Bio-Based High Functionality Polyols and Their Use in 1K Polyurethane Coatings

Thomas J. Nelson, Lindsey Bultema, Neal Eidenschink, Dean C. Webster*

Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58108, USA

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ABSTRACT: Bio-based polyols with high functionality were successfully synthesized by ring-opening epoxidized sucrose esters of soybean oil with methanol under acidic conditions, and were subsequently formulated with blocked isocyanates to form one package polyurethanes (1KPU). The bio-based polyols were characterized by gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, and Brookfield viscosity. Bio-based coatings were prepared by formulating the polyols with blocked polyisocyanates based on isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI). Two types of bio-based polyols were synthesized and the ratio of NCO:OH functional groups was varied to explore the effect of stoichiometry. The crosslinked PU coatings were characterized by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile testing, and thermogravimetric analysis (TGA). The coatings applied to steel substrates were also characterized using ASTM methods which measured hardness, adhesion, flexibility, and solvent resistance. As a control, a commercial soybean oil polyol was used and was found to have a lower modulus and a lower crosslink density and glass transition temperature (T_g) compared to coatings formulated with sucrose soyate polyols.

KEYWORDS: Sucrose soyate, soybean oil, polyol, polyurethane, coating, dynamic mechanical analysis, structure-property relationships

1 INTRODUCTION

Exploring the use of bio-based materials as potential resources for the chemical industry has emerged due to the growing safety and sustainability concerns stemming from the extensive use of petrochemicals. Recently, bio-based polyols derived from natural oils have gained a tremendous amount of interest in polyurethane production [1–5]. The high, persistent interest in bio-based polyurethanes is due, in part, to the ease of natural oil polyol preparation, as well as the low cost and abundant supply of natural oils [3]. Early attempts to make bio-based polyurethanes involved the use of castor oil since this oil has hydroxyl functionality in the oil backbone [6–8]. The castor oil triglyceride contains 90% ricinoleic acid which has 1 hydroxyl group per fatty acid chain. However, this indicates that castor oil has on average only 2.7 hydroxyl groups per molecule which is quite low and results in relatively soft materials when crosslinked. In order to boost the properties, transesterification of castor oil with pentaerythritol has been shown to result in higher functionality which results in more rigid polyurethanes [1].

Soybean oil polyols are currently being explored to make polyurethanes with better mechanical properties compared to castor oil. A common method to produce bio-based polyols with higher hydroxyl functionality is to first epoxidize soybean oil, which has on average 4.5 double bonds per molecule, followed by ring-opening with an active hydrogen compound as shown in Scheme 1 [9]. Epoxidation via the *in situ* peracid method results in a quantitative reaction with the internal double bonds on soybean oil which can then be ring-opened with a molecule like methanol with the aid of an acid catalyst to form a polyol [10]. Due to its ease of preparation, producing polyols from an epoxidized oil is commonly practiced in commercial processes [1].

Another method shown to produce molecules with even higher hydroxyl functionality is to use an

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Corresponding author: dean.webster@ndsu.edu

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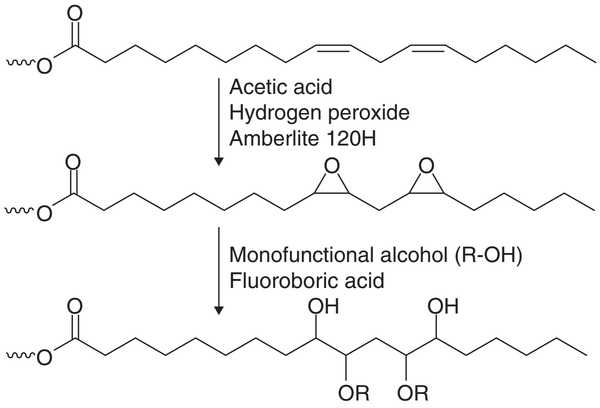
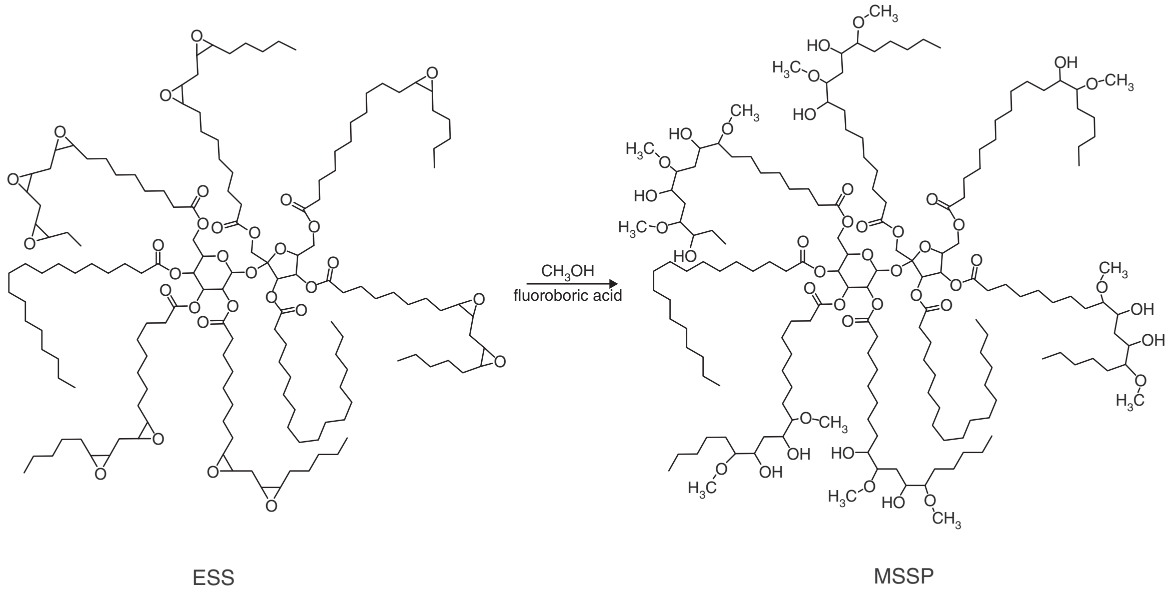


Scheme 1 Reaction scheme for polyol formation [9].



Scheme 2 Synthesis of methoxylated sucrose soyate polyol (MSSP).

epoxidized sucrose ester of soybean oil which has up to 8 fatty acid chains per molecule versus 3 for soybean oil [11]. Sucrose esters of soybean oil are currently prepared on a commercial scale by Procter & Gamble, and the epoxidation of these sucrose esters has recently been reported [11]. Epoxidized sucrose soyate can be subsequently ring-opened to produce a bio-based polyol as shown in Scheme 2.

Polyols derived from sucrose esters have a unique structure which can offer a high hydroxyl functionality of about 10 hydroxyl groups per molecule while retaining a very high bio-based content. The theoretical bio-based content for a sucrose soyate polyol ring-opened with methanol derived from petrochemicals is 94.6%. However, methanol can be bio-based if it is obtained from a source such as woody biomass which would result in a 100% bio-based sucrose soyate polyol. Epoxidized sucrose esters have already been shown to give superior properties compared to epoxidized soybean oil when crosslinked with anhydrides, which is attributed to the high epoxy group functionality [12].

The hydroxyl functionality on sucrose ester polyols can be used to formulate polyurethanes when reacted with polyisocyanate resins. In an initial study, Pan *et al.* studied 2K polyurethanes (2KPU) formulated with sucrose soyate polyols and polyisocyanate resins based on hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI). The thermosets gave very high T_g values and had modulus values exceeding 1 GPa, which is due to the high crosslink density achieved as a result of the high hydroxyl group functionality of the polyol [9].

A main disadvantage of 2K polyurethanes is that they must be applied shortly after formulating due to the reactive nature of an isocyanate group in the presence of a hydroxyl group. Stable one-package formulations can be formed if the formulation is made with a blocked isocyanate. Blocked isocyanates are used in formulations in which shelf stability is required since crosslinking reactions only occur at elevated temperatures. In blocked isocyanates, the reactive isocyanate group is blocked or protected at ambient conditions, but is regenerated at elevated temperatures due to deblocking and volatilization of the blocking group. A downside of using blocked isocyanates is that crosslinking must be done using baking conditions. On the other hand, ease of handling is enhanced since the resin will not interact with atmospheric moisture. Regardless, blocked isocyanates have found use in cationic electrodeposition coatings, powder coatings, coatings for electrical wire, and 1K automotive coatings [13].

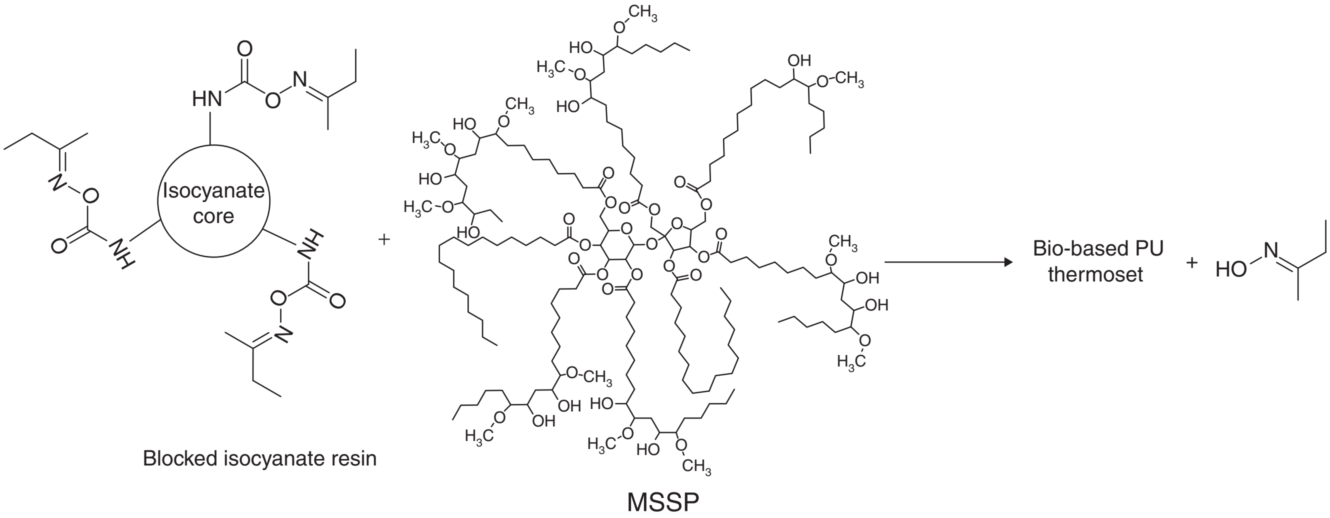
In this study, bio-based 1K polyurethanes were produced using two methyl ethyl ketoxime (MEKO)-blocked polyisocyanates based on hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI). HDI has a flexible backbone which gives rise to coatings with a low T_g and low modulus, whereas the more rigid cycloaliphatic IPDI gives coatings with a higher T_g and higher modulus [14]. The crosslinking reaction is illustrated in Scheme 3.

To further explore the effect of the ratio of isocyanate: polyol, three different NCO:OH ratios were selected at 0.6:1, 0.8:1, and 1.0:1. Having a ratio of NCO:OH < 1 is uncommon for coatings. However, a benefit to having a highly functional polyol is that coatings with sufficient crosslink density can be obtained with excess hydroxyl content. This is important since the industry is always trying to reduce its "isocyanate demand," since the polyisocyanate is usually the more expensive component in the system. For comparison, a soybean oil polyol was obtained from a commercial source which has an average hydroxyl functionality of 6–7 and was formulated to make a 1KPUs.

2 EXPERIMENTAL

Raw Materials Fully esterified sucrose soyate (Sefose 1618U) and partially esterified sucrose soyate (Sefose 1618U B6) were provided by Procter & Gamble Chemicals (Cincinnati, OH). Hexanes, glacial acetic acid, hydrogen peroxide (50% wt. solution in H_2O), and dibutyltin dilaurate (DBTDL) were obtained from Sigma Aldrich. Methanol (99.8%) was obtained from VWR. Two MEKO-blocked polyisocyanates were obtained from Bayer Material Science with one based on hexamethylene diisocyanate (HDI) Desmodur BL 3175A, and one based on isophorone diisocyanate (IPDI) Desmodur BL 4265 SN. A commercial soybean oil polyol (Agrol 7.0) was obtained from Biobased Technologies® (Springdale, AR).

Synthesis of Epoxidized Sucrose Soyate Resins Epoxidized sucrose soyate (ESS) and epoxidized sucrose soyate B6 (ESSB6) were synthesized as previously reported [11]. However, the reaction has been scaled-up to use 3.5 kg of sucrose soyate. In short, 3.5 kg of sucrose soyate along with acetic acid and Amberlite IR120 (20% wrt. sucrose soyate) was added to a 10 L jacketed reaction vessel with a valve at the bottom equipped with a Huber Unistat® for temperature control, a metering pump, and a mechanical stirrer. Once the temperature of the reactor reached 60°C with stirring, hydrogen peroxide was added with the aid of the metering pump at a



Scheme 3 Crosslinking reaction of the blocked polyisocyanates with the bio-based polyol.

rate of about 20 ml min^{-1}. The molar ratio of double bond:peroxide:acetic acid was 1:2:0.5. After the reaction was complete, the reaction temperature was allowed to rise to 40°C and hexane was added to the reactor to facilitate liquid-liquid separation. The bottom layer was drained and the solution was washed three times with water and once with a sodium bicarbonate solution to neutralize any residual acid present. Anhydrous magnesium sulfate was added to dry the resin and mixed for 20 minutes. The magnesium sulfate was filtered off and the dry resin was placed back into the 10 L reactor which was heated to 35–80°C under reduced pressure to remove the hexanes which were collected in a receiving flask. Yield, as determined by mass of sucrose soyate divided by mass of recovered product, was near 100%.

Synthesis of Sucrose Soyate Polyols Two different sucrose soyate polyols were prepared by ring-opening ESS and ESSB6 with methanol and their structures are shown in Figure 1. The product of ring-opening ESS with methanol is referred to as methoxylated sucrose soyate polyol (MSSP), and the product of ring-opening ESSB6 is referred to as methoxylated sucrose soyate B6 (MSSPB6). The reaction was carried out in a 1L reaction vessel equipped with a mechanical stirrer, reflux condenser and addition funnel. An ESS/chloroform solution was added dropwise to a solution of alcohol and catalyst to simulate "starved-feed" conditions. The molar ratio of alcohol to epoxy equivalent was 9:1. In a typical reaction, 200 g of ESS (0.746 epoxy equivalents) was dissolved in 100 g of chloroform and placed in an addition funnel. The vessel was charged with 215 g of methanol (6.72 moles), 13.4 g deionized water, and 1.8 g of the catalyst tetrafluoroboric acid and was allowed to heat up to 50°C with mechanical stirring. The ESS/chloroform solution was added dropwise at a rate of 2 mL min^{-1} once the temperature in the vessel reached 50°C. After the addition was complete, the reaction was maintained at 50°C for an additional 20 minutes. The reactor was allowed to cool to room temperature. About 6 grams of sodium bicarbonate was dissolved in 50 mL of deionized water and this solution was added to the reactor in order to neutralize the acid catalyst. After the bicarbonate solution had stirred for 20 minutes, the stirring was stopped and the reactor was allowed to sit overnight, which phase separated. The next morning, the top layer was removed. The solvent in the bottom layer was stripped with a rotovap and then the resin was rediluted with dichloromethane. The solution was placed in a separatory funnel and washed with water five times. The solution was dried by adding anhydrous magnesium sulfate which was removed by filtration. The dried solution was placed in the rotovap at 60°C to remove methylene chloride.

Characterization of Polyols Gel Permeation Chromatography (GPC) was obtained using a Waters 2410 gel permeation chromatograph equipped with a refractive index detector and calibrated with polystyrene standards. Solutions were prepared in THF at a concentration of 10 mg ml^{-1}. Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed using a Thermo Scientific Nicolet 8700 FTIR spectrometer and the data was acquired in absorbance mode. ^{1}H-NMR was performed using a JEOL-ECA 400 MHz NMR spectrometer equipped with an autosampler accessory. The samples were diluted with $CDCl_3$ at a concentration of 15 mg ml^{-1}. The data was acquired and processed using Delta NMR software. ^{1}H-^{1}H COSY was performed using a JEOL-ECA

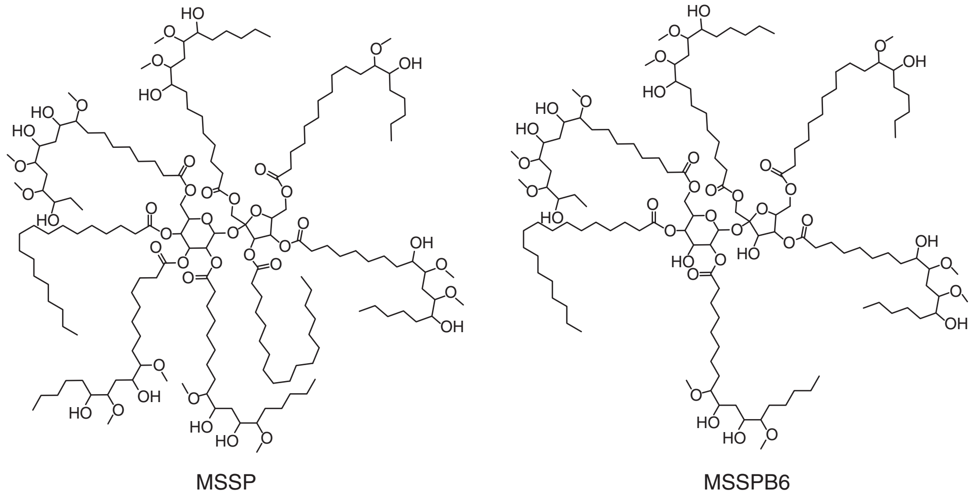


Figure 1 Typical structures of MSSP (left) and MSSPB6 (right).

400 MHz NMR spectrometer equipped with an autosampler accessory. The samples were diluted with $CDCl_3$ at a concentration of 75 mg ml^{-1}. The data was processed using ACD/Labs Specmanager software.

1K Polyurethane (1KPU) Formulation and Curing The polyols MSSP, MSSPB6 and Agrol were mixed with three different NCO:OH ratios of 0.6:1, 0.8:1, and 1.0:1 for both HDI and IPDI polyisocyanates giving a total of 18 formulations. All formulations were diluted with xylenes to obtain a formulation of 80% solids. DBTDL was added at a concentration of 1% (wt. based on solids) to the formulation. The formulations were hand mixed with a spatula for about 2 minutes followed by sonication. Coatings were applied to a steel substrate (Q-Lab, QD-36) cleaned with acetone and also a glass panel using a drawdown bar at a wet film thickness of 125 µm (5 mils). The coatings were then placed in a preheated oven at 150°C for 15 minutes. Free films were removed from the glass panel and used for tensile testing and DMA.

Characterization of PU Films The dry film thickness of PU on steel substrates was measured using a Byko-Test 8500 coating thickness gauge by taking the average of 10 points and reporting the standard deviation as the uncertainty. The hardness was determined using both König pendulum hardness and pencil hardness following ASTM D 4366 and ASTM D 3363, respectively. Adhesion was measured using the crosshatch adhesion test using ASTM 3359. Solvent resistance, which gives an indication of the crosslink density, was measured using a modified version of ASTM D 5402. Here, the head of a 26-ounce hammer was wrapped in four layers of cheesecloth and saturated with methyl ethyl ketone (MEK). The dripping wet hammer was placed at the base of the coating and allowed to rub the entire coating back and forth counting the number of double rubs until the coating failed showing the substrate. The hammer was rewet with MEK after 100 double rubs. Flexibility was measured using conical mandrel bend test (ASTM D 522) which measures a slow deformation and reverse impact (ASTM D 2794) which measures a rapid deformation. Tensile measurements were conducted using ASTM D 638 with dogbone samples cut out using a type V cutting die. At least 5 samples were used and the average was reported using the standard deviation as the uncertainty. Films based on HDI were run at a strain rate of 0.1 mm/sec and films based on IPDI were run at a strain rate of 0.0204 mm/sec. Differential scanning calorimetry (DSC) experiments were performed using a TA Instruments Q1000 DSC. PU films were placed in a hermetically sealed DSC pan. Conventional DSC was performed using a heat-cool-heat method from -80°C–200°C with 10°C heating and cooling rates. The T_g was recorded from the second heating cycle. Dynamic mechanical analysis (DMA) experiments were performed using a TA Instruments Q800 DMA. Coatings were cut to have a width of 5 mm and were loaded at 15 mm in length. In a typical run, a temperature ramp from −80°C–220°C with a ramp rate of 5°C min^{-1} was used while the oscillating frequency was 1 Hz with a strain rate of 0.02%. Additionally, a preload force of 0.02N was used. The crosslink density was determined from the storage modulus curve using Equation 1 where E is the modulus ($E' + E''$), n_e is the crosslink density, R is the gas constant and T is the temperature in Kelvin. Applying Equation 1 to the rubbery plateau regions results in $E \approx E'$ since $E'' \approx 0$.

$$E = 3\nu_e RT \tag{1}$$

The rubbery plateau region was at 125°C for coatings based on HDI and 175°C for coatings based on IPDI.

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 instrument to study the degradation of PU films. A small sample (5–15 mg) of the PU films were placed in a platinum pan and heated from 25°C–600°C under N_2 using a heating rate of 20°C/min. The instrument recorded the mass loss during the temperature ramp.

3 RESULTS AND DISCUSSION

Ring-opening of epoxidized sucrose esters was carried out in order to produce bio-based polyols capable of reacting with blocked isocyanates to produce 1KPU coatings. Ring-opening of epoxidized soy-based materials with methanol using tetrafluorboric acid catalyst has proven to be effective and has been carried out by previous researchers [5, 9, 10, 15]. The reaction conditions employed resulted in methanol ring-opening of the internal epoxy groups found on ESS and ESSB6 without side reactions such as transesterification, and resulted in only a small degree of oligomerization. The low levels of catalyst used and excess methanol was able to minimize oligomerization reactions which would increase the viscosity of the polyol. To further suppress oligomerization, "starved-feed" reaction conditions were employed by performing a dropwise addition of ESS or ESSB6 into a heated solution of methanol and acid catalyst. Chloroform was used as a solvent for ESS and ESSB6 in order to reduce the viscosity and to facilitate delivery through an addition funnel. However, the use of chloroform can be avoided if a larger capacity metering pump is used or if an addition funnel with a large opening in the stopcock is used.

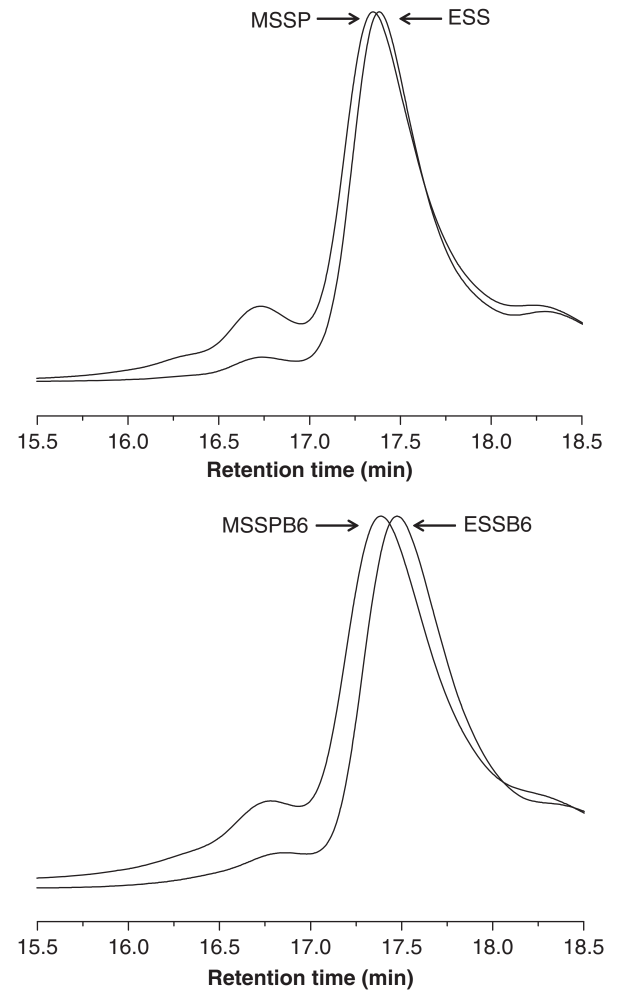


Figure 2 GPC curves of the starting epoxidized material and the ring-opened polyols.

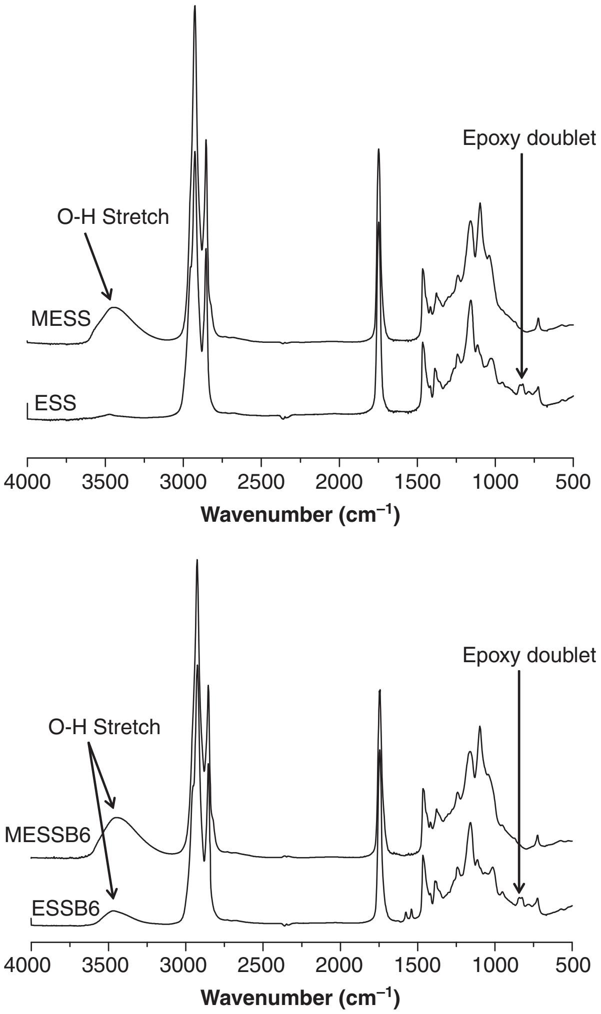


Figure 3 FTIR of the starting epoxidized material and the ring-opened polyols.

To characterize the bio-based polyols, gel permeation chromatography (GPC) was performed on the starting materials and polyols and the results are shown in Figure 2. There was a small shift to higher molecular weight after alcoholysis, which is expected since the hydrodynamic volume of the polyols is greater than the epoxidized starting materials. The shift is small since adding about 10 moles of methanol to 1 mole of ESS would only result in a mass increase of about 12%. GPC also indicated the presence of oligomers after the alcoholysis reaction indicated by the presence of a small shoulder peak at a lower retention time. Oligomerization in this reaction was attributed to a newly formed hydroxyl group reacting with an epoxy group on a different molecule, which has been observed in other soy-based polyol reactions [9]. However, the shoulder peak from the oligomers is small, indicating the extent of oligomerization is low. A newly formed hydroxyl group on sucrose soyate would be secondary, which is not as likely to ring-open an epoxy group as a primary alcohol such as methanol, which was also in excess. Overall, the reaction conditions employed are sufficient to suppress oligomerization to a significant degree. Also, the lack of additional peaks at low molecular weight indicated that transesterification did not occur, which is expected since the reaction conditions employed are mild in regards to transesterification. The shoulder peak at 18.4 min is present in the starting material and is believed to be the heptaester of sucrose soyate.

FTIR was used to detect the disappearance of the epoxy methyne near 826 cm^{-1} in the starting material and the formation of the broad O-H band near 3400 cm^{-1} in the soy-based polyol (Figure 3). The FTIR spectra were normalized with respect to the carbonyl band near 1740 cm^{-1} and were plotted in absorbance mode. After alcoholysis, the weak epoxy band is completely consumed while a broad O-H band appears near 3400 cm^{-1}. The

FTIR spectrum of the starting material ESSB6 shows a small O-H band since there are 2 hydroxyls on the starting material. The O-H band on ESSB6 increases after alcoholysis.

^{1}H-NMR was performed in order to better understand the structures of the polyols. A complete structural elucidation on the epoxidized sucrose ester resins has been performed by Pan *et al.* [11], and a partial structural elucidation for the polyols was also previously performed [9]. A more complete ^{1}H-NMR analysis is shown in Figure 4. Protons on sucrose are identified at 4.0–5.8 ppm and are constant on all the NMR spectra. The epoxidized compounds have characteristic signals at 2.9–3.2 ppm and 1.7–1.8 ppm. After alcoholysis, singlets emerge at 3.3–3.5 ppm which correspond to the methoxy protons. There is more than one singlet due to the complex mixture of fatty acids in soybean oil. New signals also emerged at 3.5–4.0 ppm which were assigned to the methyne protons near a hydroxyl. The signals near 2.9–3.2 ppm were ascribed to protons near the methoxy group and not residual epoxy methyne protons since the epoxy signals near 1.7–1.8 ppm disappeared.

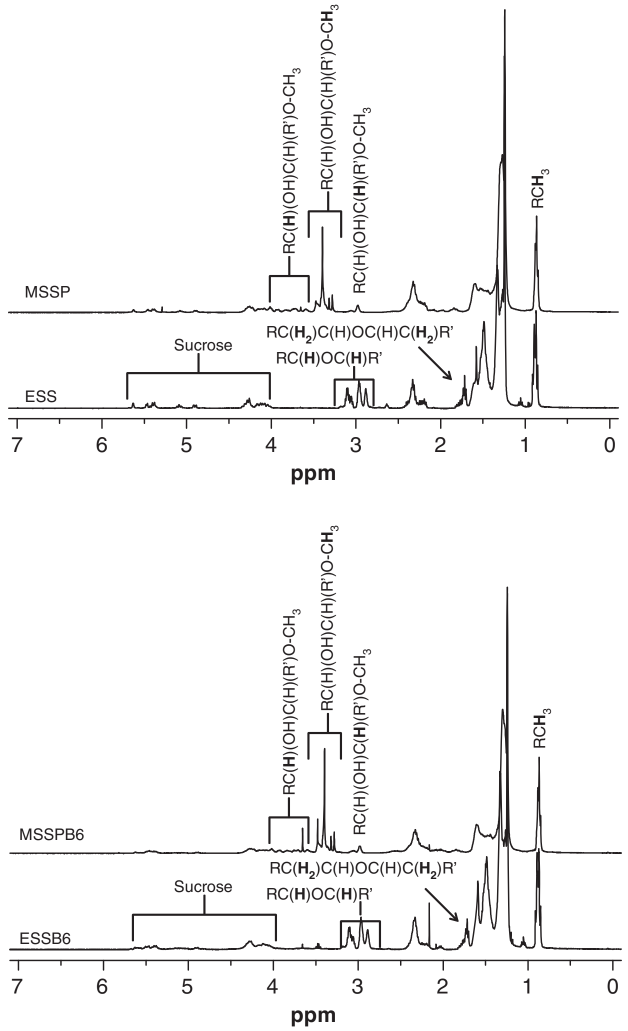


Figure 4 ^{1}H-NMR of epoxidized starting materials and ring-opened products.

To give further evidence, the signals near 2.9–3.2 ppm in MSSP and MSSPB6 were in fact protons on a ring-opened molecule as opposed to residual methyne epoxy protons and ^{1}H- ^{1}H COSY NMR was performed on MSSP. The results are shown in Figure 5. Here, the protons near 2.9–3.2 are adjacent to the hydroxyl protons near 3.5 which is clear evidence the protons are not from the epoxy since these are adjacent to only CH_2 protons upfield from 3.5 ppm. Overall, FTIR and NMR confirm there are no residual epoxy groups remaining after the alcoholysis reaction.

Table 1 gives data for the epoxidized starting materials and the three polyols synthesized. ESS and ESSB6 have relatively low viscosities at high percent solids with ESSB6 having a slightly higher viscosity. The polyol versions of these molecules had a higher viscosity than the starting epoxidized compounds which was attributed to a significantly higher degree of hydrogen bonding in the polyol resins. The small degree of oligomerization that occurred can also increase the viscosity. The viscosity of the soybean oil-based polyol, Agrol, was lower since the MW is lower and also the amount of hydroxyl groups present is lower than that of MSSP and MSSPB6. However, a lower functionality can lead to softer thermosets.

The polyol resins were mixed with two different MEKO-blocked polyisocyanate resins. One blocked polyisocyanate resin was based on HDI and the other

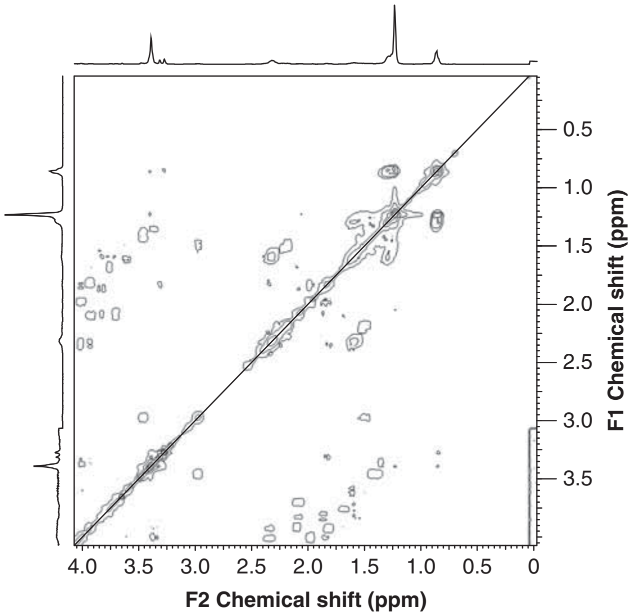


Figure 5 ^{1}H-^{1}H COSY NMR of MSSP.

Table 1 Resin data for starting materials and soy-based polyols.

Resin	M_n (g/mol)	PDI	Viscosity (mPa·s)	Percent solids (%)	Equivalent weight
ESS	2,300	1.2	2,600	98.69	250 g / epoxy eq.
MSSP	2,500	1.8	113,000	98.81	300 g / OH eq.
ESSB6	2,100	1.4	5,000	99.70	260 g / epoxy eq.
MSSPB6	2,300	1.9	195,000	98.16	232 g / OH eq.
Agrol 7.0	1,100	1.4	21,500	99.63	305 g / OH eq.

was based on IPDI. It is known that polyurethanes based on HDI form softer films with high flexibility and polyurethanes based on IPDI form harder, more brittle coatings. The compatibility of the 1KPU formulations was noted by visual observation and the results are shown in Table 2. Formulations consisting of MSSP and MSSPB6 with the HDI-based blocked polyisocyanate became cloudy during hand stirring and remained cloudy after the subsequent sonication. These formulations would eventually phase separate overnight in a sealed container, indicating an incompatible formulation. Interestingly, formulations consisting of Agrol with the HDI-based blocked polyisocyanate were compatible. It is somewhat surprising the HDI/Agrol formulation was compatible whereas HDI/MSSP and HDI/MSSPB6 were incompatible, since the chemical structures are very similar. The higher functionality of MSSP and MSSPB6 may make the molecule slightly more polar compared to Agrol. However, coatings formulated with sucrose soyate polyols and HDI-based blocked polyisocyanate could form a clear coating if the formulation was mixed well immediately prior to coating application and cured shortly thereafter. Formulations with the IPDI-based blocked polyisocyanate gave compatible mixtures for all the formulations studied.

The coating formulations were applied to substrates and cured at 150°C for 15 minutes. The T_g of the cured coatings was determined using both DSC and DMA and the results are shown in Table 3. The T_gs follow a predictable trend with the T_g increasing as the NCO:OH ratio increases with some exceptions. The exceptions include coatings formulated with sucrose soyate polyols with HDI at a ratio of 1.0:1 when the T_g was measured using DMA. Here, the soft HDI component was thought to depress the T_g of the thermoset below the T_g of the 0.8:1 coating. Although the T_gs of coatings formulated with MSSP and MSSPB6 had a lower T_g with the 1.0:1 ratio, every coating formulated with sucrose soyate polyols had a higher T_g compared to Agrol at the same NCO:OH ratio. The higher T_g of sucrose soyate containing coatings was attributed, in part, to the greater structural rigidity of the sucrose moiety which is the core of sucrose soyate versus the glycerol molecule which is the core of soybean oil. The rigidity of the sucrose moiety has been shown to give more rigid thermosets in previous studies [16]. Also, the higher functionality in MSSP and MSSPB6 was also suspected to give a higher T_g compared to coatings formulated with Agrol.

Table 2 Compatibility study of soy-based 1KPU formulations.

Formulation	Initial appearance	Appearance after 1 day
MSSP_HDI_0.6:1	Cloudy	Phase separated
MSSP_HDI_0.8:1	Cloudy	Phase separated
MSSP_HDI_1.0:1	Cloudy	Phase separated
MSSP_IPDI_0.6:1	Clear	Clear
MSSP_IPDI_0.8:1	Clear	Clear
MSSP_IPDI_1.0:1	Clear	Clear
MSSPB6_HDI_0.6:1	Cloudy	Phase separated
MSSPB6_HDI_0.8:1	Cloudy	Phase separated
MSSPB6_HDI_1.0:1	Cloudy	Phase separated
MSSPB6_IPDI_0.6:1	Clear	Clear
MSSPB6_IPDI_0.8:1	Clear	Clear
MSSPB6_IPDI_1.0:1	Clear	Clear
Agrol_HDI_0.6:1	Clear	Clear
Agrol_HDI_0.8:1	Clear	Clear
Agrol_HDI_1.0:1	Clear	Clear
Agrol_IPDI_0.6:1	Clear	Clear
Agrol_IPDI_0.8:1	Clear	Clear
Agrol_IPDI_1.0:1	Clear	Clear

Storage modulus (E′) values were obtained and increase as the ratio of NCO increases (Table 3). Crosslink densities were determined from E′ using rubber elasticity theory and were found to increase as the ratio of NCO increased, which can also give a higher T_g due to less mobility in the thermoset. The crosslink density for coatings formulated with sucrose soyate polyols was found to be significantly higher compared to coatings formulated with Agrol as determined by

Table 3 Thermal data of cured coating films obtained from DSC and DMA.

			DMA			
PU formulation (Polyol_Isocyanate)	**NCO:OH (molar ratio)**	**DSC T_g (°C)**	**T_g (°C)**	**E' at 25°C (MPa)**	**$E'_{rubbery\ plateau}$ (MPa)**	**ν_e (mol/mm^3)**
Agrol _HDI	0.6:1	2	2	1.7	1.7 @ 125°C	0.17
Agrol _HDI	0.8:1	16	16	12.1	3.6 at 125°C	0.36
Agrol _HDI	1.0:1	26	29	24.8	5.8 at 125°C	0.54
Agrol _IPDI	0.6:1	43	80	33.5	1.7 at 175°C	0.15
Agrol _IPDI	0.8:1	73	114	70.0	3.0 at 175°C	0.27
Agrol _IPDI	1.0:1	98	124	211	9.1 at 175°C	0.81
MSSP_HDI	0.6:1	18	32	44.3	4.9 at 125°C	0.49
MSSP_HDI	0.8:1	30	60	67.4	7.7 at 125°C	0.78
MSSP_HDI	1.0:1	41	41	111.2	11.5 at 125°C	1.16
MSSP_IPDI	0.6:1	82	104	239.9	9.7 at 175°C	0.87
MSSP_IPDI	0.8:1	104	131	598.8	12.9 at 175°C	1.16
MSSP_IPDI	1.0:1	110	144	824.3	18.6 at 175°C	1.67
MSSPB6_HDI	0.6:1	29	34	67.9	7.8 at 125°C	0.79
MSSPB6_HDI	0.8:1	38	51	31.6	10.1 at 125°C	1.02
MSSPB6_HDI	1.0:1	33	41	84.6	9.0 at 125°C	0.91
MSSPB6_IPDI	0.6:1	84	118	169.4	11.1 at 175°C	0.99
MSSPB6_IPDI	0.8:1	90	134	338.6	11.8 at 175°C	1.05
MSSPB6_IPDI	1.0:1	104	132	722.8	14.4 at 175°C	1.29

DMA which was attributed to the highly compact, highly functional sucrose soyate molecule.

Tan δ and storage modulus data were obtained from DMA and are shown in Figure 6. The shape of the tan δ curves is broader for coatings formulated with sucrose soyate polyols which is a result of greater heterogeneity in the crosslinked network resulting from the more complex composition of sucrose soyate versus soybean oil. The more complex composition of sucrose esters results in a wider range of crosslink densities throughout the thermoset which give a wide range of dampening mechanisms. Sucrose soyate molecules with a lower functionality give areas of lower crosslink density and sucrose soyate molecules with a higher functionality give areas with a higher crosslink density. The storage modulus curves for coatings formulated with IPDI show an interesting result. There is an increase in storage modulus at elevated temperatures which may be indicative either of residual curing reactions taking place while the DMA analysis is being performed, or of rearrangement of the polyurethane network hydrogen bonds at elevated temperatures. The increase in E′ at higher temperatures was not observed in HDI coatings to the degree it was observed in IPDI coatings. Since the T_g of IPDI coatings ranged from 104–143°C in terms of DMA, the coating may not have cured to completion when baked at 150°C for 15 minutes. Furthermore, MEKO contains a more reactive hydroxyl group compared to the secondary hydroxyls on the polyols studied which can compete with the newly formed deblocked isocyanates.

Tensile testing was also performed on cured 1KPU coatings and the results are shown in Table 4 and Figure 7. Coatings based on MSSP and MSSPB6 had a much higher modulus compared to Agrol when crosslinked with the HDI-based blocked polyisocyanate. The highest modulus value obtained for Agrol was 28 MPa at a ratio of 1.0:1, whereas MSSP had a modulus value close to 600 MPa. The elongation-at-break was higher for HDI coatings formulated with Agrol which is expected since the crosslink density was lower as determined by DMA. All coatings formulated with IPDI-based blocked polyisocyanate had high moduli and relatively low elongation-at-break. It is speculated that the high modulus values are greatly influenced by the IPDI component, whereas coatings based on HDI gave modulus values that are more influenced by the composition of the polyol.

The thermal stability of cured coatings was measured using thermogravametric analysis at a heating rate of 20°C/min in a nitrogen atmosphere (Figure 8). Coatings based on IPDI all showed a continuous degradation profile, while coatings based on HDI showed a retarded slope in 400–440°C. The slightly

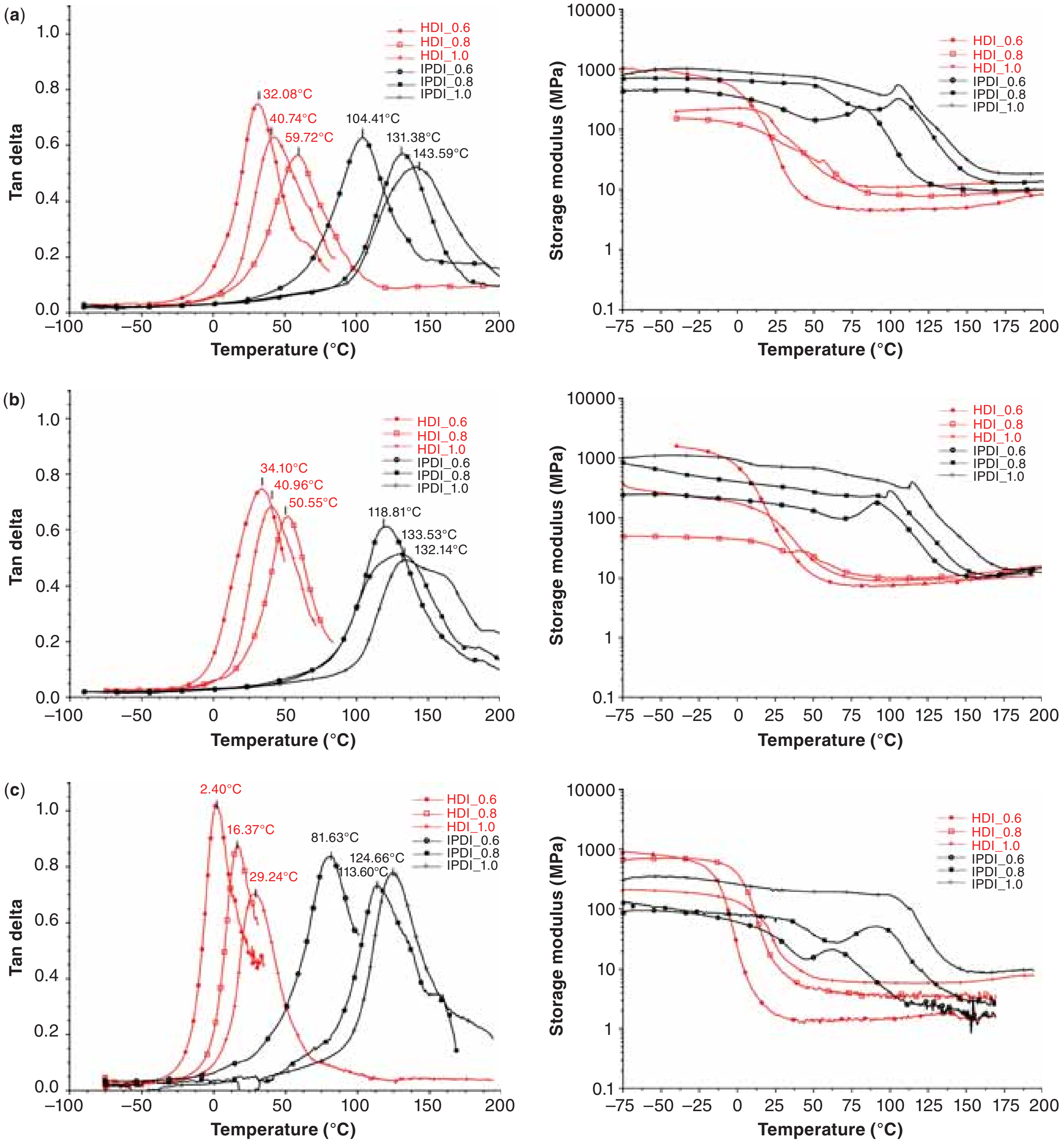


Figure 6 DMA analysis showing tan δ (left) and E′ (right) for cured 1KPU coatings: **(a)** 1KPUs using MSSP, **(b)** 1KPUs using MSSPB6, **(c)** 1KPU using Agrol.

Table 4 Tensile property data of cured coating films.

PU Formulation	NCO/OH (molar ratio)	Thickness (μm)	Modulus (MPa)	Tensile strength at Max. Load (MPa)	Elongation at break (%)
Agrol_HDI	0.6	0.10 ± 0.00	1.6 ± 0.2	1.19 ± 0.18	90 ± 11
Agrol _HDI	0.8	0.12 ± 0.01	4.2 ± 1.0	3.82 ± 1.34	118 ± 20
Agrol _HDI	1.0	0.07 ± 0.00	28 ± 4	13.97 ± 1.46	127 ± 9
Agrol _IPDI	0.6	0.07 ± 0.00	1033 ± 123	19.26 ± 1.79	33 ± 7
Agrol _IPDI	0.8	0.07 ± 0.01	1555 ± 153	33.64 ± 3.96	6.4 ± 2.2
Agrol _IPDI	1.0	0.05 ± 0.00	1650 ± 112	47.12 ± 3.41	8.9 ± 3.2
MSSPB6_HDI	0.6	0.08 ± 0.02	164 ± 56	9.33 ± 3.93	70 ± 16
MSSPB6_HDI	0.8	0.10 ± 0.02	299 ± 79	10.88 ± 0.84	57 ± 15
MSSPB6_HDI	1.0	0.08 ± 0.01	234± 30	12.87 ± 1.55	69 ± 12
MSSPB6_IPDI	0.6	0.07 ± 0.01	1403 ± 134	35.08 ± 1.57	6.8 ± 1.3
MSSPB6_IPDI	0.8	0.06 ± 0.01	1828 ± 57	43.68 ± 1.27	5.3 ± 0.5
MSSPB6_IPDI	1.0	0.06 ± 0.00	1958 ± 79	48.87 ± 2.83	4.9 ± 0.6
MSSP_HDI	0.6	0.09 ± 0.02	45 ± 14	7.03 ± 2.38	67 ± 16
MSSP_HDI	0.8	0.06 ± 0.01	504 ± 46	17.10 ± 4.34	15 ± 5
MSSP_HDI	1.0	0.07 ± 0.01	583 ± 110	19.17 ± 3.22	15 ± 8
MSSP_IPDI	0.6	0.06 ± 0.00	1413 ± 38	32.33 ± 1.42	5.9 ± 1.2
MSSP_IPDI	0.8	0.06 ± 0.00	1527 ± 142	39.66 ± 2.21	6.2 ± 0.8
MSSP_IPDI	1.0	0.07 ± 0.00	1670 ± 81	45.38 ± 1.26	6.4 ± 0.7

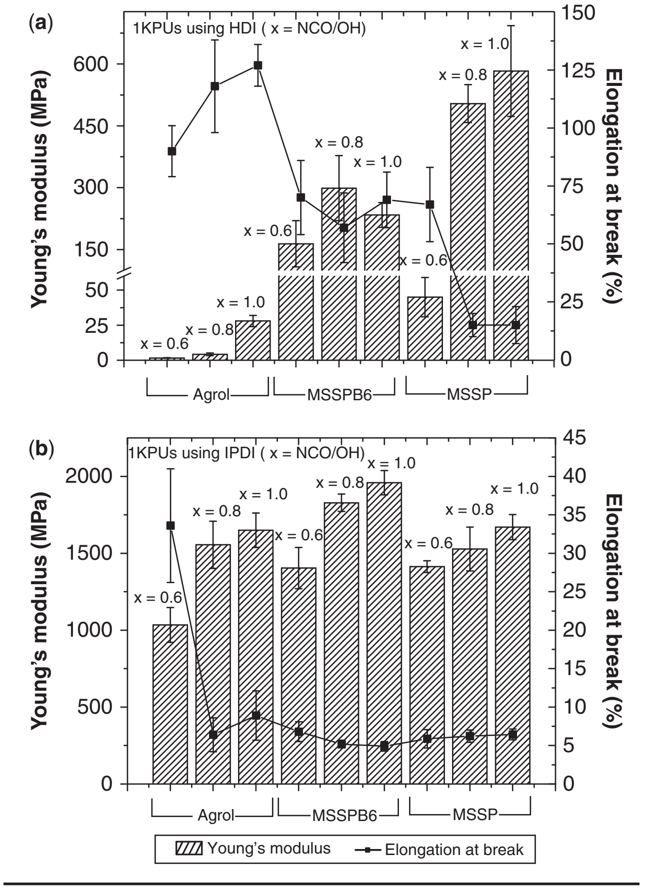


Figure 7 Young's moduli and elongations at break of 1KPUs.

better thermal stability of HDI-based coatings has been observed in a previous study [9]. Interestingly, 1KPU coatings formulated with sucrose soyate polyols had a slight mass loss at relatively low temperatures below 200°C. Pan *et al.* studied 2K HDI and IPDI coatings using similar bio-based polyols and did not notice this slight mass loss at temperatures below 200°C. Since DMA showed an increase in E′ at elevated temperature which was attributed to residual curing, the small mass loss observed in TGA was attributed to the MEKO blocking group leaving during a curing reaction.

The coatings properties are listed in Table 5. The König hardness for coatings based on MSSP and MSSPB6 were much greater compared to Agrol when formulated with HDI. The higher functionality in MSSP and MSSPB6 along with the rigid sucrose core gives higher hardness values. Interestingly, the increased hardness observed in sucrose soyate coatings formulated with HDI did not affect the flexibility, as it remained very high. All of the coatings formulated with HDI were able to withstand the maximum deformation when subjected to conical mandrel and reverse impact tests. Coatings based on IPDI were much harder as a result of the more rigid IPDI ring structure compared to the flexible HDI backbone. With IPDI, König hardness was almost identical for all the coatings. As with the tensile data, it is speculated that the IPDI component dominates the coating hardness

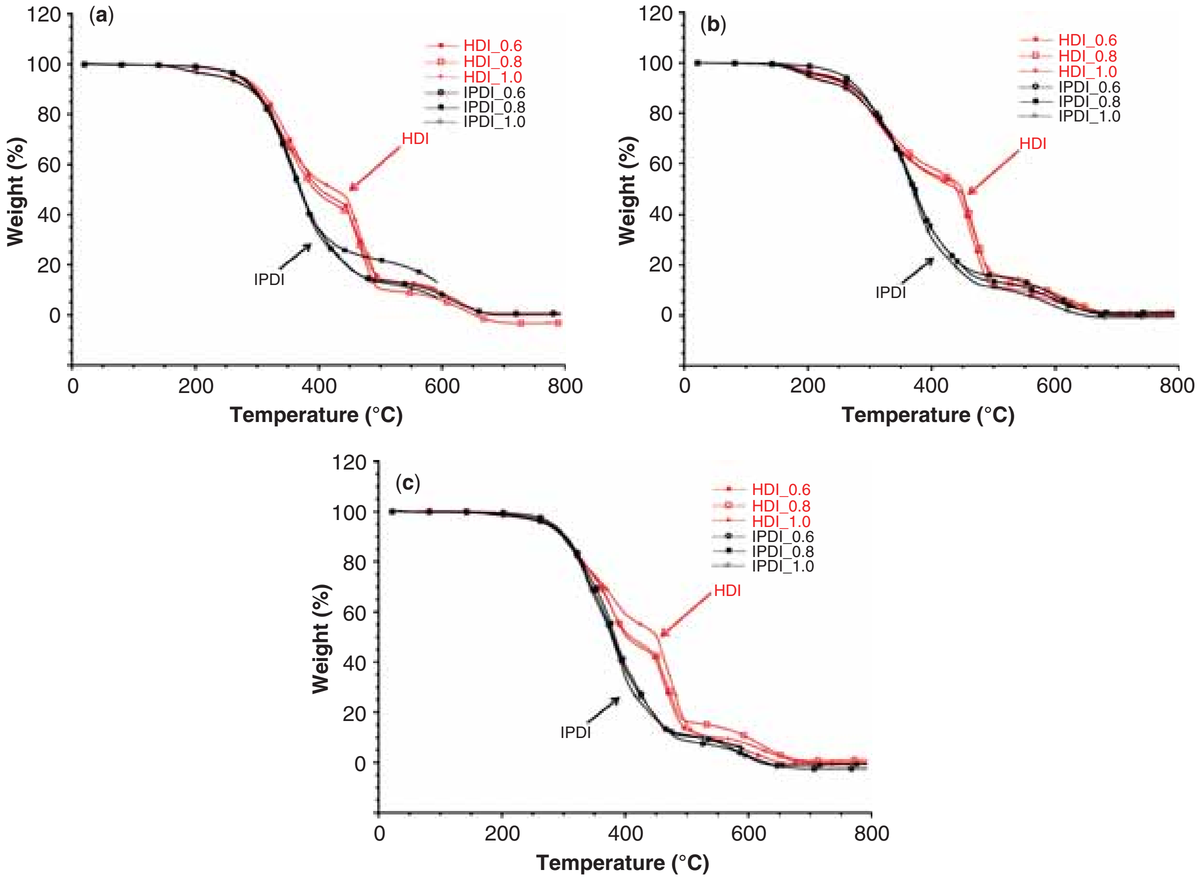


Figure 8 TGA performed in nitrogen atmosphere of 1KPU coatings: **(a)** 1KPUs using MSSP, **(b)** 1KPUs using MSSPB6, **(c)** 1KPU using Agrol.

Table 5 Coatings properties of bio-based 1KPU.

PU Formulation	NCO/OH (molar ratio)	Thickness (μm)	König pendulum hardness (s)	Pencil hardness (gouge)	Cross-hatch adhesion	MEK double rubs	Reverse Impact (in-ibs)	Mandrel bend (elongation-at-break)
Agrol_HDI	0.6	46 ± 6.0	12	HB	3B	> 400	172	> 28%
Agrol _HDI	0.8	44 ± 5.4	20	HB	4B	> 400	172	> 28%
Agrol _HDI	1.0	47 ± 6.7	56	HB	5B	> 400	172	> 28%
Agrol _IPDI	0.6	52 ± 5.2	125	HB	5B	> 400	172	> 28%
Agrol _IPDI	0.8	49 ± 3.3	184	F	5B	> 400	172	> 28%
Agrol _IPDI	1.0	40 ± 6.8	191	F	5B	> 400	40	> 28%
MSSP_HDI	0.6	68 ± 11	58	HB	3B	> 400	172	> 28%
MSSP_HDI	0.8	54 ± 6.0	106	F	5B	> 400	172	> 28%
MSSP_HDI	1.0	39 ± 7.4	118	H	5B	> 400	172	> 28%
MSSP_IPDI	0.6	41 ± 4.3	124	H	5B	> 400	100	> 28%
MSSP_IPDI	0.8	43 ± 7.8	180	H	4B	> 400	20	> 28%
MSSP_IPDI	1.0	49 ± 10	179	H	5B	> 400	20	< 3%
MSSPB6_HDI	0.6	52 ± 2.0	21	F	4B	> 400	172	> 28%
MSSPB6_HDI	0.8	48 ± 3.9	134	F	4B	> 400	172	> 28%
MSSPB6_HDI	1.0	43 ± 3.6	106	H	4B	> 400	172	> 28%
MSSPB6_IPDI	0.6	47 ± 1.6	166	H	5B	> 400	20	> 28%
MSSPB6_IPDI	0.8	60 ± 8.6	174	H	4B	> 400	< 20	< 3%
MSSPB6_IPDI	1.0	57 ± 5.7	188	H	5B	> 400	< 20	< 3%

whereas the polyol has more of an effect in HDI-based coatings. Overall, the coatings had high solvent resistance as well as good adhesion, which is typical for polyurethanes.

4 CONCLUSIONS

This study, which involved 1KPU coatings, was an extension of a previous study performed in our group which studied 2KPU coatings derived using similar bio-based polyols and polyisocyanate crosslinkers based on HDI and IPDI [9]. Here, ether polyols derived from the ring-opening of ESS and ESSB6 with methanol using an acid catalyst were successfully synthesized. PU films were prepared by crosslinking these polyols with blocked polyisocyanates. As a control, a soybean oil polyol was obtained from a commercial source and PU coatings were also prepared and studied. Overall, a wide range of coatings properties could be obtained depending on the polyol chosen, the type of blocked polyisocyanate used, and also the stoichiometry of NCO:OH. Coatings formulated with IPDI gave similar properties for all the polyols studied. However, the high functionality of MSSP and MSSPB6 allowed for coatings with higher moduli, hardness, and T_g compared to a soybean oil polyol which was formed when crosslinked with a blocked HDI-based polyisocyanate.

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