

# Characterization of Polyurethane Foams from Soybean Oil

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**ABSTRACT:** Modified soy-based vegetable oil polyols were successfully incorporated as a replacement for conventional polyols to produce flexible slabstock polyurethane foams. The oil was characterized for its hydroxyl value and fatty acid composition. The modified oils had higher hydroxyl values and lower unsaturated acids than regular unmodified oils. Three different modified polyols were used to investigate the reactivity with isocyanates. The effects on the foaming reaction of two different isocyanates, namely TDI and MDI, were investigated. The reactions were also carried out with a mixture of polyols containing synthetic polyols and vegetable oil-based polyols to delineate the effect of each component. FTIR technique was used to identify the sequence of chemical reactions during the foaming process. The effect of water levels and isocyanate content on the kinetics of the foaming reaction was investigated. Infor-

mation regarding the formation of hard and soft segments with the varying compositions was obtained. As the water content increased, the amount of the hard segment and urea formation increased in both soy oil polyols and synthetic polyols. Increased synthetic polyols in the mixture increased the rate of reaction and phase mixing due to the availability of primary hydroxyl groups. Scanning electron microscopy (SEM) and small-angle X-ray scattering (SAXS) were used to probe the morphology. As the water content increased, the cell size increased. At lower water content a more uniform cell structure was evident and at higher water levels hard domain size increased. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3097–3107, 2002

**Key words:** soybean oil; polyurethanes; FTIR; NMR; gel permeation chromatography (GPC)

## INTRODUCTION

Soybean oil is an inexpensive, readily available renewable resource. The oil, comprised of triglycerides of fatty acids, provides an excellent platform for valuable polymeric materials like polyepoxides, polyurethanes, and similar compounds. Soybean oil triglycerides contain both saturated and unsaturated fatty acids. The unsaturated fatty acid composition exceeds 80%, depending on the variety and climatic conditions of harvest.<sup>1</sup> The unsaturated sites in oil can be utilized to introduce functional groups. Petrovic and coworkers<sup>2</sup> reported that functional groups can be introduced at the positions of double bonds. Thus, the number of functional groups will vary with the type of vegetable oil as well as the degree of conversion.

In recent decades, there has been an increased demand for urethane materials.<sup>3</sup> There are several references<sup>4,5</sup> that indicates vegetable oils can be used as integral parts of urethane materials. The properties of a castor oil–diisocyanate coatings were found to improve when treated with low molecular polyols by alcoholysis.<sup>6</sup> Our interest in polyurethanes stems from the fact that soy oil can be modified to react with isocyanate to produce urethane products that will add

value to the soy oil and decrease the cost of the system. A second important aspect is the fact that soybean oil is a renewable resource. Because most of our oil is imported from politically unstable regions, this has the potential to increase our national security.

The objective of this research is to conduct a systematic study comparing the reaction kinetics to the morphology of urethane foams made from vegetable oils. In the present study, functionalized soybean oil was used to prepare polyurethane foam. The oil was characterized using FTIR, NMR, and gas chromatography (GC). Hydroxyl value, acid value, and iodine value were determined using AOCS methods. The reaction was monitored using FTIR. The polyols were also mixed with synthetic polyols water mixtures to examine the rate of foaming reaction. The isocyanate index and water content in the foam formulation was varied to examine the properties of the foam. The morphology of the foams was examined with the help of a scanning electron microscope. Small-angle X-ray scattering was used to investigate the hard domain structure.

## EXPERIMENTAL

### Materials

Three different soy polyol samples were obtained from Urethane Soy Systems Inc. (Illinois) and labeled as P38.05, P38-GC5, and P3805. Crude soybean oil

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samples supplied by Volga Oil Processing Company, Volga, SD, and commercial edible soybean oil obtained from a grocery store were also analyzed for comparative purposes. These oils were subjected to various spectroscopic and chemical analyses to evaluate the structural and physical characteristics.

Toluene Diisocyanate, an 80 : 20 mixture of 2,4- and 2,6-isomers of toluene diisocyanate (TDI) and spectroscopic grade solvent was obtained from Aldrich Chemicals, Milwaukee, WI. ISONATE 143L, a modified MDI, is a polycarbodiimide-modified diphenylmethane diisocyanate that is liquid at room temperature, was supplied by Dow Chemicals, Midlands, MI. Dabco T-9 (Stannous Octoate catalyst) and Dabco 33-LV (Amine catalyst, 33% triethylenediamine in 67% dipropylene glycol) catalysts were supplied by Air Products, PA. HPLC grade standards were obtained from Sigma Aldrich, St. Louis, MO. Deionized water was obtained using the Millipore water purification system.

### Hydroxyl value

The hydroxyl value is defined as the number of milligrams potassium hydroxide equivalent to the hydroxyl content of 1 g of sample. The AOCS official method Cd 13-60 was used to determine the hydroxyl value of the oil samples. Acid value and iodine value were determined according to AOCS procedures Cd 3d-63 and Cd 1c-85, respectively.

### Fatty acid composition

The fatty acid components were separated and identified with the help of gas chromatography. To determine the fatty acid concentration, fatty acids are converted to corresponding methyl esters according to AOCS method Ce 2-66. The oil sample was taken in a 125-mL flask. A specific amount of  $\text{BF}_3$ -methanol mixture was added, and a reflux condenser was attached and the mixture was boiled for 2 min. Five milliliters of heptane was added through the condenser, and the mixture was boiled for an additional minute. After removing from heat, 15 mL of saturated sodium chloride solution was added. The mixture was shaken vigorously for 15 s. The ester layer was separated from the flask into a small test tube, and a small amount of anhydrous sodium sulfate was added. This dry mixture was then directly injected into the gas chromatograph (Hewlett Packard 5890). A DBWAX column (L = 30 m, d = 0.32 cm, size = 0.5  $\mu\text{m}$ ) obtained from J&W Scientific Inc (Folsom, CA) was used with a temperature ramp of 60 to 230°C at the rate of 8°C/min. The detector temperature was 230°C, and the carrier gas used was helium. A standard was run before the sample was injected, and the percent-

age composition was directly obtained from the chromatogram.

### FTIR measurements

The FTIR measurements of the oil samples were conducted using a Nicolet 7000 series spectrometer. The samples were dissolved in chloroform and casted on a sodium chloride crystal to obtain a thin film, and the spectra of the films were taken.

### NMR spectra

The NMR spectra of the oil and polyol samples were obtained at 300 MHz using a Varian VXR300 instrument with a 12.2- $\mu\text{s}$  (90 degree) pulse and an acquisition time of 2.0 s. The samples were dissolved in deuterated chloroform, and  $^1\text{H}$ -NMR spectra were obtained at room temperature.

### Foam formulation

The basic foam formulation contains a polyol, surfactant, water, catalyst, and isocyanate. Hence, there are several variables that can play a significant role in the final foam quality. The components were mixed in a Styrofoam cup, and the volume and temperature rise monitored. To account for traces of water, an excess isocyanate index (1.10) was used to obtain good quality foam.

### Infrared measurements during foaming reaction

The foaming reactions were also monitored using the same spectrometer with the help of the experimental setup described in detail by Artavia.<sup>7</sup> The reaction mixture (soy polyol, water, catalysts, and surfactant) were mixed together and required amount of TDI was added. The mixture was again mixed well and immediately transferred in to the reaction cell (45–50 s). The cell was equipped with a 45° KRS-5 single-pass parallelogram prism with a dimension of 50 × 5 × 2 mm. The technique used was attenuated total reflectance infrared spectroscopy (ATR). As the ATR crystal touches the reactive form, it can act like a cold sink altering the reaction exotherm. Hence, the cell and the crystal were heated at the same rate as the reaction progressed with the help of previously saved reaction data. This was achieved with a temperature controller and a heating element attached to the cell. The changes taking place during the foaming reaction were monitored with a Nicolet FTIR instrument using a MCT detector. Infrared spectra were collected at 4  $\text{cm}^{-1}$  resolutions and the scanning time was 15 s per file. A background spectrum was also collected before heating the probe. The FTIR data was collected for 20 min from the start of the reaction, and it was found

**TABLE I**  
Average Fatty Acid Composition of Soybean Oil from Literature Data

Component acid	Average composition %
Saturated	
Lauric	0.1
Myristic	0.2
Palmitic	10.7
Stearic	3.9
Arachidic	0.2
Behenic	<0.5
Total	~15.0
Unsaturated	
Palmitoleic	0.3
Oleic	22.8
Linoleic	50.8
Linolenic	6.8
Eicosenic	<1.0
Total	~80.7

that the visible spectral changes ceases after 10 min from the start.

#### Gel permeation chromatography (GPC)

A Waters 150 LC/GPC was used with a refractive index detector to measure the molecular mass. A Phenogel (Phenomenex, Torrance, CA) column (300 × 7.8 mm) with 500- $\mu$ m particles was used for separation. HPLC grade tetrahydrofuran (THF) was used as the mobile phase. The experiment was carried out at room temperature with a solvent flow rate of 1 mL/min with 35 bars pressure. The refractive index versus the elution volume was obtained for each sample and correlated to the elution volume vs. molecular weight for the polystyrene standard.

#### Mass spectroscopy

Matrix-Assisted Laser Desorption/Ionization (MALDI-TOF) mass spectroscopy was used to determine the absolute molecular weight of selected oil samples. A Bruker reflex IV machine was used for this purpose.

#### Small angle X-ray scattering

The data was collected on the 2D small-angle X-ray lines with copper radiation. Two sample-to-detector distances were run: 112 and 232 cm. The detector used is a Bruker GADDS. Data was collected at room temperature for 10 min per sample.

#### Morphology

The morphology of the foam samples was examined with the help of a Hitachi S-800 scanning electron microscope. A small portion of the foam was cut from the appropriate foam block and frozen in liquid nitrogen. A thin piece of foam was then carefully sliced with a sharp blade and stuck to aluminum stubs. The samples were then sputter-coated with a total of 15 nm of Au/Pd and observed under the microscope employing an accelerating voltage of 10 kV and a probe current of  $6 \times 10^{-11}$  amps.

## RESULTS AND DISCUSSION

#### Composition

Soybean oil is less expensive than corn, safflower, and sunflower oils, yet it has many of the desirable characteristics of premium vegetable oils. It also has a higher level of unsaturation compared to some other vegetable oils. Crude soybean oil contains approximately 95–97% triglycerides.<sup>8</sup> The fatty acid composi-

**TABLE II**  
Fatty Acid Profile for the Soybean Oil and Polyol Samples Obtained from GC

Component acid	Store soy oil	P38.05	P38-GC5	P3805
Saturated				
Lauric	0.103	0.098	0.11	0.042
Myristic (14 : 0)	13.12	0.165	0.087	0.086
Palmitic (16 : 0)	5.07	21.29	20.81	19.56
Stearic (18 : 0)	0.256	5.92	6.26	5.79
Arachidic (20 : 0)	0.147	0.312	0.183	0.31
Behenic (22 : 0)	0.101	0.435	0.184	0.125
Total	18.69	27.78	27.45	25.78
Unsaturated				
Palmitoleic (16 : 1)	0.118	0.131	0.114	0.113
Oleic (18 : 1)	22.51	26.19	30.41	29.63
Linoleic (18 : 2)	48.90	32.36	37.24	39.71
Linolenic (18 : 3)	5.49	2.53	2.49	3.15
Eicosenic (20 : 1)	0.225	0.505	0.174	0.151
Total	77.24	61.72	70.42	72.75

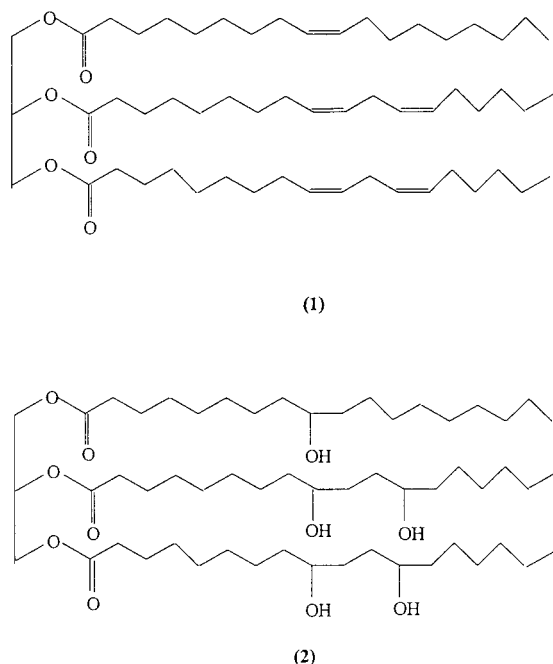


Figure 1 Structure of (1) soy oil, and (2) soy polyol.

tion of soybean oil is shown in Table I. As evident from the table, the soybean oil triglycerides contain both saturated and unsaturated fatty acids. It was found that the soybean oil did not generate any foam when used in the unmodified form. Attempts were made to modify the soybean oil by introducing hydroxyl groups so that it could be used in polyurethane formulations. Guo and coworkers<sup>9</sup> reported the preparation of soy polyols via the oxirane ring-opening reaction of epoxidized soybean oil with methanol. The fatty acid composition of modified and unmodified soybean oils obtained from GC analysis are given in Table II. A schematic representation of soy oil molecule is given in Figure 1. The unsaturated fatty acids are viable to oxidation and hydroxyl groups can be added to the oil chain after oxidation. Figure 1(b) shows an idealized soy polyol obtained after oxidation. It is not necessary that all the double bonds will be converted to hydroxyl groups during air oxidation process and needs further investigation to assert the chemical changes.

Changes in fatty acid composition can be observed while examining the three different polyols and the soybean oil. There is a decrease in percentage composition of unsaturated fatty acids. This is particularly true in the case of linolenic (18 : 3) and linoleic (18 : 2) acid, which is reduced by a third and a quarter, respectively, for all the three modified polyols when compared to unmodified soybean oil. From Table II, it is clear that linoleic acid, which is the largest of the unsaturated acids, is the most susceptible to functionalization compared to other unsaturated fatty acids.<sup>10,11</sup> Neff et al.<sup>11</sup> observed trilinoleoylglycerol and dilinoleoyl-oleoylglycerol were the major product precursors during photooxidation of soybean oil. Similar observation was also reported during the oxidative stability studies of polyunsaturated fatty acids of soybean oil in presence of emulsifiers and found that linoleic acid was more unstable.<sup>11</sup> This could be due to the oxidation of linoleic to oleic acid.<sup>12</sup> Fatty acid profile indicates that the saturated acid composition, especially palmitic acid (16 : 0) and stearic acid (18 : 0) content increased.<sup>12</sup> The increase in saturated fatty acid content could also be due to the conversion of unsaturated to saturated during a oxidation process. It was also reported that linolenate polymerizes very rapidly into a complex mixture of oxygen-containing compounds. These materials include dimers, trimers, and higher polymers responsible for a higher molecular weight fraction.<sup>1</sup>

The viscosities of the polyols were much higher (~2800 cps at 72°F) than the regular soybean oil (~50.5 cps at 77°F). The hydroxyl numbers of the soy polyols were also higher (Table III), indicating the introduction of OH functionality to the molecule. Guo and coworkers<sup>13</sup> also reported an increase in viscosity, even with a single OH group per double bond. Linoleic acid, comprise about 50% of the total fatty acids, has two double bonds and oleic acid (~25% by weight) has one double bond. The fatty acid content of the polyols indicates that as the linoleic acid content decreases, the oleic acid and stearic acid content increases. Table III shows the acid values for the polyol samples, which is a measure of the free acids per gram of the sample. Hence, in samples that contain virtually no free acids other than fatty acids, the acid value may

TABLE III  
Acid Value and Iodine Value and Hydroxyl Value of Oil Samples

Sample	Acid value mgKOH/g	Iodine value cent. g of iodine/g	Hydroxyl value mgKOH equiva/g	Functionality	Molecular weight (Mn)	Polydispersity (Mw/Mn)
Crude Soy	1.28	133.39	35.4	1.0	1587	1.01
Store Soy	0.45	124.17	32.5	1.0	1583	1.01
P38.05	7.04	89.90	53.2	2.85	3008	4.81
P38-GC5,	4.84	101.96	91.8	5.08	3110	5.35
P3805	6.76	107.48	92.5	5.20	3161	8.33

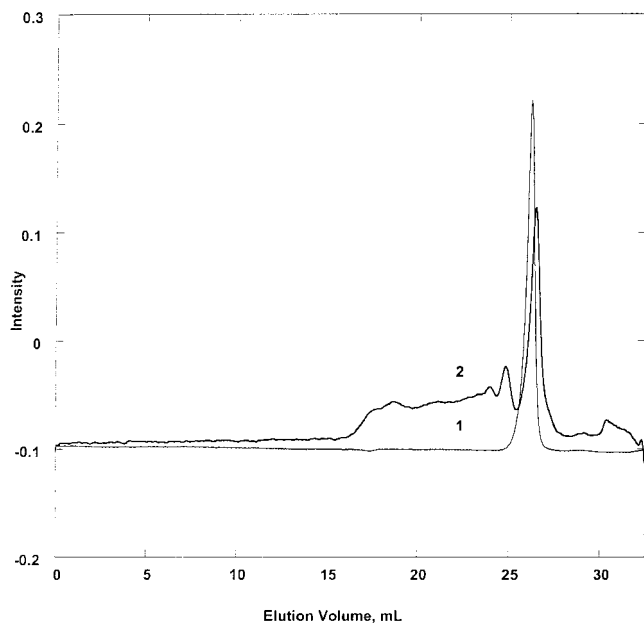


Figure 2 GPC chromatogram of (1) soy oil and (2) soy polyol.

be directly converted to percent free fatty acids. It was noticed that the acid values were higher for polyols when compared to the soybean oil samples. The iodine value represents the magnitude of unsaturation in the molecule. While examining the iodine values for the polyols and the oil, it is evident that the unsaturation decreases after the functionalization process.

### Molecular weight

The molecular weight determinations of the polyol samples are recorded in Table III. A typical chromatogram obtained from GPC is shown in Figure 2. The molecular weight data reported were calculated using polystyrene as the standard. The GPC chromatogram showed lower retention volumes when compared to crude soybean oil, the starting material. The peaks were also broader for polyols with left shoulders increasing the molecular weight. There appears to be an aberration in molecular weight when using the polystyrene as standard. As triglycerides are star shaped, as opposed to linear polymers, a correction is needed to obtain the actual molecular weight. Thus, standards of several triglycerides with known molecular weights were analyzed using GPC. It was found that samples with lower molecular weights did not show any aberration, while higher molecular weight standards showed higher values than the actual molecular weight. The values obtained for standards and the actual molecular weights are given in Table IV. Thus, it appears to be necessary to apply a correction to the values obtained from GPC for reporting the actual

TABLE IV  
Molecular Weight Obtained of Standards from GPC

Standard	Molecular weight	Obtained from GPC	Aberration in mol wt
Palmitic acid	256.4	263	6.6
Oleic acid	282.5	267	15.4
Linoleic acid	280.4	295	14.6
Linolenic acid	278.4	248	30.4
Tristearin	891.5	1560	668.5
Tripalmitin	807.3	1386	578.7
Triolein	885.4	1499	613.6
Trilinolein	879.4	1335	455.6
Trilinolenin	873.4	1397	523.6

molecular weight. However, no correction was applied to the reported molecular weight in Table III.

The molecular weight obtained using a GPC was compared with the molecular weight using mass spectroscopic analysis. The value obtained for crude soy oil was 878.07, and that for P38.05 was 2722.44. These values are in agreement with values obtained from GPC, once the correction was applied. Thus, it appears to be necessary to apply a correction to the values obtained from GPC for reporting the actual molecular weight.

### FTIR and NMR spectra

The FTIR spectra of the oil samples and the polyols are shown in Figure 3. The polyols showed hydroxy peak at around  $3342\text{ cm}^{-1}$ . The increase in the intensity of hydroxyl peak also indicates an increase in hydroxyl number for the polyols. The figure shows the FTIR of

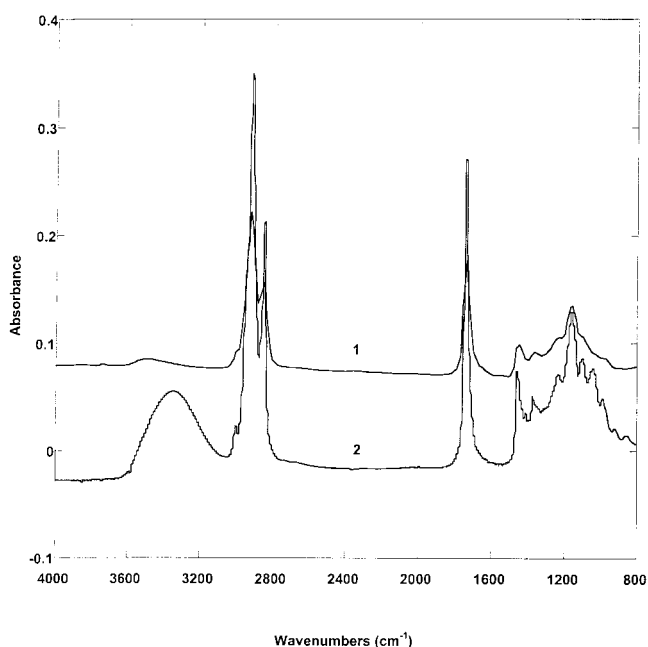


Figure 3 FTIR spectra: (1) spectra of soybean oil, (2) spectra of soy polyol P3805.

TABLE V  
Typical Soy Polyol Foam Formulation

Soy polyol	100
Water	2-6
Surfactant	1.0
Dabco T-9 catalyst	0.1-0.2
Dabco 33-LV catalyst	0.3
TDI/MDI index	0.9-1.1

P38-GC5, as the spectra were similar for other polyols. The FTIR of polyols also showed a peak near  $1098\text{ cm}^{-1}$ , which is characteristic to the presence of secondary hydroxyl group.

NMR spectra of the polyols and the oil samples reveal information regarding different functional groups. The proton NMR spectra of polyols showed characteristic peaks and are compiled as follows:  $\delta$  0.92 ppm—(triplet,  $-\text{CH}_3$ );  $\delta$  1.29 ppm—(broad singlet,  $-\text{CH}_2$ );  $\delta$  2.06 ppm—(broad singlet,  $-\text{CH}_2-\text{C}=\text{C}$ );  $\delta$  2.33–2.38 ppm—(triplet,  $\text{CH}_2-\text{C}=\text{O}$ );  $\delta$  2.8 ppm—(triplet,  $=\text{CH}-\text{CH}_2-\text{OH}$ );  $\delta$  3.8 ppm—(mid chain  $\text{CH}-\text{OH}$ );  $\delta$  4.149–4.282—(triacylglycerols or glyceryl carbons);  $\delta$  5.344—(olefinic, *trans* carbon originating from ricinoleic acid).

The peak at 3.8 ppm was not visible for soybean oil. It is evident from the NMR data that the functionalization process of soybean oil hydroxylated the fatty acid glycerides. These hydroxylated chains were exploited to react with the isocyanate to produce polyurethane linkages during foaming reactions.

## Foams

The basic ingredients of a flexible foam formulation include: polyol, diisocyanate, catalysts, and a surfactant. The catalysts used were organotin compounds [typically tin(II) caprylate or octoate] with tertiary amines. The relative catalytic activity and the surfactant of these components affects the foaming process and resultant cellular structure of the foams. Increasing the amount of organotin catalysts in the foam formulation shortens the gelation time and increases the rigidity and the number of closed cells in the foaming reaction. Several experiments were conducted to determine the required amount of these catalysts, and the typical foam formulation is given in Table V. The amount and type of catalyst was not optimized for this article.

The foam formation reaction involves a complex combination of chemical reactions and physical changes. These changes can be monitored by evaluation of the chemical reactions as well as the simultaneous examination of morphologic changes. During the foaming process, the chemical reaction was monitored using infrared spectroscopy (FTIR). Such techniques have been successfully used without disturb-

ing the reaction medium.<sup>7,13,14</sup> The primary purpose was to correlate the conversion of isocyanate groups using their decreasing infrared absorbance and to measure the foam exotherm as a function of time. The formation of hydrogen bonding and other chemical interactions were examined with the help of this technique.

Foams obtained using MDI were rigid and the reaction was slower when compared to that of TDI. The 80:20 mixture of 2,4-TDI and 2,6-TDI gave a faster foam rise and was easier to elevate the reaction exotherm. Reactions with TDI were carried out to determine the reactivity of the three different polyols.

Several experiments were conducted by changing the amount of water in the reaction and keeping a constant isocyanate index (1.1). Figure 4 shows a typical FTIR plot for the foaming reaction. Water content of the reaction mixture was varied from 2, 3, 4, 5, and 6%. As the water content was increased while keeping the isocyanate index constant, it was observed that the amount of carbon dioxide released also increased. As a result, both the weight percent of hard segment and the ratio of polyurea to polyurethane in the foam increased. It was also evident that the foam became less dense as more gas was released. However, above 6% water the reaction was extremely fast and the foam properties declined. The changes in the spectra taking place during the reaction showed a similar trend except the reaction rate increased as the water content increased.

Figures 5 shows the spectral data for the trend of hard and soft segment formation reaction during the reaction of soy polyol. The peaks at  $1715$ ,  $1663$ , and  $1640\text{ cm}^{-1}$  were monitored. The trends for all the three polyols used were similar. As the water content in the reaction mixture increased, the reaction was faster; the changes can be observed in the figure. Initially, soluble urea ( $1715\text{ cm}^{-1}$ ) was formed. As the reaction proceeds, increased urea is formed and starts to organize into loose hydrogen bonded structures<sup>15</sup> and segregate into hard segment domains ( $1640\text{ cm}^{-1}$ ). The urea intermediate was monitored at  $1663\text{ cm}^{-1}$ . These observations are clearly visible when the relative absorbance intensities of the individual peaks were plotted against time. The figure illustrates the onset of urea formation and the development of hard segments as a function of time.

The FTIR also showed the disappearance of the isocyanate peak, and the appearance of the hydrogen-bonding peak grew with time (Fig. 6). The isocyanate disappearance was plotted against time for foaming reactions, and the trend was similar in all the various reactions studied. The rate of depletion of isocyanate decreased with time and reached a constant trend after 600 s from the start of the reaction.

Experiments were conducted to study the reactivity of the soy polyols with the isocyanate by introducing

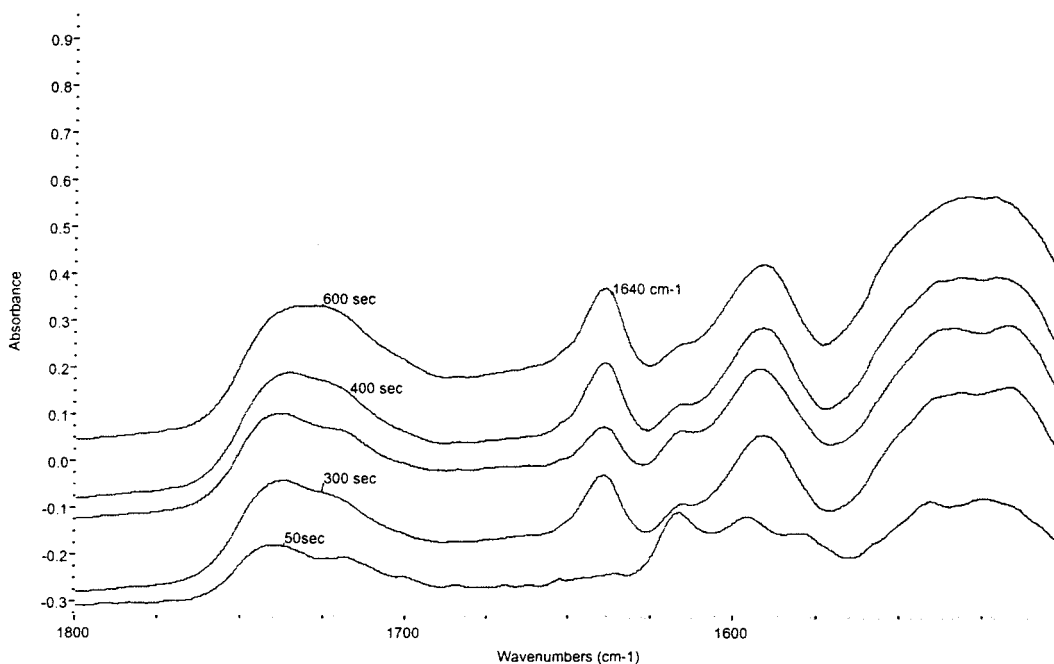


Figure 4 FTIR spectral data during the foaming reaction with 1.1 TDI index and 5% water with P3805.

more primary hydroxyl groups. Two approaches were considered. In the first approach, the polyol was mixed with varying amounts of synthetic polyol, namely Voranol, a 3000 molecular weight polyol with primary hydroxyl groups (hydroxyl #  $\sim$ 58.0). Generally, the primary hydroxyl groups are more reactive than the secondary hydroxyl groups in soy polyol. Thus, 20, 50, and 80% Voranol was mixed with the polyol and the foaming reactions examined. It was observed that as the amount of synthetic polyol in the reaction mixture increased, the reaction rate also increased due to the primary hydroxyl. Figure 7 shows the trend for 80% soy polyol and 20% voranol mixture. The figure also reveals a higher intensity for urea hard segments when 20% voranol was added to the mix-

ture. This indicates the instant availability of primary hydroxyl groups when compared to the soy polyols.

The plot of isocyanate disappearance against time revealed that the mixture with a higher voranol content reacted faster with the isocyanate. This is also clearly visible from the plot of urea hard segment formation. In the case of the 20/80 soy polyol/voranol mixture, the onset of urea hard segment formation showed a steep increase and reached the maximum then reached a stable value at around 600 s. For the 50/50 and 80/20 soy polyol/voranol mixture, the onset of urea hard segment formation did not show a sharp increase at the start of the reaction. However, this reaction increased at approximately 170 s after the start of the reaction for 50/50 mixture. In the case of 80/20 mixture, the increase started around 300 s after the start of the reaction. These observations indicate that the kinetics of the foaming reaction can be controlled by changing the polyol content in the reaction mixture.

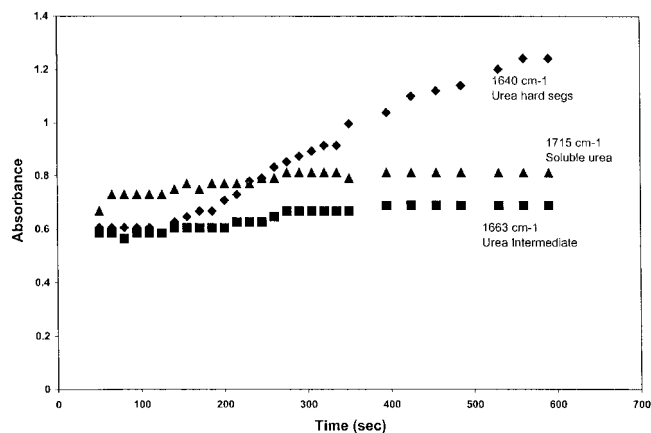
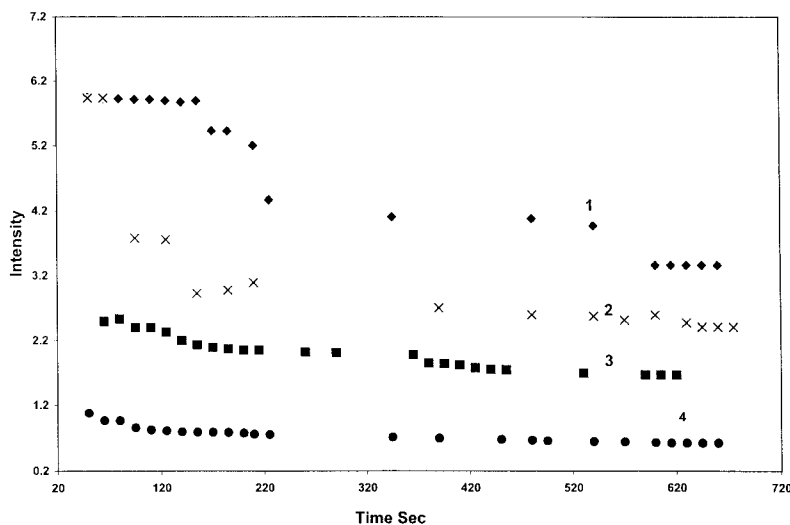


Figure 5 Trend of urea segment formation for soy polyol at 5% water and 1.1 TDI index using P3805.

In the second approach, starch was added to increase the functionality of the polyol. Each molecule of starch has one primary and three secondary hydroxyl groups. As starch was insoluble in soy oil, it was dissolved in ethylene glycol before adding to the foam formulation. Thus, the pregel starch was dissolved (10 phr) in ethylene glycol. Twenty-five parts of the starch/ethylene glycol mixture and 75 parts water was added. The hydroxyl number for this starch/ethylene glycol/water mixture was determined and found to be 139.7 mgKOH equivalent/g. Five percent of this mixture was added to the soy polyol and the foaming

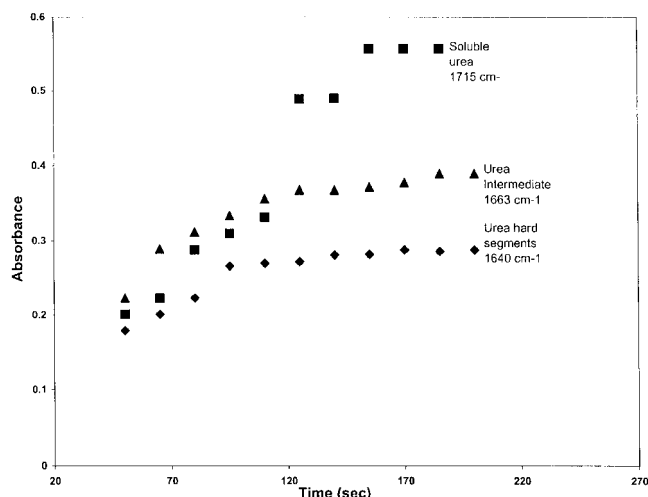


**Figure 6** Isocyanate disappearance during the foaming reaction at 5% water and 1.1 TDI index for (1) starch:polyol mixture, (2) 80 : 20 soy : voranol mixtures, (3) 50 : 50 soy voranol mixtures, and (4) 20 : 80 soy voranol mixtures.

reaction was examined. The results are shown in Figure 8. The reaction started gradually and increased momentum after 300 s. It was also noticed that the relative intensity onset of urea hard segment formation showed a significant increase at around 350 s from the start of the reaction. This could be attributed to the increased number of hydroxyl groups available for reaction. The reaction showed increased hard segment formation and a more rigid foam was obtained as opposed to soy polyol samples.

### X-ray scattering

Small-angle X-ray scattering (SAXS) was carried out for samples with different water levels for foam formulation with a TDI index of 1.1. Figure 9 shows that



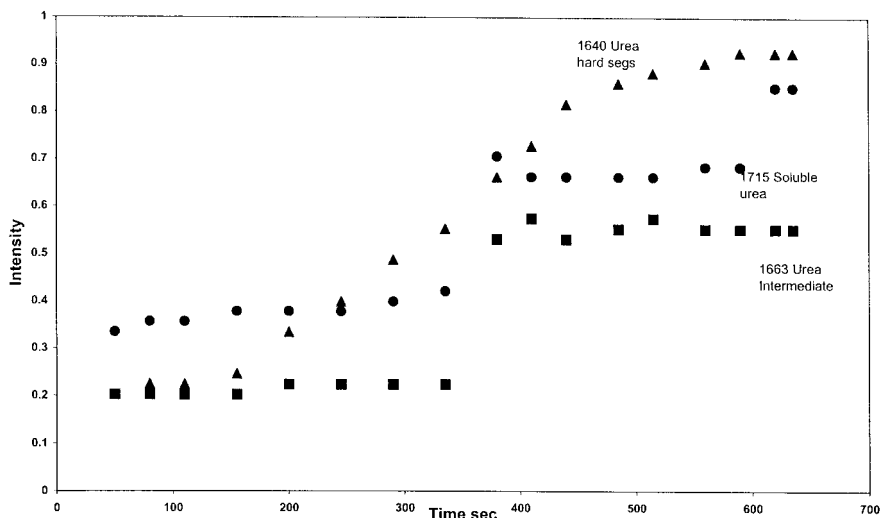
**Figure 7** Trend of urea segment formation for 80/20 mixture of soy polyol and voranol at 5% water at 1.1 TDI index using P3805.

as the water content increased the crystal structure or the scattered intensity diminished. This shows that the primary OH increases phase mixing. This was also in agreement when the foam samples were examined with the help of SEM. The two-dimensional images were integrated and converted to  $q$  vs. intensity plot as shown in Figure 9. For foams obtained using MDI with 4% water, the intensity showed a maximum when compared to foams obtained using TDI. This type of SAXS curve attributes to a two-phase system comprising of a soft one and a hard segment. Spirkova et.al. also describes a two-phase system while examining SAXS curve. This indicates the increased rigidity of the foam when MDI was used and is due to the structure of MDI. The  $q$ -value obtained for MDI samples was  $0.34 \text{ nm}^{-1}$ . The SAXS data for 80/20 and 50/50 soypolol/voranol and starch/ethylene glycol/water/polyol were identical for all three foam samples and similar to the pure soypolyol data. As the voranol content increased the scattering showed a slight increase in intensity but did not show any peak as obtained in the case of case of foam samples with MDI.

### Scanning electron microscopy

Morphology of the foam reveals important information such as cell shape and domain size. Fractured surfaces of the foam were examined under magnification and are shown in Figures 10–14. As the water content increased from 4 to 6%, it is clear that the cell size also increased and the foam became less dense. It is also evident from the micrograph that the cell structure became more uniform and similar with lower water content. The texture of the foam was uniform in the case of MDI foam (Fig. 10). In the case of foams with both MDI and TDI (Fig. 11), open cells and closed



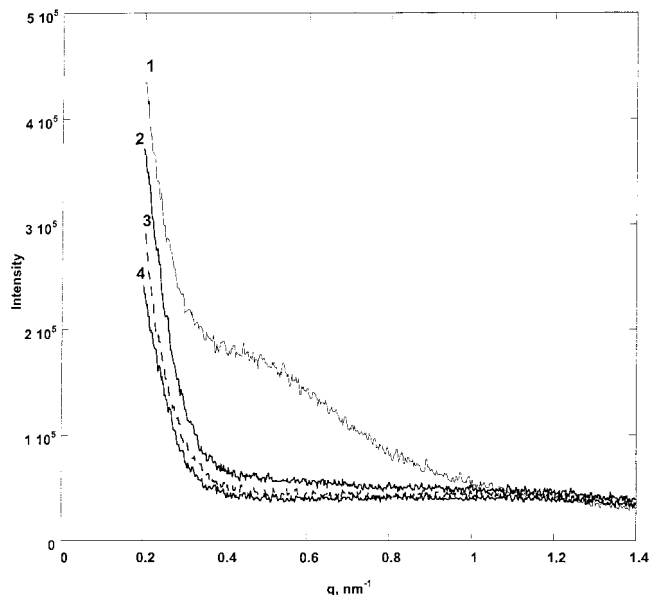


**Figure 8** Trend of urea segment formation for mixture of soy polyol and starch at 5% water at 1.1 TDI index using P3805.

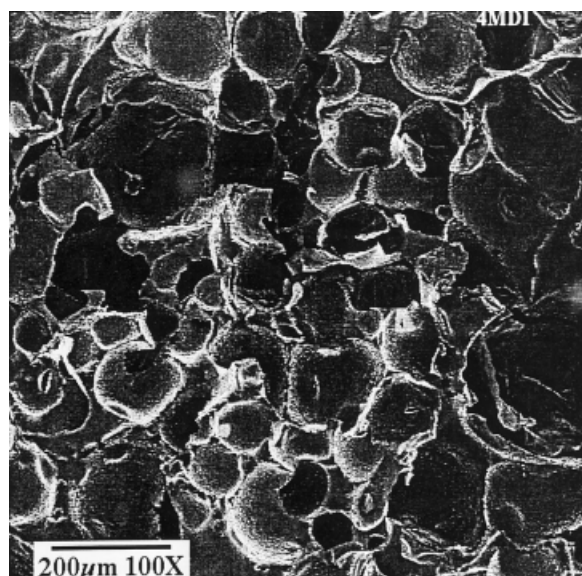
cells are clearly visible. The cell structure was not altered when the TDI index was changed from 0.9 to 1.1, and hence, the figures are not shown. Similar results were also observed by Dimitrios et al.<sup>17</sup> when changing the TDI index in the formulation. However, Armistead et al.<sup>18</sup> noticed increased texture to the foam while using synthetic polyols. In the case of soy polyols, the texture was more consistent with water levels of 3–4%, and the reaction was slower at these levels. At 5–6% water level, cells showed some rupture and the cell sizes varied. This could be due to the lack of an optimized surfactant.

The SEM of foam samples with the mixture of soy polyol and Voranol are shown in Figures 12 and 13.

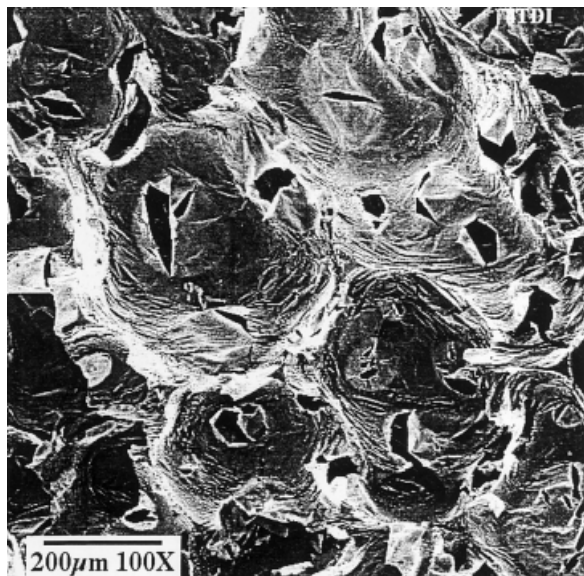
For samples with 80 : 20 mixture of soy and voranol (Fig. 12) had more well-organized cell shapes than foam samples with regular soy polyol. For samples with 50 : 50 mixture of soy polyol and voranol (Fig. 13), the cell shapes were apparently bigger in size when compared to 80 : 20 mixture with identical experimental conditions showing the need for a new surfactant. For foam samples containing starch (Fig. 14), the cell size and shape were more opaque when compared to the other foam samples without starch. The foams obtained were more rigid, and the texture was clearly visible from the micrograph after the addition of starch. However, there was no phase separation visible in the domain structure, and this is explained by the fact that the functional groups in



**Figure 9** SAXS data for different foam samples (1) 4% water MDI foam, (2) 4% water TDI foam, (3) 5% water TDI foam, (4) 6% water TDI foam.



**Figure 10** SEM for the foam sample with 4% water at MDI index 1.1.

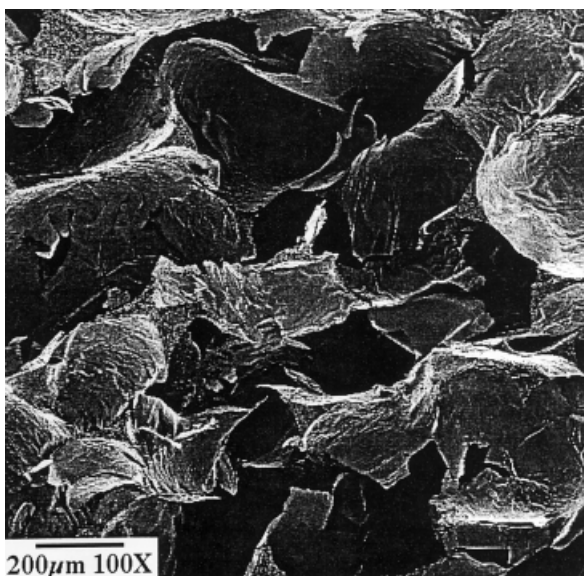


**Figure 11** SEM for the foam sample with 4% water at TDI index 1.1.

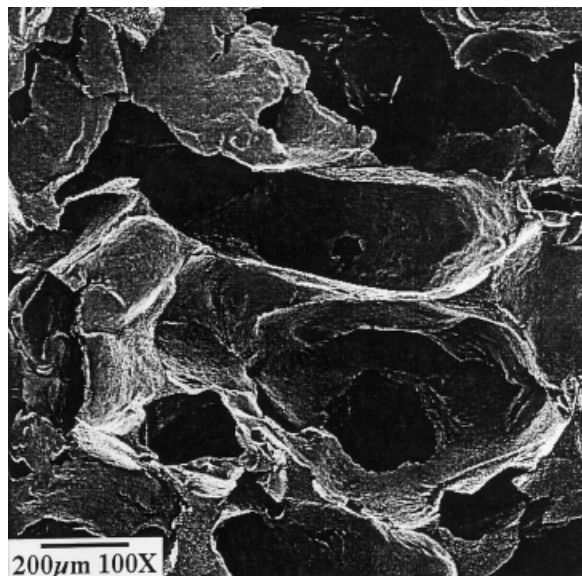
starch also takes part in the foaming reaction. Experimental observations and the scanning electron micrographs reveal that the rigidity of the foam can be controlled by changing the amount of starch in the foam formulation and also serves as a method to enhance the foaming reaction by supplementing functional groups in the polyol.

### CONCLUSIONS

Functionalized soybean oils have increased hydroxyl and acid values, increased molecular weight but reduced iodine values, lower than regular soybean oil.

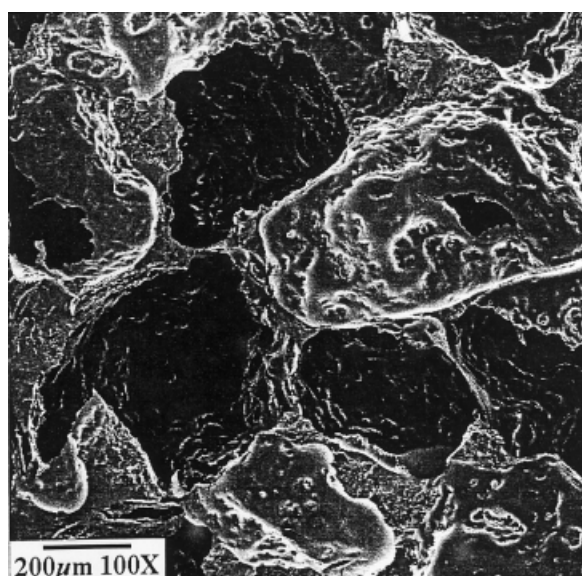


**Figure 12** SEM for the foam sample of 80:20 soy: voranol at TDI index 1.1.



**Figure 13** SEM for the foam sample of 50:50 soy: voranol at TDI index 1.1.

After the functionalization, there is a decrease in the unsaturated fatty acids particularly linolenic and linoleic and an increase in the saturated acid content. Flexible slabstock foam can be obtained from soy polyols, and the properties can be changed by controlling several variables like water content, isocyanate index, and catalysts. Soybean based polyols showed enhanced reactivity and the foaming reactions proceeded in a very similar fashion to synthetic polyols. FTIR was used to probe into the real-time chemical changes occurring as the foam reaction progresses. The rate of foaming reaction was controlled mainly by water and isocyanate content in the formulation. As



**Figure 14** SEM for the foam sample of soy polyol starch mixture at TDI index 1.1.

the water content increased, the amount of the hard segment and urea formation increased. Both MDI and TDI can be used with soy polyol to produce foam with varying physical properties, depending on the end use. Foams with MDI were more rigid than foams with TDI. The addition of synthetic polyol with primary hydroxyl group increased the rate of reaction and phase mixing in the foam.

Increased water content also increased the cell size. This work shows that vegetable oils can be successfully used in place of synthetic polyols, thereby adding value to agricultural resources.

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