

# Effect of Different Isocyanates on the Properties of Soy-Based Polyurethanes

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**ABSTRACT:** New types of polyurethanes were prepared by reacting soybean oil-based polyol and different isocyanates. The polyurethanes can be used as foams, elastomers, coatings, adhesives, etc. Their properties strongly depend on crosslinking density and the structure of isocyanates. Aromatic triisocyanates impart the highest density, glass transition, modulus, and tensile strength, but have the lowest elongation at break, swelling in toluene, and impact resis-

tance. Aliphatic triisocyanates and diisocyanates give rubbery materials with the highest elongation at break, highest swelling, and the lowest tensile strength. Polyurethanes with aromatic and cycloaliphatic diisocyanates were similar in properties, with values between those of the two groups. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2912–2916, 2003

**Key words:** polyurethanes; renewable resources, structure

## INTRODUCTION

Polyols derived from vegetable oils are new raw materials from renewable resources.<sup>1–3</sup> Combined with isocyanates these polyols produce polyurethanes (PUs) that can compete in many aspects with PUs derived from petrochemical polyols. Thermal and oxidative stability of the soybean oil-based PUs are better than those of the polypropyleneoxide-based PUs.<sup>4</sup> Soybean oil is highly hydrophobic, so an excellent weather stability of the derived PUs can be expected. These PUs can be used in the production of polyurethane foams,<sup>5, 6</sup> elastomers, coatings,<sup>7, 8</sup> etc.

Soybean oil-based polyol used in this work is a tetrol of approximate structure shown in Figure 1. Hydroxyl groups are located on 9<sup>th</sup> or 10<sup>th</sup> and 12<sup>th</sup> or 13<sup>th</sup> carbon atom in a fatty acid. Thus, when crosslinking is completed, a portion of the chains (from 10<sup>th</sup> to 18<sup>th</sup> carbons, for example) is not included in the network and is left dangling, acting as a plasticizer.

Properties of polymer networks are determined by their chemical structure and crosslinking density. It has been found that the crosslinking density of networks from such polyols and methane diisocyanate (MDI) is not very high, rendering PUs with moderate glass transition temperatures ( $T_g \sim 50\text{--}70^\circ\text{C}$ ) and moduli.<sup>9</sup> Crosslinking density can be varied by varying the OH number of the polyol or varying the functionality of isocyanates. Because the properties of PU networks are also affected by chemical structure of isocyanates, we have elected to examine both the effect of functionality (difunctional versus trifunctional)

and chemical structure (aliphatic versus cycloaliphatic and aromatic) of isocyanates on PU properties. All PUs were prepared with a single, soybean oil-based polyol.

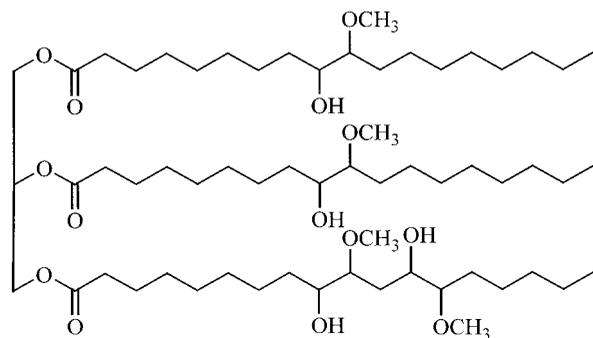
There is a broad range of isocyanates used in the production of PUs,<sup>10</sup> and they contribute to the PU properties in different ways. Aromatic isocyanates give more rigid PUs than do aliphatic ones, but their oxidative and ultraviolet (UV) stability are lower.<sup>11</sup> We used two aromatic diisocyanates [MDI and toluene diisocyanate (TDI)], two cycloaliphatic diisocyanates [hydrogenated MDI (HMDI) and isophorone diisocyanate (IPDI)], one aliphatic diisocyanate [hexamethylene diisocyanate (HDI)], and four commercial triisocyanates (two aromatic and two aliphatic). The chemical structures of the isocyanates are presented in Table I.

## EXPERIMENTAL

### Materials

Soy-206-polyol, with OH# = 206 mg KOH/g and functionality 3.9, was synthesized in our institute. Distilled MDI (MDI), TDI 80:20 isomer mixture (TDI), hydrogenated MDI (RMDI), isophorone diisocyanate (IPDI), and 1,6-hexamethylene diisocyanate (HDI) were used as supplied. Desmodur N-100 (N100) and Desmodur N-3300 (N3300) are biuret-based triisocyanates derived from 1,6-hexamethylene diisocyanate. Desmodur RF-E is *tris*(*p*-isocyanatophenyl)thiophosphate and Desmodur CB 75N is a TDI-trimethylol propane-based triisocyanate. All isocyanates were supplied by Bayer (Pittsburgh, PA). Triisocyanates were supplied as solutions but they were used in the dry state after solvent removal. Mercury catalyst Cocure 44 was supplied by CasChem (Bayonne, NJ).

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**Figure 1** Schematic representation of the soy-polyol structure.

## Methods

The samples were prepared by mixing a proper amount of polyol, isocyanate and catalyst and pouring in the mold. The mixture was cured at 110°C overnight. Den-

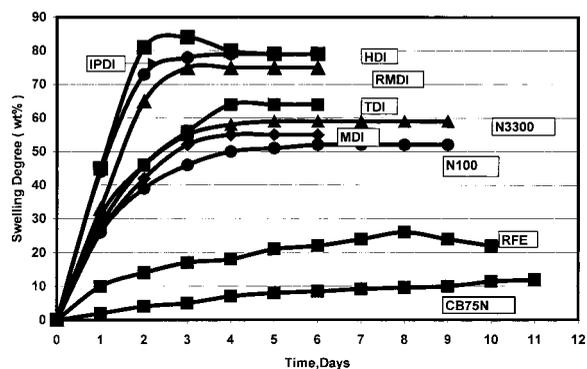
sity was measured by immersion in water according to ASTM 792. A thermal analyst system from TA Instruments, consisting of the Controller 3100 with DSC 2910 module and TMA 2940 module, was used to measure glass transition. Dynamic mechanical analysis (DMA) tests were carried out on DMA 2980 from TA Instruments (New Castle, DE). The heating rate with both DMA and thermomechanical analysis (TMA) was 5°C/min, and that with differential scanning calorimetry (DSC) was 10°C/min. Tensile properties were measured on an Instron model 4467 (Canton, MA) according to ASTM D882-97, and notched Izod impact strength was measured on a Resil Impactor from CEAST USA, Inc. (Fort Mill, SC) (model P/N 6957.000).

## RESULTS AND DISCUSSION

The structure of PUs is defined by two structural units: polyol and isocyanate.<sup>11, 12</sup> Our four functional

**TABLE I**  
Chemical Structures of Isocyanate

Isocyanate	Structure
4,4'-Diphenylmethane diisocyanate, MDI (Desmodur M)	
2,4:2,6-Toluene diisocyanate, TDI 80:20 isomer mixture (Desmodur TD 80)	
RMADI, hydrogenated MDI (Desmodur W)	
Isophorone diisocyanate, IPDI (Desmodur I)	
Hexamethylene diisocyanate, HDI (Desmodur H)	
Desmodur N-100 and Desmodur N-3300, triisocyanates derived from 1,6-hexamethylene diisocyanate	
Desmodur RF-E, a tris(p-isocyanato-phenyl)-thiophosphate	
Desmodur CB 75N, a trimethylol propane TDI-based prepolymer	



**Figure 2** Effect of the isocyanate structure on the degree of swelling of polyurethanes in toluene.

soy-polyol complexes have high enough structural irregularity to prevent crystallization of PUs and give single-phase, amorphous, thermosetting compounds with di- and triisocyanates. The chemical structure of the isocyanates affects the rigidity and crosslinking density of the PU network. The rigidity of the PU network is supposed to increase by varying the isocyanate structure in the following order: aliphatic < cycloaliphatic < aromatic.<sup>13</sup> The triisocyanates give higher crosslinking density of the PU networks in comparison with diisocyanates, which affects density,  $T_g$ , and mechanical and swelling properties of the prepared samples. Crosslinking density can be estimated from swelling in a solvent if the solvent-polymer interaction parameter is known.<sup>14</sup> Generally, higher swelling is obtained for networks with lower crosslinking density and those in better solvents for the polymer.<sup>15</sup> The results in Figure 2 show that the highest degree of swelling in toluene is obtained with aliphatic and cycloaliphatic diisocyanates, followed by aromatic diisocyanates, which were close to aliphatic triisocyanates. Two aromatic triisocyanates showed very low swelling, with Desmodur RFE swelling more than CB75N. Assuming approximately the same degree of crosslinking in aliphatic and aromatic triisocyanates, higher swelling in the former suggests that toluene is a better solvent for aliphatics than aromatics and about the same for aliphatics and cycloaliphatics.

The effect of different isocyanates on density is displayed in Table II. The PUs based on aromatic triisocyanates RFE and CB75N had the highest density. Heavy phosphorus in Desmodur RFE was responsible for the higher density of its polymers compared with the polymers with CB75N. Aromatic diisocyanates MDI and TDI and aliphatic triisocyanates N100 and N3300 gave PUs of lower density. The PUs of lowest density came from cycloaliphatic and aliphatic diisocyanates. Apparently, the aromatic structure of isocyanates had a stronger effect on density than crosslinking density.

Dynamic mechanical properties are displayed in Figures 3 and 4. Storage modulus versus temperature curves, shown in Figure 3, display a characteristic increase in modulus at the  $T_g$  before transitioning to the rubbery modulus in samples with aromatic and cycloaliphatic diisocyanates. This effect during heating was ascribed to the volume relaxation and shrinking at  $T_g$  before strong expansion. This effect was much weaker with aromatic triisocyanates and was not observed with aliphatic di- and triisocyanates. The magnitude of the glassy modulus did not follow a regular pattern but it was lower in HDI polyurethane.

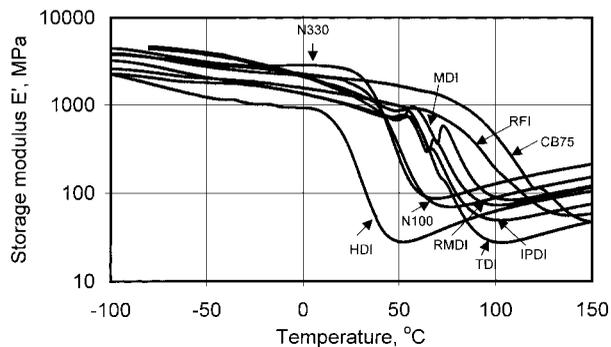
All samples displayed a strong increase in rubbery modulus with temperature. This phenomenon was examined both in the bending and stretching mode, and it was proved to be real. Rubber elasticity theory predicts increase of modulus with temperature:

$$E = 3\nu RT = 3\rho RT/M_c \quad (1)$$

where  $\nu$  is the concentration of elastically active chains,  $R$  is the gas constant,  $T$  is the absolute temperature,  $\rho$  is the density, and  $M_c$  is the number average molecular weight of network chains. The molecular basis for the increased modulus is the contraction of molecular coils due to increased entropy and thus increased retractive force. Thermoelasticity or increased retractive force with increasing temperature is observed in rubbers, but only in the extended state above the thermoelastic inversion point, which in natural rubber is at  $\sim 7\%$  elongation.<sup>16</sup> Below this extension, the thermal expansion contribution

**TABLE II**  
Density, Glass Transition Temperature (Measured by DSC, TMA, and DMA), and Degree of Swelling in Toluene

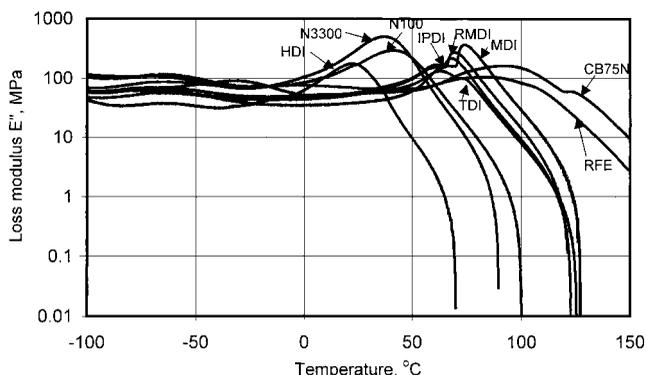
Isocyanate	Density (kg/m <sup>3</sup> )	$T_g$ by DSC, °C	$T_g$ by TMA, °C	$T_g$ by DMA, °C	Swelling degree, %
MDI	1104	59	55	74	55
TDI	1104	47	53	62	64
RMDI	1062	50	47	69	75
IPDI	1061	48	48	68	79
HDI	1066	10	15	22	79
N100	1082	26	25	41	52
N3300	1096	25	25	37	59
RFE	1272	NA	64	84	22
CB 75N	1186	93	85	92	12



**Figure 3** Storage modulus–temperature curves of soy-polyurethanes.

is larger than that of entropic contraction, whereas above this point, the latter becomes dominating factor. Because dynamic mechanical tests are performed in the linear elastic region, at extension of  $<1\%$  and where thermal expansion should dominate, it is reasonable to assume that the polyol chains were crosslinked in the extended state and that retractive force dominates even at such low extensions.

The rubbery modulus in these networks did not vary with frequency, suggesting that equilibrium was reached. Crosslinking density varied from sample to sample, but the order of magnitude was fairly correct. The  $M_c$  value for the network crosslinked with triisocyanate N3300 was 662, the value for the network based on N100 triisocyanate was 929, and the values for diisocyanates HDI and TDI were 1427 and 2229, respectively. All values were obtained from the modulus measured at  $\sim 100^\circ\text{C}$  except for the TDI-cured sample, which had a measurement temperature of  $149^\circ\text{C}$ . These temperatures were  $\sim 100^\circ\text{C}$  above their  $T_g$ s. As a reference,  $M_c$  for a network from the trifunctional soy polyol and HDI calculated from the structure should be 874. The difference between the measured and calculated  $M_c$  is caused partly by the inadequacy of the theory (it depends on the network model assumed — phantom or affined — and the chains may not be long enough to assume Gaussian



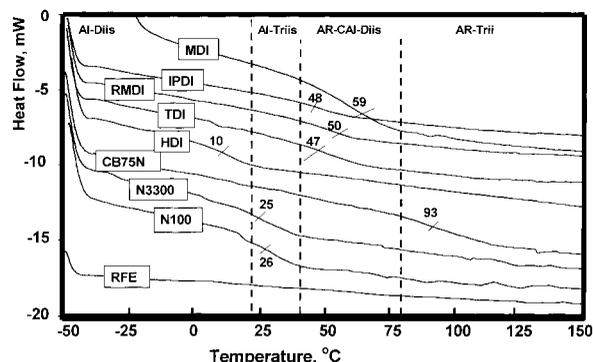
**Figure 4** Loss modulus–temperature curves of soy-polyurethanes.

distribution of end-to-end distances implied in the theory) and experimental difficulties, but they both reflect the correct order of magnitude.

Although the structure of isocyanates and experimental parameters such as the clamp force may affect somewhat the values of the modulus, two triisocyanate crosslinked networks displayed higher crosslinking density than the two networks with diisocyanates. Measurements of the moduli in aromatic and cycloaliphatic polyurethanes, high above  $T_g$ , was not possible because of thermal degradation, which starts at  $>150^\circ\text{C}$ . Loss modulus curves, shown in Figure 4, were characterized by two maxima: one in the temperature range  $20\text{--}100^\circ\text{C}$  that is related to the glass transition, and the other at  $-65^\circ\text{C}$  that is related to the beta transition. Temperatures of the maxima (glass transitions) followed the order: CB75N  $>$  RFE  $>$  MDI  $>$  RMDI  $>$  IPDI  $>$  TDI  $>$  N100  $>$  N3300  $>$  HDI. As expected, the highest  $T_g$  was obtained with the two aromatic triisocyanates, followed by aromatic and cycloaliphatic diisocyanates having two rings, then cycloaliphatic and aromatic diisocyanates with a single ring structure. Aliphatic triisocyanates gave very soft leathery polymers and HDI gave rubber.

Beta transition PUs occurred between  $-80$  and  $-40^\circ\text{C}$ , with a maximum at about  $-65^\circ\text{C}$  in all polymers except in the RMDI-cured PUs, where the maximum was shifted to  $-30^\circ\text{C}$ . This transition is obviously related to the molecular motions in the polyol main chains because it was observed even in PUs where dangling chains were cut by metathesis.<sup>17</sup> In contrast, in the RMDI PUs, this transition may be related to the conformational changes in the cyclohexyl groups of the diisocyanate.

The values of  $T_g$  determined by DSC, TMA, and DMA showed the same trend, as demonstrated in Table II. DSC curves of all samples are given in Figure 5. Values of  $T_g$  determined by DSC and TMA values are somewhat lower than those obtained by DMA due to the frequency effect. The  $T_g$  values determined by DSC and TMA for PUs with aromatic triisocyanate CB75N were 93 and  $85^\circ\text{C}$ , respectively, and  $\sim 64$  for the



**Figure 5** DSC curves of polyurethanes with different isocyanates.

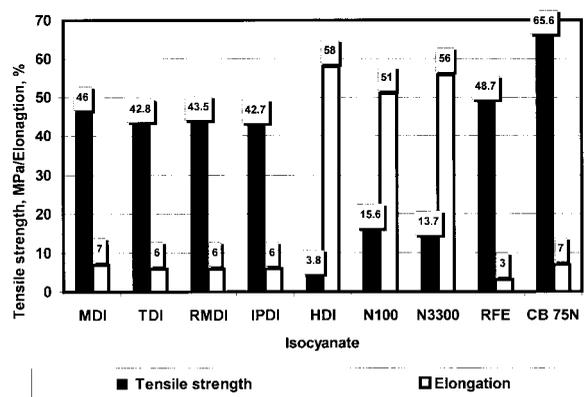
**TABLE III**  
Flexural Modulus and Izod Impact Strength of Polyurethanes

Isocyanate	Flexural modulus, MPa	Izod impact strength, J/m
MDI	1380	28
TDI	1180	33
RMDI	1190	39
IPDI	1220	37
HDI	0	0
N100	29	59
N3300	23	57
RFE	2480	13
CB 75N	2040	12

PU with RFE. Aromatic and cycloaliphatic diisocyanates gave  $T_g$  values between 48 and 59°C. Aliphatic triisocyanate-based PUs had a  $T_g$  at 25°C, whereas HDI gave a polymer with  $T_g$  at 10 or 15°C.

Mechanical properties of the samples (Fig. 6) are influenced by crosslinking density and rigidity of the PU network as well. Glassy polymers displayed brittle fracture characterized by elongation at break below 10%, whereas that of rubbery PUs cured with aliphatic diisocyanate and triisocyanates showed elongations at break of 52–58%. The samples based on aromatic triisocyanates showed the highest tensile strength of 65 MPa (CB75N) and 48 MPa (RFE). Aromatic and cycloaliphatic diisocyanates impart tensile strength of the same magnitude of ~45 MPa. Two aliphatic triisocyanate-cured PUs have tensile strength of ~15 MPa, and HDI-based PU breaks at ~4 MPa. Low strength and high elongations of all aliphatic PUs are characteristic of rubbers.

As already mentioned, these polymers have moderate or low moduli due to their moderate crosslinking density. The data in Table III show that triisocyanate-cured PUs have flexural moduli between 2000 and 2500 MPa, which is typical for thermoplastic and thermosetting resins. These values are somewhat lower than those of polystyrene and polymethylmethacrylate, higher than



**Figure 6** Tensile strengths and elongations at break of soy-polyurethanes.

that of polypropylene, and equal to those of epoxy resins. Aromatic and cycloaliphatic diisocyanate-cured polyurethanes have flexural moduli of ~1200 MPa (corresponding to rigidity of high density polyethylene), whereas aliphatic isocyanates are rubbers, and flexural modulus cannot be measured. Modulus values are dependent of  $T_g$  and of the difference between  $T_g$  and measuring temperature (room temperature in our case).

Impact strength appeared to be inversely proportional to the modulus. The lowest values (Notched Izod was 12 J/m) were displayed by CB75N- and RFE-cured PUs, followed by PUs with aromatic (28 and 33 J/m) and cycloaliphatic diisocyanates (37 and 39 J/m). Rubbers are not usually tested for impact.

## CONCLUSIONS

The properties of the soy-based PUs strongly depend on crosslinking density and the structure of isocyanates. Aromatic triisocyanates impart the highest density, glass transition, and modulus and tensile strength, but the lowest elongation at break, swelling in toluene, and impact resistance. Aliphatic triisocyanates and diisocyanates give rubbery materials with the highest elongation at break, highest swelling, and the lowest tensile strength. PUs with aromatic and cycloaliphatic diisocyanates showed values similar between those of the two previous groups.

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