offered sol fractions as low as 6.8% and T_g 's (determined from each network's primary $\tan \delta$ peak) ranging from 18 to 43°C, which depended on the amine-based crosslinker used to develop the network.

Petrovic et al.¹⁵ were able to show that ozonolysis could be used to obtain SBPs. This technique has the advantage of providing a polyol with a primary terminal hydroxyl group, unlike the secondary hydroxyl group located near the center of a triglyceride arm, which is common in other synthetic approaches. The authors used this mechanism to produce polyols from soybean oil and trilinolein, the latter of which possesses carbon–carbon double bonds on all three arms of the triglyceride. Using these two polyols would allow one to judge the influence of the approximately 16% of triglyceride arms in soybean oil that have no carbon–carbon double bonds and thus may behave as a plasticizer in the network in addition to not being able to support any equilibrium mechanical stresses applied to the final network material.

The SBPs synthesized in the aforementioned study showed a lower functionality than the trilinolein polyol (i.e., 2.55 vs 3.00, respectively) and similar number-average molecular weight (M_n) values (628 vs 560 g/mol, respectively), which, as stated earlier, were less than raw soybean oil's molecular weight near 900 g/mol. When both polyols were reacted with MDI to make PUNs, the SPUN displayed a lower T_g (22°C) and higher swelling (61%) than those of the trilinolein network (52°C and 30%). The authors attributed these results to the differences in the crosslink density (lower in the soy-based material) and the number of dangling ends (higher in the soy-based system) in both systems.

Petrovic et al.¹⁶ also performed a study in which segmented crosslinked PUs were prepared from SBPs, and the influence of the amount of the hard segment within these systems was examined. They found that a phase-separated morphology existed for samples with 40% hard segment, but they saw no evidence of this same behavior at lower hard-segment

contents. Furthermore, small angle X-ray scattering studies showed that the chain extender of the hard segment had an impact on the domain spacing of the materials. When butanediol was used a chain extender, a domain spacing of 124 Å was realized, which is in the range of typical values for an uncrosslinked thermoplastic elastomer.¹⁷ When the shorter ethylene glycol was substituted as a chain extender, the peak was replaced by a shoulder with a domain spacing of about 100 Å. Increasing the hard-segment content of these materials led to networks with lower crosslink densities, impact strengths, and swelling but higher T_g 's and moduli than those of their lower hard segment counterparts.

Mannari and Massingill¹⁸ derived SBPs containing phosphate ester groups with various degrees of functionality by reacting epoxidized soybean oil with phosphoric acid. These polyols were used to prepare PU coatings and compared with conventional polyester polyol based systems. The authors noted reduced hardness and solvent resistance with their soy-based systems; however, they also noted reduced costs and reduced volatile contents (%) with the soy systems. In addition, they found that the higher functionality SBPs could be substituted for up to 25% of the conventional polyols without any noticeable compromise in the film properties.

Our previous work investigated the structure-property relationships of SBP-based SPUNs synthesized with either an air oxidation route or an epoxidation route followed by an acid treatment.¹⁹ Both types of SBPs contained secondary hydroxyl groups located toward the center of the arms of the triglycerides. The use of a catalyst was avoided in this earlier work, as the epoxidized polyols possessed a relatively high functionality and viscosity that did not allow them to be easily processed into networks suitable for mechanical testing. Specifically, these two properties led to the entrapment of air during the mixing of the monomers, which did not have sufficient time to escape from the mixture after it was cast if a tin catalyst was used because the gelation was achieved more rapidly. In addition, some of these polyols were blended with a petroleum-based polyol to determine if these systems properties could be improved. It was shown that the high sol fractions associated with the networks prepared with the air-oxidized polyols could be reduced either through blending with a petroleum polyol or through the substitution of the air-oxidized SBPs with those prepared with the epoxidation route, which led to a higher functionality SBP. Despite the improvements offered by the epoxidation route, this approach still did not lead to low sol fractions comparable to what would be obtained in pure petroleum-based systems. It was also shown that removing the high levels of sol from the pure soy networks distinctly raised the T_g . Furthermore, a linear

relationship between the T_g of the PUN and the hydroxyl number of the SBP from which it was synthesized was realized.

The objective of the work presented here was to investigate a new series of SPUNs that were synthesized from SBPs prepared by BioBased Technologies (BBT; Rogers, AR). BBT employs a synthetic scheme that involves first epoxidizing the raw soybean oil with hydrogen peroxide and acetic acid and later hydroxylating the oil with the same components. To determine if the same linear relationship between the hydroxyl number and T_g would be observed, a series of SPUNs were prepared from BBT polyols that had different hydroxyl numbers and Isonate 143L (i.e., the diisocyanate used in our previous study) without the aid of a catalyst. Another series of SPUNs was prepared with the same polyols but with different diisocyanates as well as a polyisocyanate (i.e., PAPI 27). A tin-based catalyst was also included in this portion of the study because air entrapment was not a problem in the preparation of these networks. Finally, a series of blends of SBPs and a petroleum-based polyol were used to prepare PUNs to learn if the hydrophobic SBP would display miscibility with the more polar petroleum-based polyol.

EXPERIMENTAL

Materials

BBT generously donated four different soy-based polyols for this study, labeled SB126, SB145, SB171, and SB189A, with hydroxyl numbers of 126, 145, 171, and 189 mg of KOH/g, respectively. Two other soy-based polyols that were supplied to the authors by BBT, labeled SB117 and SB189B, were used to make blends with a petroleum-based polyol and possessed hydroxyl numbers of 117 and 189 mg of KOH/g, respectively. The SB189B polyol that was used in the study covering blends of SBPs with petroleum-based polyols was taken from a different batch than the SB189A used to make the pure soy networks. There were some small differences noted in the properties of the pure soy networks prepared with the two different batches of soy-based polyol with a hydroxyl number of 189, and they have therefore been given different names in this article.

Dow Chemical Co. (Midland, MI) generously supplied a petroleum-based, propylene oxide extended polyether polyol, Voranol 4701 ($M_n \sim 5000$ g/mol, average functionality ~ 2.5 , $\sim 74\%$ ethylene oxide end-capped), and Isonate 143L (a polycarbodiimide-modified diphenylmethane diisocyanate) having an isocyanate equivalent weight of 144.5. Additionally, they donated PAPI 27, a polyisocyanate (MDI-based) with an average functionality of 2.7, which was used as received.

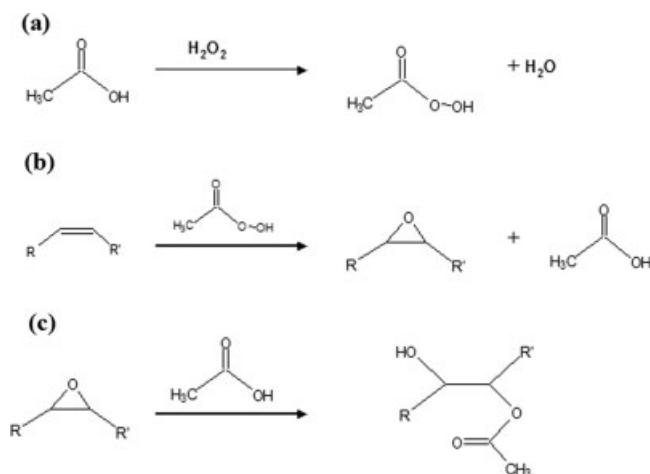


Figure 1 Synthetic route followed to prepare the soy-based polyols. (a) Acetic acid is treated with hydrogen peroxide to form peroxyacetic acid and water. The peroxyacetic acid reacts with the double bond of (b) a triglyceride to epoxidize the soybean oil. Here R and R' are different parts of a fatty acid that may or may not contain additional unsaturation. (c) Epoxidized soybean oil reacts with acetic acid to hydroxylate the soybean oil and adds an ester side chain. This figure was adapted from ref. 19.

Toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) were purchased from Sigma–Aldrich (St. Louis, MO). MDI was purchased from Alpha Aesar. No further purification steps were given for these monomers.

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

Dimethylacetamide (DMAC) was used as the solvent in the swelling experiments and for the extraction of the sol to determine the sol fraction. DMAC was purchased from Sigma–Aldrich, and no steps were taken to further purify it.

Hydroxylation of soybean oil

Hydroxylated soybean oil was prepared by BBT as described in detail in the appropriate patent.²⁰ The synthetic route followed by BBT to functionalize the soybean oil with hydrogen peroxide and acetic acid is shown in Figure 1. This process was used to prepare all the SBPs used in this study.

Determination of the hydroxyl number

The hydroxyl number for each soybean-based polyol was determined using the AOCS Official Method Cd 13–60.

Dow Chemical provided the hydroxyl number of Voranol 4701, which was determined with ASTM D 4272.

PU synthesis

The PUNs were synthesized as follows. Equivalent weights were determined for each polyol with the hydroxyl numbers provided by the two suppliers (i.e., BBT and Dow Chemical). Calculations for the required masses of the reactants were determined on a 20-g polyol basis and with an isocyanate index of 105. Equation (1) was used to determine the mass of diisocyanate needed for the synthesis:

$$\frac{M_{\text{NCO}}}{\text{EW}_{\text{NCO}}} = \sum_{i=1}^n \left(\frac{M_{\text{polyol}_i}}{\text{EW}_{\text{polyol}_i}} \right) \cdot 1.05 \quad (1)$$

where M is the mass of the reactant, EW is its equivalent weight, and n is the total number of blend components used in the synthesis. To make comparisons with our previous work, a series of SPUNs were prepared with Isonate 143L and SBP, but without the use of a catalyst, as was done in the previous work. In all other cases, a catalyst (DABCO T-12) was added at a weight equal to 0.1% of the mass of the polyol used in the synthesis of PUs. Networks were also made with a 100 or 50 wt % soybean based polyol with the balance being Voranol 4701.

The determined masses of the reactants were mixed together and carefully hand-stirred to minimize the presence of air bubbles in the mixture. For the systems prepared with MDI, MDI was first melted with a hot plate (~50°C) and then mixed with the polyol and catalyst, which were also preheated to the same temperature. The mixture was cast onto glass Petri dishes, placed in a hood, and allowed to sit for at most 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 at a rate of 20°C/min to 100°C and were held at that temperature for 3 h before being cooled to 35°C at a rate of 2°C/min.

In some cases, the rigid networks could not be removed from the glass dishes after curing. For these cases, the mixtures of the reactants were cast onto smooth Kapton sheets. The mixtures were smoothed with a doctor blade and then cured according to the procedure listed previously.

Characterization

Gel permeation chromatography (GPC)

The relative molecular weights and molecular weight distributions of the SBPs were determined by GPC performed on a Waters Breeze GPC system, which was equipped with Styragel[®] HR 0.5 and HR 2 columns and Waters 2414 UV absorbance and 2487 refractive-index detectors. Tetrahydrofuran (THF) served as the eluting solvent, and the flow rate was set at 1 mL/min. The operation temperature was set to be 40°C. SBPs were directly dissolved in the THF

TABLE I
Molecular Weight Data and Calculated Average Functionality for Some BBT Soy-Based Polyols

	SB126	SB145	SB171	SB189A
M_n (Da)	1790	1810	1900	2070
Polydispersity index	1.23	1.24	1.23	1.24
Average functionality	4.02	4.68	5.79	6.97

solvent at a concentration of approximately 1 wt % without filtration. The molecular weights and molecular weight distributions were calibrated with low-molecular-weight polystyrene standards (Shodex SL 105, Kawasaki, Japan). The data were analyzed with Breeze software from Waters.

Sol fraction measurements

Thin PU samples (0.3 mm or less) were cut from each PU used in this study and weighed and then were 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 a 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 a vacuum normalized to the mass before immersion in DMAC.

Dynamic mechanical analysis (DMA) tests

DMA was carried out in the tensile mode with a Seiko model DMA 210 over a temperature range of -110 to 180°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 $\tan \delta$ was assigned to T_g for each sample.

Stress-strain measurements

Stress-strain measurements were gathered at room temperature with an Instron model 4400R tensile testing instrument. Dog-bone samples were cut from each PUN with a mechanical die. This allowed multiple specimens to be cut, each with a testing length of 10 mm and a width of 2.9 mm. The crosshead speed was kept constant at 25 mm/min for all tests.

RESULTS AND DISCUSSION

PUNs from soy-based polyols and modified MDI

Soybean oil was hydroxylated by BBT as discussed previously and used to synthesize PUNs as outlined in the Experimental section. The full details of the hydroxylation process are proprietary.

GPC curves were gathered for each of the SBPs to determine their respective molecular weight distributions. The M_n values and polydispersities are given in

Table I. As is evident upon an examination of the table, there is an increase in the polyol molecular weight as the functionality increases. Despite this increase, all of the polyols possess almost the same polydispersity index. The average functionality of each polyol (also shown in Table I) was calculated with the polyol's equivalent weight and M_n . As can be seen, these polyols offer functionalities as low as ~ 4 to as high as ~ 7 . Although the latter may appear quite high, it does not surpass the theoretical maximum of a triglyceride, which is ~ 7.4 , determined by multiplication of the average number of C=C groups in a triglyceride (i.e., 4.6) and the average number of -OH groups (i.e., 1.6) obtained from the olefin groups.^{3,21} The emphasis of the GPC data in this work is focused on the trends in the molecular weight distributions of the polyols rather than their absolute values. The M_n values reported for the SBPs are likely underestimates of their true values. One must recall that the polyols are branched, unlike the linear polystyrene standards used to calibrate GPC. As such, for the same solubility parameters, the polyols will have a smaller hydrodynamic volume than the polystyrene standards. This results in the molecular weights of the SBPs being underestimated and also accounts for their reported higher average functionality.

PUNs were prepared from each of the four SBPs and the modified MDI Isonate 143L as outlined previously. Samples of each network were immersed in DMAC to extract the sol fraction from the network; our previous work indicated that the solubility parameter of DMAC closely matched that of SPUNs.¹⁹ The recorded sol fractions for each network are listed by the SBP designations in Figure 2. As one would expect, when the hydroxyl number of the polyol was

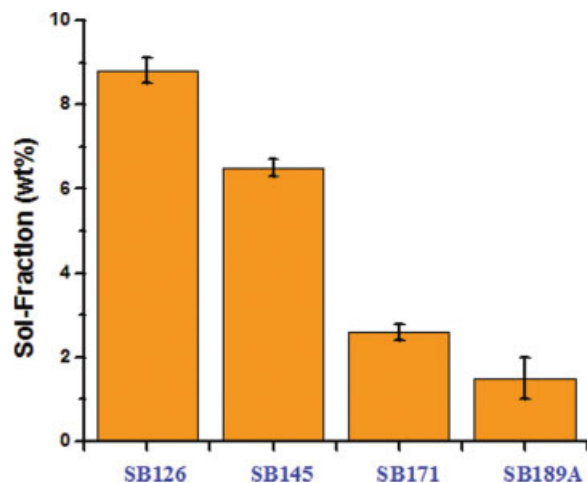


Figure 2 Sol fractions (wt %) of PUNs prepared with soy-based polyols of different hydroxyl numbers with a modified MDI. Each network was immersed in excess DMAC for 24 h at 50°C to extract the sol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

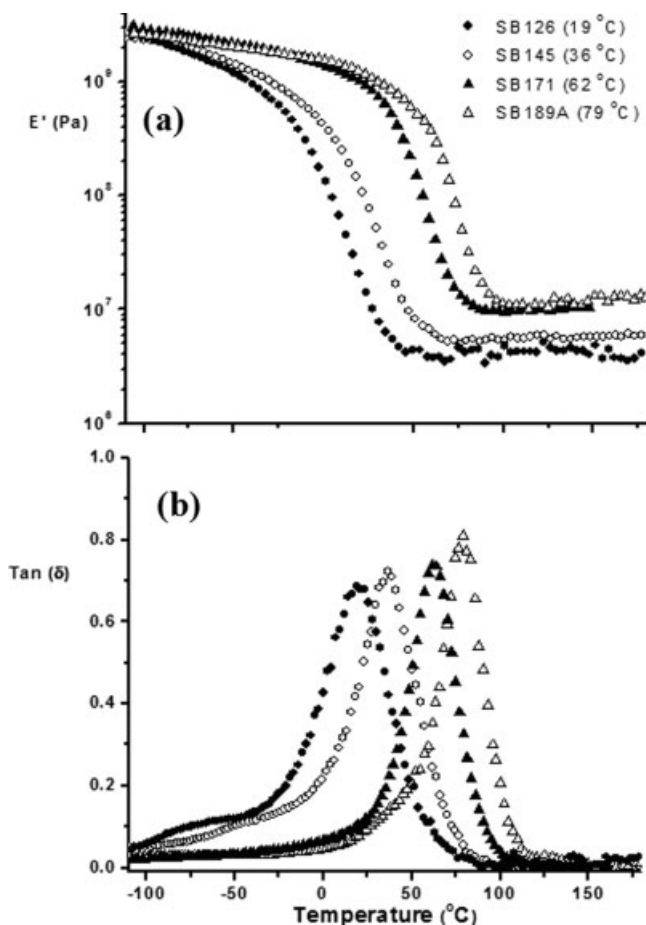


Figure 3 (a) E' as a function of temperature for PUNs synthesized from soy-based polyols of various hydroxyl numbers and (b) $\tan \delta$ as a function of temperature for PUs synthesized with the same soy-based polyols. The reader may note the presence of a small shoulder at lower temperatures for the lower hydroxyl number polyol networks. The T_g 's of each network are listed in the legend of part a.

increased, the sol fraction of the corresponding network decreased because of the higher functionality polyols having a greater chance of becoming incorporated into the network due to more reactive sites than a lower functionality polyol. The lowest functionality polyol, SB126, contained less than 9 wt % sol, and the highest functionality polyol, SB189A, offered sol fractions under 2%.

DMA was employed to determine the temperature dependence of the storage modulus (E') and the general thermal transition behavior of each network PU. The changes in E' (stiffness) with the temperature for PUs synthesized with these polyols and their blends are shown in Figure 3(a). Each material experienced a typical drop in stiffness of roughly 3 orders of magnitude when the network passed through its T_g (indicated by the principal $\tan \delta$ peak, which is discussed later), and its location systematically increased with the SBP hydroxyl number. In addition, the rubbery

plateau modulus was shown to increase with the hydroxyl number as well, and the temperature service window, or temperature range over which the stiffness of a material is a weak function of temperature, gradually decreased. The rubbery plateau modulus behavior is explained by qualitative consideration of the molecular weight between crosslinks (M_c) of the systems. As the average functionality of these polyols increases, more parts of the triglyceride arms are becoming attached to the network, and there are fewer free arms in the network. This reduces M_c of the system and thus provides a stiffer material above T_g . Furthermore, it was shown by Zlatanic et al.²² that the unattached regions of a triglyceride can depress T_g of the network. There are expected to be a higher number of these free arms in our systems prepared from those using lower hydroxyl number polyols; however, some level of dangling ends will be present in all of the systems, as the —OH groups on the SBP are secondary and are located toward the centers of the triglyceride arms. Thus, when an —OH group reacts with an isocyanate group to form a urethane linkage, there is a short dangling end of roughly six carbons that is attached to the network only at one point. In addition to these shorter dangling ends, approximately 16% of all the triglyceride arms in soybean oil are saturated and, as such, contain no hydroxyl functionality. Both the shorter dangling ends and the saturated arms are expected to be in each system.

The DMA experiments also provided the trends in $\tan \delta$ for these networks, which are shown in Figure 3(b). As reflected in the E' profiles, the T_g of the networks systematically increased as the hydroxyl number of the polyol used in the synthesis of the SPUN increased. Although many of the same arguments presented to explain the observations of each material's E' behavior still apply, the diisocyanate content should also be considered when we discuss the trends in T_g . As the hydroxyl number of the polyol increases, the amount of diisocyanate in the system also increases. As such, the diisocyanate content of these PUNs is not constant and increases with the SBP functionality. The higher diisocyanate content in the network will undoubtedly increase the material's T_g (provided that the reaction goes to completion). It is also evident from the curves that the breadth of the $\tan \delta$ peaks decreases and the magnitude of the same peaks increases with the polyol functionality. This may be due to the fact that as the average functionality of the polyol increases, there will be fewer arms of the triglyceride that are not covalently attached to the network, which may have somewhat different levels of molecular mobility than those of the arms, which are covalently bonded to the network. It is also evident from the DMA curves that the two PUNs prepared from the lower average functionality polyols

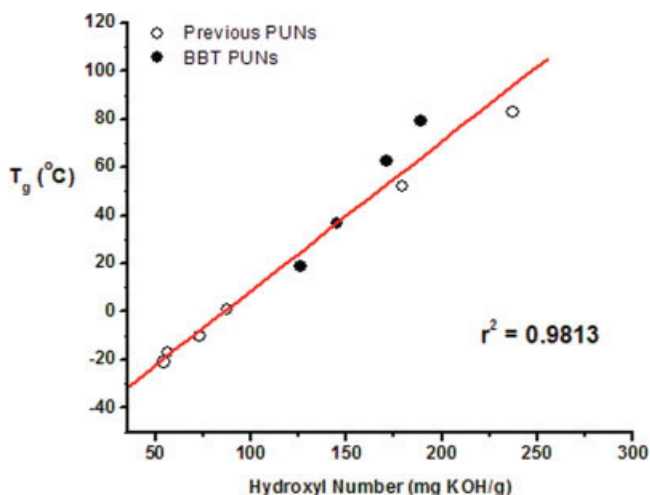


Figure 4 Relationship between T_g (the $\tan \delta$ peak) of a PU containing its sol and the hydroxyl number of the polyol from which it was synthesized. Data from our previous work¹⁹ are included and are represented by open circles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

SB126 and SB145 each had a lower temperature shoulder adjacent to the primary $\tan \delta$ peaks. The origin of this sub- T_g shoulder was not determined; however, others have speculated that it may be related to rotational motions of short units in the fatty acid chain.¹⁵ It appears from the curves that as the polyol functionality was increased, this shoulder reduced in size and ultimately disappeared with the higher hydroxyl number polyols.

In our previous work,¹⁹ we reported an observation of a linear relationship between the hydroxyl number of a soy-based polyol and the T_g of its corresponding PUN (prepared without a tin catalyst) over the range of hydroxyl numbers and conditions used in that study both in the synthesis of the polyol and in the curing of the materials. One objective of this study was to determine if this relationship still held upon being expanded with the addition of the BBT PUN data. The resulting relationship is shown in Figure 4. As one can readily observe, three of the four new data points fall closely on the line. Despite the use of different synthetic schemes to produce the soy-based polyol and the application of slightly different curing treatments to prepare the networks, the resulting relationship still offers a respectable r^2 value of 0.9813. Even though these four new BBT data points follow the general trend in Figure 4, they may in reality more closely follow a slightly different linear relationship. When a linear regression analysis is applied to only these four points, a very impressive r^2 value of 0.9999 is obtained. This linear behavior of T_g with the hydroxyl number is similar to what was reported earlier by Wool et al. in their work with acrylated soy-based network materials.²¹

Stress–strain curves of the BBT materials were gathered under the ambient conditions to provide insight into the ultimate tensile strength and modulus of these systems. The experimental results are shown in Figure 5. The temperature of the experiment in relation to the T_g of the network has an enormous influence in determining the stress–strain curve. If one were to draw a vertical line at 25°C in Figure 4(a), it would be evident that some of these materials are in the glassy state, whereas others are much more rubbery. For example, although the SB189A PUN displays a much higher ultimate tensile test than SB126 PUN, the former's T_g is roughly 50°C above the ambient temperature, whereas that of the latter is roughly 6°C below ambient temperature. Hence, if this same test were performed for the SB189A system at a temperature of 85°C, its curve may more closely resemble that of the SB126 system.

As shown in Figure 5, the SBP4 PUN, as expected, displays the highest modulus and ultimate tensile strength (at ca. 37 MPa) of any of the materials. It also displays the lowest strain at break of the materials as well. This behavior is a result of the material's high T_g and anticipated lower M_c due to the higher average functionality of the polyol. Interestingly, when the average functionality of the polyol is reduced slightly, such as the case of SB171, the resulting network is still quite rigid at room temperature and offers a high tensile strength (~ 21 MPa) but elongates somewhat before failure.

It is evident that the SB126 PU, which represents the lower end of polyol functionality, displays a much lower modulus and ultimate tensile strength (~ 5 MPa) in addition to a much higher strain at break ($\sim 105\%$) than the SB189A system. Overall, the

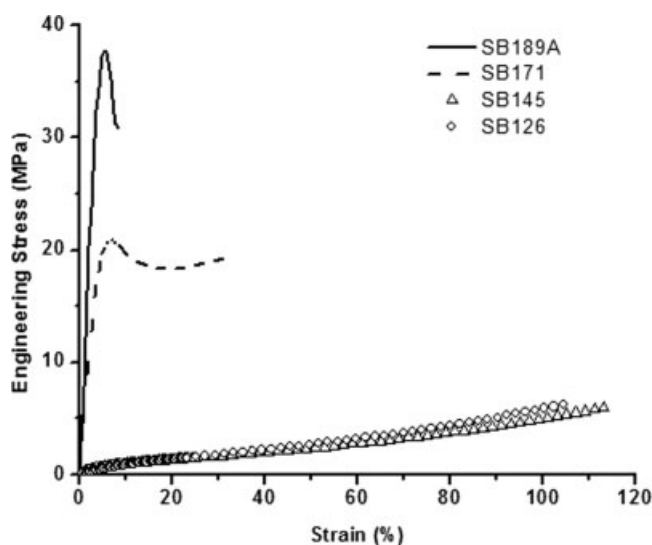


Figure 5 Stress–strain curves collected under the ambient conditions for PUNs prepared from soy-based polyols of various hydroxyl numbers with a modified MDI.

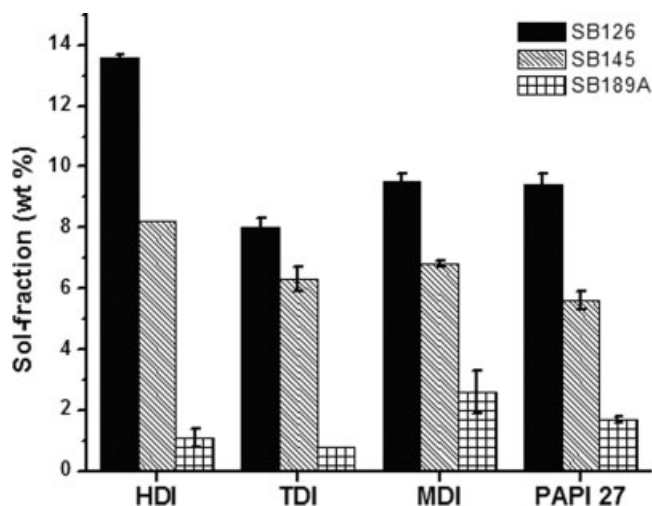


Figure 6 Sol fractions of PUNs prepared with different isocyanates.

trends in the tensile strength, modulus, and strain at break are very systematic; however, the SB145 PUN shows a higher strain at break than the SB126 network, which is quite weak. This is certainly believed to be due to the higher degree of network connectivity in the former network, which apparently allows it to stretch further before mechanical failure.

PUNs from soy-based polyols with different isocyanates

Four different isocyanates were reacted with three of the four SBPs (i.e., SB126, SB145, and SB189A) to investigate the effect of the nature of the crosslinker on the properties of the PUNs. The crosslinkers included HDI, TDI, and MDI (all difunctional) and the polyisocyanate PAPI 27 (average functionality ~ 2.7). The networks were prepared as outlined in the Experimental section. A tin catalyst was also used in this portion of the work because, as mentioned earlier, the retention of air bubbles caused by mixing was not a limitation before gelation in comparison with the epoxidized SBPs in our earlier work.

The sol fractions for these systems are reported in Figure 6. In some cases, there are no error bars to accompany the data. This is due to identical results among the many samples that were tested. Upon an investigation of the data, it becomes evident that regardless of which SBP was used in the synthesis, the largest sol fractions were most often observed for networks prepared with HDI. The systems generally showed lower sol fractions when HDI was replaced with TDI, although the reason for this is not yet understood. The sol fractions of the TDI and MDI series were similar for all systems. The PUNs prepared with the higher functionality PAPI 27 showed the lowest sol fractions of all systems. This was not sur-

prising, given that the higher average functionality of PAPI 27 should allow gelation to occur earlier. This property of the polyisocyanate is believed to explain why there did not appear to be a significant difference in the sol fractions, regardless of the SBP included in the synthesis. In the case of the networks prepared with SB189A, which possessed the highest hydroxyl number, the sol fractions were very low for each isocyanate ($\sim 1\%$). Measuring such a small change in the mass of a sample can introduce error, and thus one must certainly use caution in implying that one network has a lower sol fraction than another.

The DMA curves of each SBP for the entire series of isocyanates are shown in Figures 7–9. The T_g transition in E' [Figs. 7(a), 8(a), and 9(a)] shows that the difunctional isocyanate materials softened before the PAPI 27 network softened. This was not unexpected, as the polyisocyanate should form a network with a higher crosslink density than any of the diisocyanate-based networks. When the functionality of the crosslinker is held constant, as is the case for the HDI, TDI, and MDI systems, the HDI material softens somewhat before the aromatic materials even though HDI and

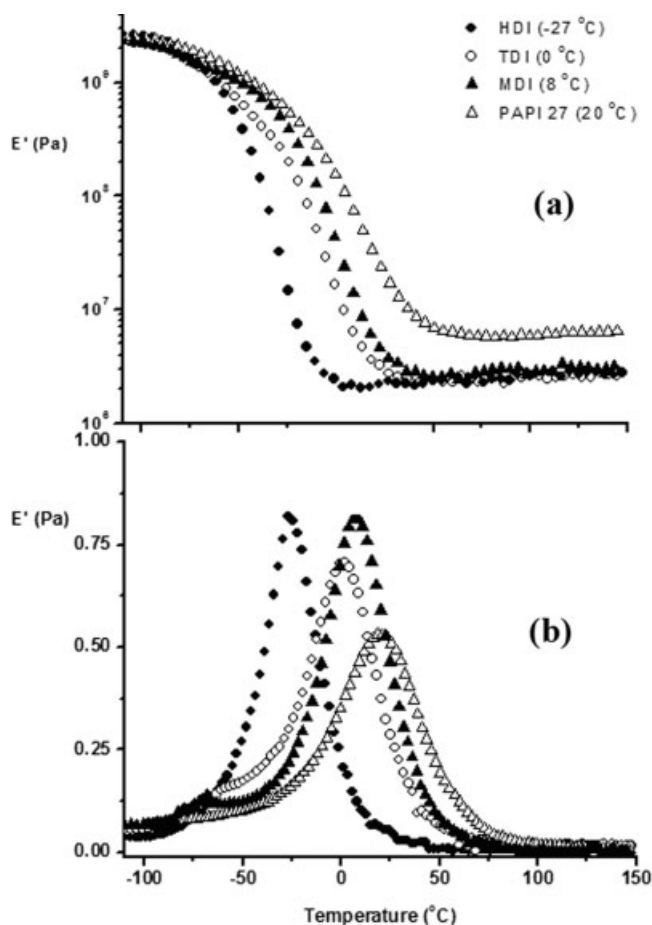


Figure 7 DMA curves of PUNs prepared with SB126 and different isocyanates. The T_g 's of each network are listed.

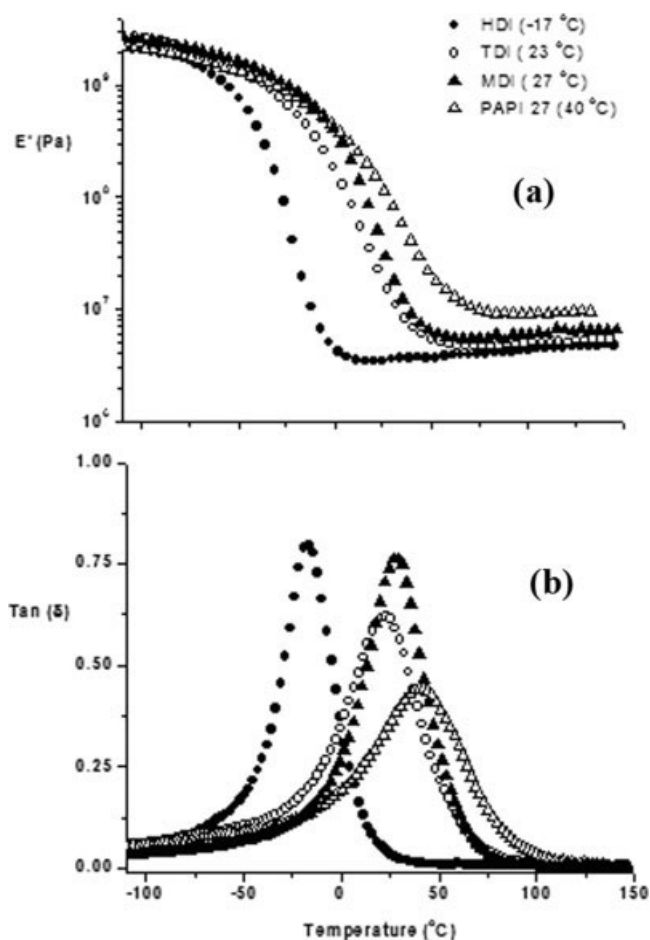


Figure 8 DMA curves of PUNs prepared with SB145 and different isocyanates. The T_g 's of each network are listed.

TDI have very similar molecular weights. This is likely due to the flexible sp^3 nature of the carbons in HDI in comparison with the more rigid aromatic sp^2 character of the other systems. When the two aromatic systems, TDI and MDI, are contrasted, it is apparent that the TDI network softens at a lower temperature. This can be explained by the higher molecular weight of the MDI unit, which is almost twice that of TDI and thus provides a higher diisocyanate weight content in the network.

The $\tan \delta$ peaks of the same PUNs are shown in Figures 7(b), 8(b), and 9(b). Reflecting the trends observed in the E' profiles, the T_g 's of the PAPI 27 systems were shown to be the highest, followed by those of the MDI systems, the TDI systems, and the HDI systems. The trend in locations of the primary peaks (i.e., T_g 's) can be justified using the same arguments presented for the trends in E' , crosslink density, diisocyanate weight content, and diisocyanate flexibility.

When the value of E' of each network is reported as a function of the average functionality of the SBP from which it was synthesized and at a temperature

of 125 $^{\circ}\text{C}$, at which all of the systems are in their rubbery regions, a striking relationship is revealed. As shown in Figure 10, a linear relationship between E' and the average functionality can be observed for each isocyanate. Despite our intent in the section to highlight changes in the soy-based networks due to the incorporation of isocyanates other than 143L, PUNs prepared with the three SBPs and Isonate 143L were included in this plot to demonstrate that this diisocyanate also displays the same linearly based relationship as is observed for the other four isocyanate PU systems. It is well established through the Gaussian theory of rubber elasticity that M_c of a polymeric material is a function of that material's equilibrium modulus (E), temperature (T), and density (ρ):

$$M_c = \frac{3\rho RT}{E} \quad (2)$$

where R is the ideal gas constant.²³ Although E' is not the same as the true equilibrium value of E , which is the basis of eq. (2), it does provide an approximation, and the trends in E' and E with increasing average

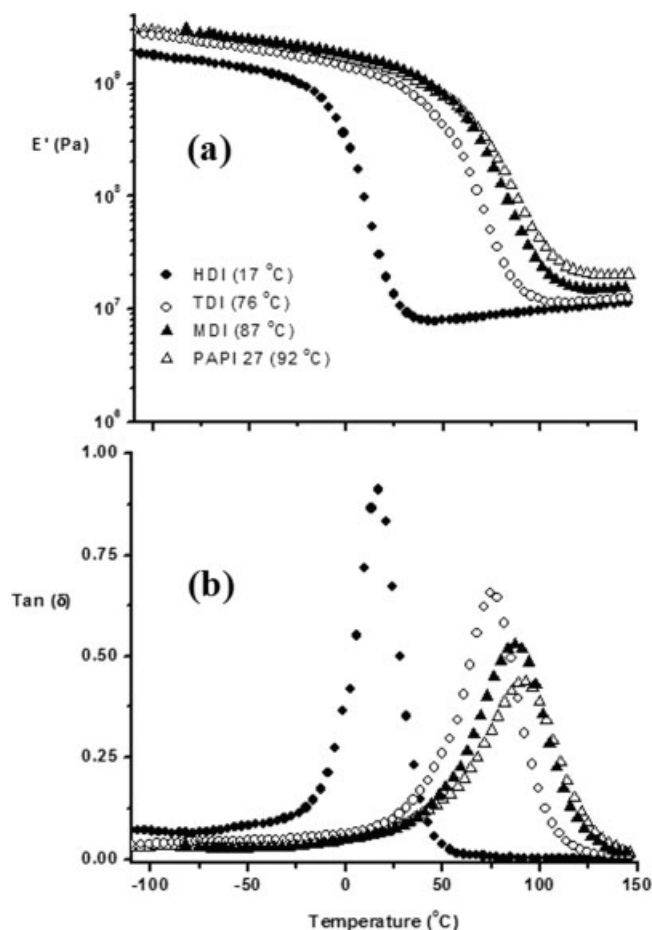


Figure 9 DMA curves of PUNs prepared with SB189A and different isocyanates. The T_g 's of each network are listed.

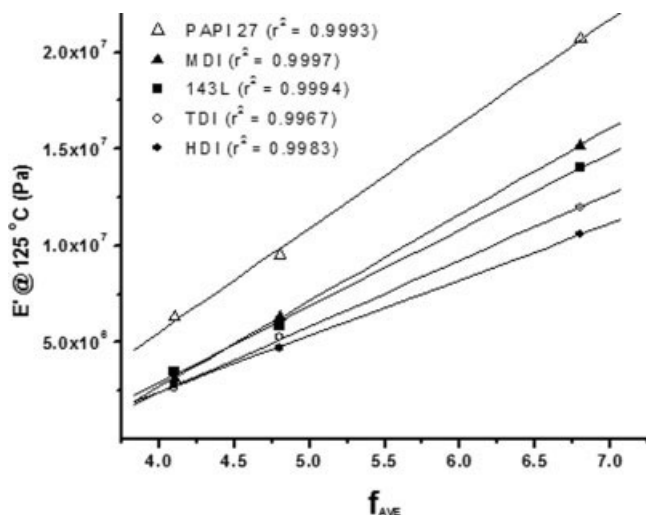


Figure 10 Relationship between E' (at 125°C) of networks made from different isocyanates and the average functionality (f_{ave}) of the soy-based polyol from which they were synthesized.

functionality are certainly expected to be similar. Given that the densities of the networks were not expected to vary widely, the data state that M_c is indeed decreasing with both the SBP average functionality and the functionality of the crosslinker, as would be expected.

The stress–strain curves for each series of PUNs were gathered under the ambient conditions and are shown in Figures 11–13. As stated previously, the T_g of a material strongly influences its mechanical behavior, and as such, the reader should consider each material's T_g relative to ambient temperature when reviewing the figures. In every case, as one replaces HDI with TDI, TDI with MDI, and then MDI

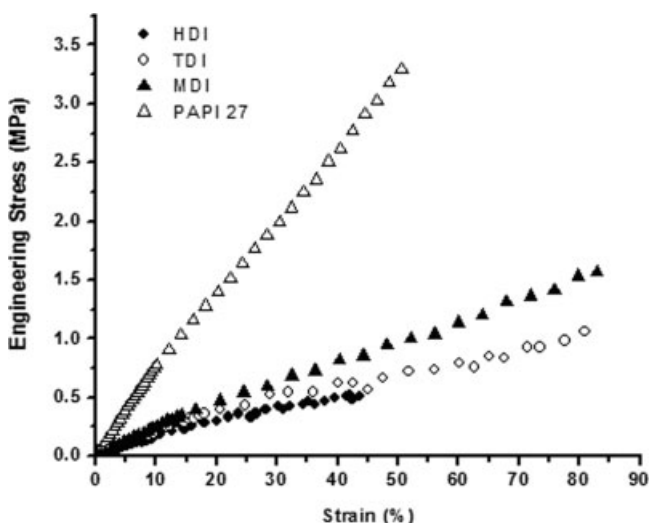


Figure 11 Stress–strain curves gathered under the ambient conditions for PUNs prepared with SB126 and different isocyanates.

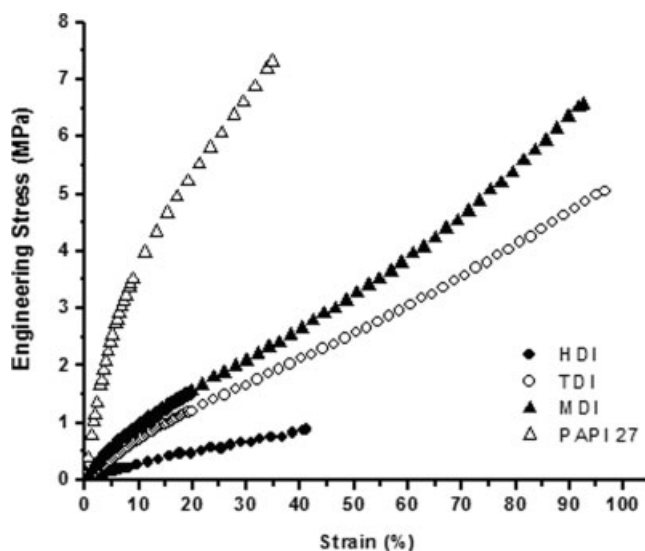


Figure 12 Stress–strain curves gathered under the ambient conditions for PUNs prepared with SB145 and different isocyanates.

with PAPI 27, the tensile strength and Young's modulus of a given network increase. The TDI-based and MDI-based PUNs offered the highest strains at break, except in the case of SB189A, for which both were well below their respective T_g 's under the ambient conditions and therefore did not deform appreciably. In this case, the HDI-based system offered the highest strain at break.

PUNs from blends of petroleum-based and soy-based polyols and modified MDI

As discussed in the Introduction section, SBPs are most often synthesized in a manner that results in

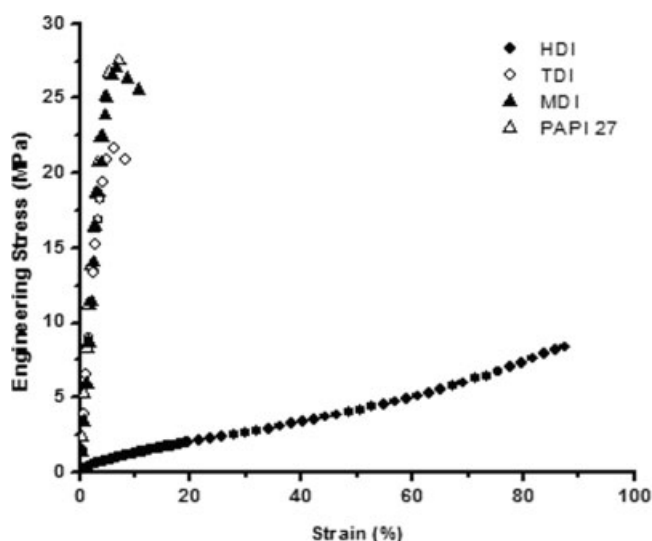


Figure 13 Stress–strain curves gathered under the ambient conditions for PUNs prepared with SB189A and different isocyanates.

secondary —OH groups located toward the center of the arms of the triglyceride, as is the case for the polyols used in this study. In many cases, the SBP will have an average functionality greater than 3. These characteristics of the polyol often lead to PUNs with higher T_g 's higher than those prepared with a glycerin extended propylene oxide petroleum-based polyol of comparable molecular weight, as the petroleum-based polyol will typically have terminal primary hydroxyl groups providing a network with a higher M_c .

The range of applications for which the SPUNs prepared with Isonate 143L are suitable could be expanded if the systems' service temperature windows were larger. Often the beginning of the service temperature window for the rubbery behavior of a pure SPUN is near or above room temperature. One method that could lengthen this window would be to blend a given SBP with a petroleum-based polyol that is known to be capable of making a network with a relatively low T_g under the conditions listed in the Experimental section. However, when we employ this method, we must recognize that blends of petroleum- and soy-based polyols possess somewhat chemically different backbone structures and, as such, could promote some level of chemical incompatibility. This ultimately has the potential to lead to a partially heterogeneous or nonuniform network in the final material, particularly if any partitioning of the polyols occurs before gelation of the network.

The petroleum-based polyol Voranol 4701 is a glycerin-extended propylene oxide (with some ethylene oxide end capping) polyol that is known to possess a polyether backbone that is more polar than the triglyceride backbone. This is in contrast to that of the soy-based polyols prepared by BBT, which are more olefinic in nature and hydrophobic. Although it may appear that these two may not blend well, our previous work with 4701 and other SBPs suggests that the solubility parameters of the two are quite similar.¹⁹

A series of PUNs were prepared by the blending of Voranol 4701 in equal amounts (i.e., 50–50 wt %) with two BBT SBPs of different hydroxyl numbers: SB117 and SB189B. The reader is reminded that the SB189B used for making blends is from a different batch than the SB189A polyol used to make pure SPUNs discussed earlier, and some small differences in properties (e.g., T_g) were noted between the two batches. The conditions for preparing the PUNs are listed in the Experimental section. The resulting networks, while showing signs of coloration, were transparent and rubbery at room temperature. The viscosity of SB189B is high enough that it does not lend itself to be as easily mixed as its lower viscosity counterpart SB117. Both systems were slowly and carefully hand-mixed to prevent the inclusion of air bubbles in the mixture, which can result in voids within the PUN.

However, because of its higher viscosity, the 4701 SB189B was noticeably more difficult to mix and, while visually appearing to be well-mixed, may not have been fully mixed on a molecular level, as addressed shortly.

The DMA profiles of the 4701 SB117 system and the two pure polyol systems are shown in Figure 14. E' of the 50–50 network [Fig. 14(a)] shows a sharp drop over a temperature range between those of the two homopolyol systems, as one would expect. Additionally, there appears to be only one systematic drop in E' from $\sim 10^9$ to $\sim 10^6$ Pa with increasing temperature, which indirectly implies a well-mixed miscible blend, as opposed to two separate glass transitions being observed over the same range with increasing temperature, which would indicate the presence of a two-phase network morphology. The trends in $\tan \delta$, shown in Figure 14(b), also indicate a well-mixed system. The 50–50 mixture network shows a single $\tan \delta$ peak at -32°C , which lies between the two peaks of

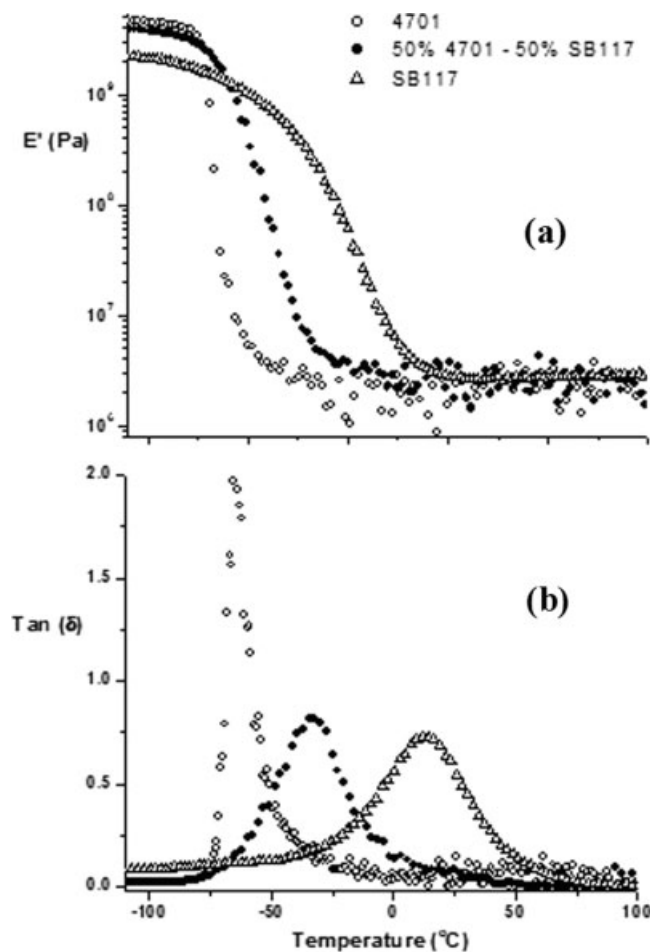


Figure 14 (a) E' as a function of temperature for PUNs synthesized from a petroleum-based polyol (Voranol 4701), a soy-based polyol with a hydroxyl number of 117 (i.e., SB117), or a 50–50 blend of the two and (b) $\tan \delta$ as a function of temperature for the same PUNs.

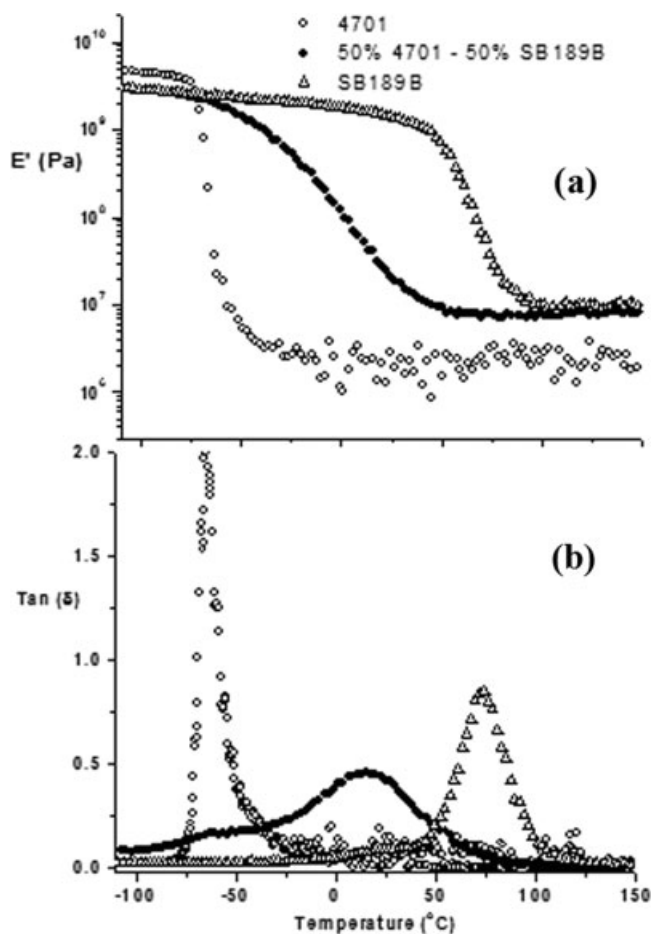


Figure 15 (a) E' as a function of temperature for PUNs synthesized from a petroleum-based polyol (Voranol 4701), a soy-based polyol with a hydroxyl number of 189 (i.e., SB189B), or a 50–50 blend of the two and (b) $\tan \delta$ as a function of temperature for the same PUNs. The reader may note the presence of a secondary peak in the 50–50 system located at the same temperature of the primary peak of the 4701 network.

the pure polyol systems, and it is less broad than that of the pure SB117 system. For well-separated systems, one would expect to see two distinct $\tan \delta$ peaks close to the location of each pure system's peak or at least significant broadening of a single $\tan \delta$ peak in the 50–50 system, both of which are absent in the 50–50 profile.

A well-known and useful relationship that can be used to estimate the T_g of random copolymers and miscible blends is the Fox equation.²⁴ The Fox equation states that the T_g of a miscible blend is a function of each T_g of the pure homopolymers (in this case, the pure 4701 PUN and the pure SB117 PUN) and their respective weight fractions in the blend:

$$\frac{1}{T_g} = \left(\frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \right) \quad (3)$$

where T_g is the glass-transition temperature of the 50–50 network, w_i is the weight fraction of one com-

ponent, and T_{gi} is the glass-transition temperature of the pure PUN. For the systems shown in Figure 14(b), the T_g of the pure 4701 network is -64°C , and that of the pure SB117 network is 12°C . At equal weight fractions, the Fox equation predicts a T_g of -32°C for a well-mixed network, which matches what was observed experimentally (i.e., the primary peak in $\tan \delta$ for the 50–50 system was located at -32°C).

When the functionality of the SBP is increased, as is the case in SB189B, a different behavior is observed. The DMA profile for the pure 4701, pure SB189B, and 50–50 blend networks are shown in Figure 15. Unlike what was observed in the previous blended network, this network's drop in E' , a single drop from $\sim 10^9$ to $\sim 10^6$ Pa, is considerably broader than those of the pure polyol systems. Furthermore, its $\tan \delta$ peak is broader than that of both of the pure networks and appears to show the presence of a shoulder that lies beneath the location of the 4701 network's primary $\tan \delta$ peak.

The $\tan \delta$ peak of the blended system is located at 15°C , and that of the pure SB189B material is located at 74°C . When the Fox equation is applied to this system, the agreement is very poor. The Fox equation predicts a T_g value of -12°C for a well-mixed PUN. This result combined with the DMA profile behavior suggests there is incomplete compatibility between the higher functionality SBP and the petroleum-based polyol, although the optical clarity of these materials is still good. Further studies to determine the origin of the deviation from the Fox equation have not yet been undertaken. They may be chemical in nature or simply a consequence of incomplete distributive and dispersive mixing.

To determine the tendency, if any, of the SBPs to spontaneously phase-separate from the petroleum-based polyols, several 50–50 mixtures of SB117 and SB189B with 4701 were prepared in 20-mL glass vials

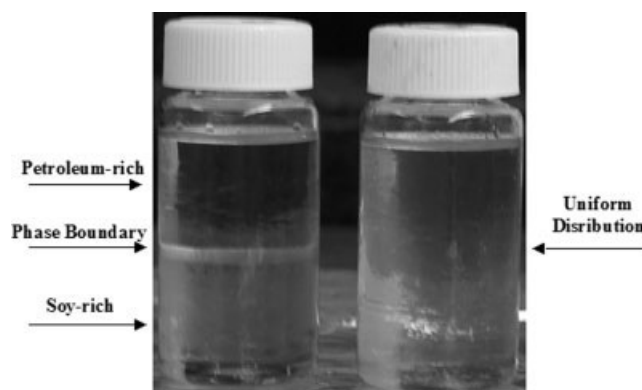


Figure 16 Image of two 50–50 mixtures of 4701 and SB189B. The left vial received no hand mixing or heat treatment and showed an SBP-rich phase at the bottom of the vial and a petroleum-rich phase at the top of the vial. The right vial was hand-mixed and then heated for 3 h at 100°C and appeared homogeneous throughout the vial. The two mixtures did not change visibly even weeks after being prepared.

without the addition of any other additives (e.g., a diisocyanate or catalyst). Some of the mixtures were blended without any mixing or heat treatment. It was found that in this case that mixing did not occur spontaneously, and there was a clearly visible phase separation between the two polyols in the vial for both types of 50–50 mixtures. When the two types of mixtures were hand-mixed and then heated to 100°C for 3 h, as was done in the preparation of the networks in this study, the two polyols showed no signs of separating even after cooling. An image taken of two 50–50 blends of 4701 and SB189B is shown in Figure 16. The vial on the left received no mixing or heat treatment, and the vial on the right was subjected to both hand mixing and heat treatment. The vial on the left showed no signs of changing even after being allowed weeks to mix, whereas the vial on the right remained stable over the same time period. The same experiment was performed for a 50–50 blend of 4701 and SB117, and the same outcome was observed.

CONCLUSIONS

Four soy-based polyols with different hydroxyl numbers were prepared with a synthetic scheme involving hydrogen peroxide and acetic acid. The polyols possessed an M_n that increased with the hydroxyl number and had values ranging from 1790 to 2020 Da. These polyols were used to prepare PUNs through their reaction with a modified MDI and the application of heat to promote curing. Sol fractions for each network were determined by immersing the materials in excess DMAC. The sol fraction of the network decreased as the hydroxyl number of the polyol from which it was synthesized increased. The modulus and $\tan \delta$ of each PU were recorded as a function of temperature. The drop in modulus associated with the T_g of the PUs became sharper as the average functionality of the polyol increased. This trend was repeated in the $\tan \delta$ peaks for the same materials, and the location of the primary $\tan \delta$ peak also increased in the same manner.

Three of the four SBPs were used to make networks with different isocyanates. The PUNs prepared from polyisocyanate PAPI 27 were shown to possess the lowest sol fractions, and in general HDI offered the largest sol fraction, followed by the TDI- and MDI-based systems. In all cases, for a given SBP, the HDI-based network displayed the lowest T_g , followed by TDI and then MDI, whereas the PAPI 27 systems offered the highest T_g 's for a given polyol. The same trend was observed for the ultimate tensile strength for the same polyol. When the values of E' at 125°C of the networks (a temperature at which all of the systems were in their rubbery regions) for a given isocyanate were reported as a function of the SBP's average functionality, a linear relationship was recorded.

Two different SBPs with different hydroxyl numbers were each blended with a petroleum-based polyol to investigate how compatible the components were in terms of making a well-mixed PUN system. The DMA curve for the network composed of 50% of the lower hydroxyl number SBP provided an experimental value of T_g that exactly matched the predictions of the Fox equation, thereby implying good homogeneity of the mixing of the two polyols. However, the network composed of 50% of the higher hydroxyl number SBP showed poor agreement between the experimental value and the value of T_g predicted by the Fox equation. Furthermore, there appeared to be a broadening of the primary peak and the appearance of a small secondary peak in the $\tan \delta$ curve in the same location as that of the principle $\tan \delta$ peak of the pure petroleum network system.

The authors thank Dow Chemical for donating some of the monomers used in this study. They also thank Air Products for donating the catalyst used in this study. In addition, the authors would like to thank the United Soybean Board for their financial support of this work.

References

1. Uhlig, K. *Discovering Polyurethane*; Hanser/Gardner: Cincinnati, 1999.
2. Herrington, R.; Hock, K. *Flexible Polyurethane Foams*; 1997.
3. Liu, K. *Soybeans: Chemistry, Technology, and Utilization*; Chapman & Hall: New York, 1997.
4. Wool, R. P.; Sun, X. S. *Bio-Based Polymers and Composites*; Academic: New York, 2005.
5. Singh, A. P.; Bhattacharya, M. *Polym Eng Sci* 2004, 44, 1977.
6. John, J.; Bhattacharya, M.; Turner, R. *J Appl Polym Sci* 2002, 86, 3097.
7. Guo, A.; Ivan, J.; Petrovic, Z. *J Appl Polym Sci* 2000, 77, 467.
8. Husic, S.; Javini, I.; Petrovic, Z. *Compos Sci Technol* 2005, 65, 19.
9. Khot, S. N.; Lascalea, J. J.; Can, E.; Morye, S. S.; Williams, G. I.; Palmese, R. G.; Kusefoglu, S. H.; Wool, R. P. *J Appl Polym Sci* 2001, 82, 702.
10. Petrovic, Z.; Zhang, W.; Zlatanovic, A.; Lava, C. *Polym Mater Sci Eng* 2002, 86, 377.
11. Petrovic, Z. S.; Zhang, W.; Zlatanovic, A.; Lava, C.; Ilavsky, M. *J Polym Environ* 2002, 10, 5.
12. Javini, I.; Zhang, W.; Petrovic, Z. *Polym Mater Sci Eng* 2002, 86, 387.
13. Tamami, B.; Sohn, S.; Wilkes, G. L. *J Appl Polym Sci* 2004, 92, 883.
14. Wilkes, G. L.; Sohn, S.; Tamami, B. U.S. Pat. 7,045,577.
15. Petrovic, Z.; Zhang, W.; Javini, I. *Biomacromolecules* 2005, 6, 713.
16. Petrovic, Z.; Cevallos, M.; Javini, I.; Schaefer, D.; Justice, R. *J Polym Sci Part B: Polym Phys* 2005, 43, 3178.
17. Abouzahr, S.; Wilkes, G. L. *Processing, Structure, and Properties of Block Copolymers*; Elsevier: London, 1985; p 165.
18. Mannari, V. M.; Massingill, J. L., Jr. *JCT Res* 2006, 3, 151.
19. Pechar, T. W.; Sohn, S.; Wilkes, G. L.; Gosh, S.; Frazier, C. E.; Fornof, A.; Long, T. E. *J Appl Polym Sci* 2006, 101, 1432.
20. Casper, D. M.; Newbold, T. U.S. Pat. 20060041156 (2006).
21. La Scala, J.; Wool, R. P. *Polymer* 2005, 46, 61.
22. Zlatanovic, A.; Petrovic, Z.; Dusek, K. *Biomacromolecules* 2002, 3, 1048.
23. Rosen, S. *Fundamental Principles of Polymeric Materials*; Wiley: New York, 1993.
24. Sperling, L. *Introduction to Physical Polymer Science*; Wiley: New York, 1992.