Polyester Polyols and Polyurethanes from Ricinoleic Acid

Zoran S. Petrović,[1] Ivana Cvetković,[1] DooPyo Hong,[1] Xianmei Wan,[1] Wei Zhang,[2]
Tim Abraham,[2] Jeff Malsam[2]

[1]*Kansas Polymer Research Center, Pittsburg State University, Pittsburg, Kansas 66762*
[2]*Cargill Inc., Minnetonka, Minnesota 55391*

ABSTRACT: Triols of molecular weights (MWs) 1000–4000, suitable for flexible foams, were prepared by transesterification of methyl esters of ricinoleic acid with trimethylol propane. These polyols were noncrystallizing, relatively low-viscosity liquids. They were reacted with diphenylmethane diisocyanate (MDI) to obtain elastomers having glass transition temperatures below −60°C. Polymer networks from high-MW polyols exhibited relatively high sol fractions suggesting that some cyclization occurred during polyol preparation. The low Shore hardness, relatively low strength and modest elongation of the elastomers were attributed to the specific structure of polyricinoleic chains and the presence of dangling chains, serving as plasticizers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1184–1190, 2008

Key words: polyurethanes; vegetable oil; structure; properties; biopolymers; elastomers; structure–property relations

INTRODUCTION

Concerns about sustainability and the high cost of petrochemicals have increased interest in bio-based materials. Polyols from vegetable oils have already found applications in the polyurethane foam industry. However, in the area of flexible foams they are usually used in conjunction with petrochemical polyols. Typical polyether polyols for flexible foams are triols with molecular weights (MWs) ranging from 3000 to 6000. The main issue with vegetable oil based polyols is their heterogeneity in functionality within the same polyol, as well as their relatively lower MW than necessary for flexible foams. In this work, we have addressed both issues and tried to prepare triols with high MW suitable for foams and elastomers. Because foams are very complex systems, testing of polyols was carried out in elastomers. New elastomeric networks allow the analysis of the effect of regular functionality of polyols on polymer properties and reveal advantages and disadvantages of bio-based materials. The polyols were prepared from ricinoleic acid obtained from castor oil. Ricinoleic acid is an 18-carbon hydroxy-fatty acid having the hydroxyl group on the 12th carbon, and an MW of 298.25. The MW of its methyl ester is 312.49. When self-esterified to a higher MW, ricinoleic acid gives polyester chains with six carbon

atoms in the side chains. Such long side chains are known as "dangling chains" and they influence the behavior of polymers. They act as plasticizers by reducing the glass transition of the polyesters, and prevent crystallization even at very low temperatures. An illustration of the structure of triols obtained from polyricinoleic acid and trimethylolpropane (TMP) is shown in Figure 1.

Ricinoleic acid and hydrogenated ricinoleic acid (also known as 12-hydroxystearic acid) are excellent precursors for the preparation of polyesters and a number of patents deal with this topic.[1–3] Polyols for foams from ricinoleic acid were reported almost half a century ago.[4] US patent 3,741,941 describes the preparation of polyesters from 12-hydroxystearic acid, and their use as film forming coatings. British patent[1] discloses a process for preparing polyols containing basic nitrogen, in which 12-hydroxystearic acid is first self-polymerized to poly(12-hydroxystearic acid) to a degree of polymerization of 2–10. Subsequently, the polymer is transesterified with an alkanol having 1–4 carbons, and then reacted with a dialkanolamine or trialkanolamine. A European patent[5] discloses the use of a polyester condensate formed from diols, such as an alkanediol or polyethylene glycol, and 12-hydroxystearic acid, for use as an internal release agent in the manufacture of polyurethane elastomers. A US patent describes the preparation of composites using polyesters formed from the self-condensation of ricinoleic acid alone, or condensation of ricinoleic acid in the presence of a C2–C20 starter polyol.[2] Another patent describes the synthesis of low-viscosity polyol compositions
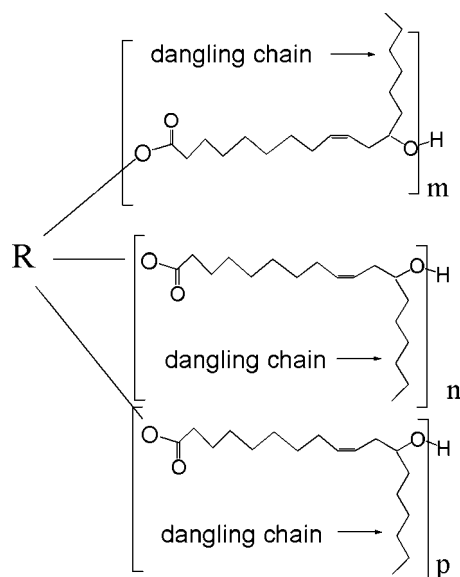
Figure 1 Polyester triol obtained from methyl ricinoleate and trimethylolpropane.

containing a polyol made from hydrogenated castor oil fatty acids and TMP.[6] Polyols made from ricinoleic acid and glycerol for use in seat pads of vehicles are disclosed in a recent patent.[7] In many of the above disclosures, the starting monomer 12-hydroxystearic acid actually contains about 10% of nonhydroxylated fatty acids, because the starting material is obtained from castor oil, i.e., the nonhydroxylated fatty acids present in the castor oil are not removed before they are used to make polyols. Dow Chemical discloses a process for purifying methyl 12-hydroxystearate by recrystallization from a solvent, and polymerizing the purified methyl 12-hydroxystearate onto a variety of initiators to synthesize polyols for polyurethane foams.[3] Commercial polyols for polyurethane foam applications produced from ricinoleic acid were reported recently.[8] Polyesters from ricinoleic acid have also been prepared recently using enzymes as catalysts.[9] However, very little information of the structure and properties of polyols and polyurethanes can be found in the literature.

The objective of this study was to investigate the technical feasibility of creating new triols of varying MWs, by transesterification of substantially pure polyricinoleic acid methyl esters with TMP, and examining the properties of the products. The methyl ester of ricinoleic acid was obtained by transesterification of castor oil with methanol and removal of glycerin. Typically, the content of ricinoleic acid in castor oil fatty acid mixtures is about 90%, and the rest are nonhydroxyl containing fatty acids, which can be separated from ricinoleic acid by fractional distillation.

EXPERIMENTAL

Materials

Castor oil, medical grade, was purchased from Walgreen. Methanol, Certified A.C.S, was obtained from Fisher Scientific (Pittsburg, PA). Potassium methoxide (CH_3OK), 95–99%, was obtained from Alfa Aesar (Ward Hill, PA). Fascat® 4350, a tin-based transesterification catalyst, was kindly supplied by Arkema Inc. (Philadelphia, PA). Trimethylol propane (TMP) was obtained from Aldrich. ISONATE® 143 L is a polycarbodiimide-modified diphenylmethane diisocyanate from Dow Chemical (Midland, MI). It is a light yellow liquid with NCO content of 29% (measured NCO = 28.5%; equivalent weight = 149.70). It was used to make polyurethanes with the MRCN triols.

Methods

The IR spectra were recorded on a Perkin–Elmer (Waltham, MA) Spectrum-1000 Fourier transform infrared (FT-IR) spectrometer. The GPC chromatograms were acquired on a Waters system consisting of a 510 pump and 410 differential refractometer. Tetrahydrofuran was used as the eluent at a flow rate of 1.00 mL/min at 30°C. Four Phenogel columns plus a guard Phenogel column from Phenomenex (Torrance, CA) covering an MW range of 10^2 to 5×10^5 were used and calibrated with eight narrow MWD polystyrene standards from BF Goodrich (Richfield, OH). The viscosities were measured on a Rheometrics Scientific Inc. (Piscataway, NJ) SR-500 Dynamic Stress Rheometer between two parallel plates, 25 mm in diameter with a gap of 1 mm. The hydroxyl values of the polyols were determined according to the ASTM E 1899-97 standard test method for hydroxyl groups, using the reaction with p-toluenesulfonyl isocyanate (TSI) and potentiometric titration of the resulting carbamate with tetrabutylammonium hydroxide.

A differential scanning calorimeter, model Q100, from TA Instruments, New Castle, DE, was used to measure glass transition and melting at a heating rate of 10°C/min. Dynamic mechanical tests were carried out on DMA 2980 from TA Instruments at 10 Hz and heating rate of 5°C/min. Tensile properties were measured according to ASTM D882-97 using a tensile tester model 4467 from Instron, Canton, MA.

Synthesis of polyols

Preparation of methyl ricinoleate from castor oil

Methyl ricinoleate (MRCN) was obtained by methanolysis of castor oil catalyzed by 1 wt % CH_3OK. A large excess of methanol (the molar ratio of methanol to ester bonds of triglyceride was 10 : 1) was used for

TABLE I
Designation and Properties of Triols

Polyol ID	MRCN/TMP molar ratio	Targeted M_n	M_n from OH#	OH# (mg KOH/g)	Viscosity (Pa s)
MRCN-1K	3.1	1003	1163	144.6	1.03
MRCN-2K	6.7	2013	2395	70.3	1.49
MRCN-3K	10	2939	3764	44.7	2.14
MRCN-4K	14	4061	5492	30.6	3.34

the process. The reaction was carried out under refluxing conditions of the mixture (temperature was 65–70°C) for 2 h. After cooling to room temperature, diethyl ether was added to the mixture, and then washed with water several times, until the pH value of the water phase was 7. The diethyl ether was then removed on a rotary evaporator.

Purification of MRCN

The methyl ester mixture obtained by transesterification with methanol as described above contained about 87% MRCN. A high vacuum distillation of the methyl ester was employed to obtain high purity MRCN as starting material for the polycondensation reaction. The distillation was carried out under high vacuum at about 230–250°C. The methyl esters obtained directly from castor oil were separated by distillation into three fractions, designated A, B, and C. Fraction A (about 15–20 wt % of the total mixture) was the initial fraction. Fraction B, about 65 wt %, was the second and purest fraction. Fraction C was the residue from the distillation (about 15 wt % of the total methyl ester mixture), containing some oligomers. Fraction B was redistilled to obtain the pure methyl ester of ricinoleic acid. GPC showed a single MRCN peak (no dimers). The hydroxyl (OH) number of the distillate was close to the theoretical value of 179.5 mg KOH/g.

Polycondensation of MRCN

Four polyricinoleate triols were prepared by reacting MRCN with TMP in different molar ratios. Targeted MWs of the triols were 1000, 2000, 3000, and 4000. Table I shows the MRCN/TMP molar ratios for the four polyols. The polycondensation of MRCN with TMP was carried out in a round bottom flask at 220°C with stirring. A medium vacuum was applied to the polycondensation system for about 20–40 min after the beginning of the polycondensation reaction, to remove the methanol that was generated. Fascat 4350 (0.5 wt %) was used as the catalyst. The reaction time was 3 h for the MRCN-1K and MRCN-2 K polyols, and 4 and 6 h for the MRCN-3K and MRCN-4K polyols, respectively. During the first hour, the reaction was carried out under atmos-

pheric pressure to avoid loss of TMP. During the second hour, a mild vacuum was applied and toward the end the reaction was continued under high vacuum. When the polycondensation reaction was complete, the polyols were cooled to room temperature, and used to prepare the cast resins without removing the catalyst. The polyols were light yellow liquids of relatively low viscosity as shown in Table I. The MW of the polyols is related to the molar ratio, x, and the MW of MRCN (= 312.49), loss of one mole of methanol ($M = 32$) per mole of MRCN and MW of TMP (134.17):

$$M_n = 312.49x - 32x + 134.17 \qquad (1)$$

The MWs of the triols are related to the hydroxyl number, OH#, by the following relationship:

$$M_n = 168,300/\text{OH\#} \qquad (2)$$

Hydroxyl numbers were lower than theoretical (16% for MRCN-1K, 19% for MRCN-2K, 28% for MRCN 3K, and 35% for MRCN-4K), possibly due to some dehydration at high temperature or due to the loss of monomers by evaporation. Cyclization does not affect OH number but gives lower MW than calculated from OH content.

The GPC curves of the triols in Figure 2 show no residual monomers and relatively narrow MW distribution ($M_w/M_n \sim 1.2$ from GPC). In the MRCM-1K polyol one observes a discrete MW distribution with
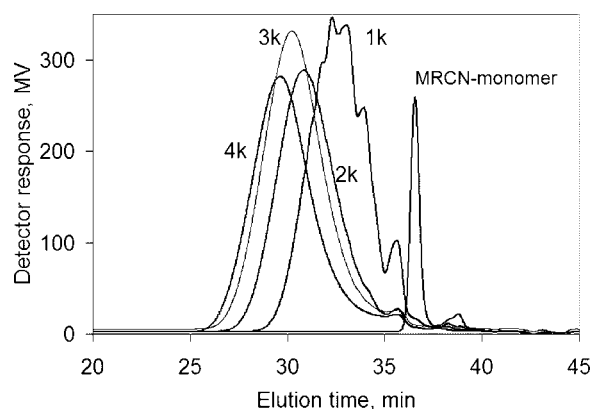
Figure 2 GPC curves of polyricinoleate-based triols. Designations 1K, 2K, 3K, and 4K refer to MRCN-1K, MRCN-2K, MRCN-3K, and MRCN-4K.
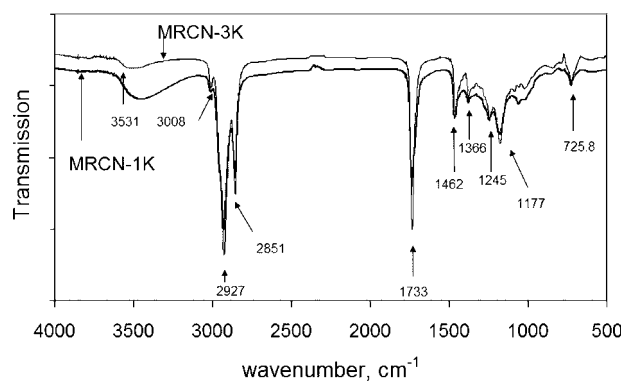
Figure 3 FT-IR spectra of the polyricinoleate triols MRCN-1K and MRCN-3K.

peaks for Individual species like dimer, trimer, tetramer, etc., but a continuous distribution is observed for the higher MW polyols.

Infrared spectra of polyester triols MRCN-1K and MRCN-3K are shown in Figure 3. They differ only in the area of the hydroxyl group, displaying in MRCN-3K two merged hydroxyl peaks at 3528 and 3463 cm^{-1}. The former was assigned to the non-hydrogen bonded OH, indicating that some OH groups in the very nonpolar environment could not form hydrogen bonds. Other characteristic bands are at 3010 cm^{-1} for double bonds, 1734 cm^{-1} for carbonyl and ester C—O vibrations at 1243 and 1177 cm^{-1}.

Preparation of polyurethanes

The procedure for making cast polyurethanes consisted of drying the polyols under vacuum, mixing Isonate 143 L with the polyol in a cup, pouring the reaction mixture into a preheated mold at 60°C, curing for several hours at 60°C, and finally raising the temperature to 110°C for a final cure of over 12 h. Because of the presence of residual catalyst from the polyol synthesis, the reaction with isocyanates was rather fast. The 1-mm thick cast films were clear and completely transparent.

For comparison purposes we prepared two more polyurethanes, one with castor oil and the other with a polypropylene oxide triol (Arcol F 3022 from Bayer) of 3000 MW.

RESULTS AND DISCUSSION

Ricinoleic acid methyl esters were of high purity, suitable for self-polymerization. The TMP, which was used as a starter, has primary hydroxyl groups which would preferentially react with the fatty acid methyl esters. Polycondensation had to be carried out at a very high temperature of 220°C because of the less reactive secondary hydroxyl groups in the ricinoleic acid. Transesterification is an equilibrium

reaction and methanol was removed to force the equilibrium toward polymer formation. However, this is a complex reaction and the outcome is dependent on time, because the reaction between ester groups and methyl esters (transesterification) or ester interchange (interesterification) also takes place, affecting MW distribution. Also, dehydration and cyclization reactions are possible, resulting in lower hydroxyl numbers and a mixture of different species. The polyol MRCN-1K (designation in Table I) was essentially an analog of castor oil with TMP instead of glycerin, but the OH number was lower than in castor oil (145 vs. 160 mg KOH/g). In a system consisting of a triol and hydroxyl fatty acids there are different possibilities for MW distribution. Hydroxy fatty acids may homopolymerize to a very high MW linear species or they may react with the starter triol (TMP). Chain growth on the three branches in triols may be uneven. Although the number average MW can be precisely calculated from the reactant ratio, weight average MW depends on the reactivity ratio of primary and secondary hydroxyl groups and the degree of conversion. The final distribution affecting the properties of polyols was simulated using the Monte–Carlo method. The simulation of polycondensation, ignoring side reactions, has shown relatively narrow MW distribution with M_w/M_n = 1.2–1.25. This is similar to the distribution in petrochemical polyols made by anionic polymerization of propylene oxide. The MW distribution of polyols made at different molar ratios of MRCN/TMP is given in Figure 4 for the case of 95% conversion and a reactivity ratio of primary to secondary hydroxyls = 100 : 30. The conversion of 95% was chosen since transesterification is never complete, but simulation at 100% conversion gave us similar values. The widest distribution was obtained for the equal reactivity of the groups, being about 1.5, whereas for the reactivity ratio 10 : 1 M_w/M_n was only 1.1. However, the
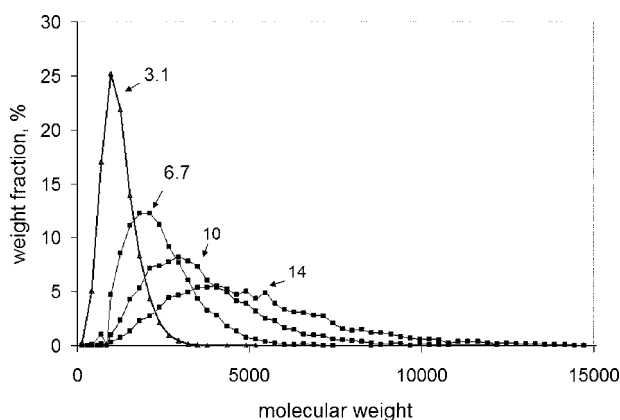

Figure 4 Molecular weight distribution for four triols at different MRCN/TMP molar ratios shown on curves obtained from Monte–Carlo simulation.
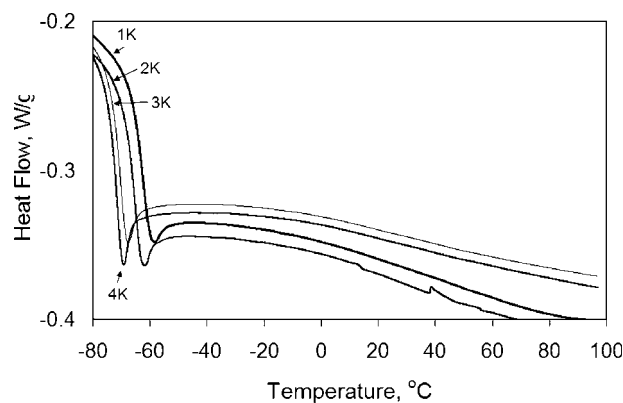
Figure 5 DSC curve of MRCN polyols. Designations 1K, 2K, 3K, and 4K refer to MRCN-1K, MRCN-2K, MRCN-3K, and MRCN-4K.

reactivity ratio 100 : 30 gave results closest to the experimental values. It should be mentioned that the difference in reactivity is very temperature dependent and at some high temperature the rate constant will eventually become equal. Incomplete reaction may lead to the formation of some monols. DSC curves of the polyols presented in Figure 5 show no melting points on the curves but they show MW dependent, very low glass transitions (T_g) from -63 to $-72°C$. The absence of melting, and low T_g values, are attributed to the presence of dangling chains.

Triols crosslinked with Isonate 143 give polymer networks whose quality can be assessed from the sol fraction, after swelling in toluene. The degree of swelling and sol fraction for the four polyurethane networks are given in Table II. Although the sol fraction of the castor oil and Arcol-based polyurethanes, together with PU-MRCN-1K, was within expected low limits, PU-MRCN-2K, 3K, and 4K displayed high sol fractions, possibly as a result of the presence of cyclics and monols. This was especially evident at higher MWs. This shows that cyclization proceeds to a considerable degree at higher MRCN/TMP ratios and presents a difficulty in preparing well-defined high MW samples. It is interesting that the polyricinoleate polyol at the MRCN/TMP ratio 10.5 revealed in Bayer's patent[2] (Polyester B8) had the same OH number as our analog MRCN-3K, in spite of the different synthesis conditions.

TABLE II
Degree of Swelling and Sol Fractions of Polymers Swollen in Toluene

Sample ID	Degree of swelling (%)	Sol fraction (%)
PU-MRCN-1K	96	1.6
PU-MRCN-2K	285	8.6
PU-MRCN-3K	450	13.6
PU-MRCN-4K	686	26
PU-Castor	98	0.9
PU-Arcol	255	3

The swelling degree of PU MRCN-1K was almost identical to that of castor oil. The higher swelling of PU MRCN-3K relative to its petrochemical analog PU-Arcol is not only partly due to the better solubility of oil-based chains in toluene but also due to the lower cross-linking density of the former.

DSC curves of the polyurethanes show only a single transition ascribed to the glass transition, Figure 6. The transitions are not always well defined, and reading the exact values may be a challenge, especially in the case of PU MRCN-1K. Glass transition and mechanical properties of the polyurethanes are displayed in Table III. Figure 6 shows a fairly broad glass transition for PU-MRCN-1K, a sign of a broader MW distribution of network chains than predicted by simulation.

Table III reveals that the T_g values of the MRCN polyurethanes are lower than even that of PU Arcol, which has flexible polyether chains. The T_g of PU MRCN-1K is about 25°C lower T_g than that of the castor oil-based polyurethane. However, this should be taken with caution because of the uncertainty of the T_g measurement of the PU MRCN-1K by DSC (DMA gave T_g of 7°C for this polymer). Also, MRCN polyurethanes 3K and 4K show lower hardness than the PPO-based network. Low hardness is probably the result of the presence of dangling chains and their plasticizing effect, but also lower cross-linking density and the presence of extractable fractions.

Dynamic mechanical curves for the four polyricinoleate polyurethanes, given in Figure 7, show higher glassy moduli of polyurethanes from lower MW triols, which is consistent with a higher content of aromatic MDI. The level of rubbery moduli decreases with increasing MW of the polyols.

The cross-linking density was estimated from the storage modulus at 50°C using the affine model rela-
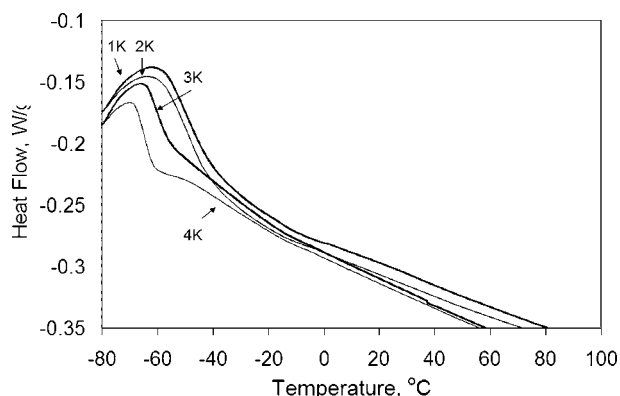

Figure 6 DSC curves of polyurethanes. Designations 1K, 2K, 3K, and 4K refer to polyurethanes based on polyols MRCN-1K, MRCN-2K, MRCN-3K, and MRCN-4K.

TABLE III
Properties of Polyurethanes

Sample ID	T_g (DSC) (°C)	Hardness Shore A	Tensile strength (MPa)	Elongation (%)	Tensile modulus (MPa)
PU-MRCN-1K	−17	67	3.22	81	5.75
PU-MRCN-2K	−50	48	0.88	68	2.01
PU-MRCN-3K	−59	36	0.49	170	0.49
PU-MRCN-4K	−64	27	0.37	196	0.33
PU-Castor	7	66	4.11	112	5.51
PU-Arcol	−51	44	0.85	68	1.89

tionship between the equilibrium modulus, E, and the MW of network chains, M_c:

$$E = 3\rho RT/M_c \qquad (3)$$

Here ρ is the sample density, R is the gas constant and T is the absolute temperature. Strictly speaking, the equilibrium modulus is not equal to the storage modulus, but when 70–100°C above glass transition they should not be far apart. The MW of the network chains can be calculated from the MWs of the polyols, being equal to two branches of a triol and an MDI unit: $M_c = 2M_{pol}/3 + 250$. Calculated M_c values from the structure are 1025 for MRCN-1K, 1846 for MRCN-2K, 2759 for MRC-3K, and 3911 for MRCN-4K. These values are significantly lower than the those calculated from the modulus using expression (3), which gives 1768, 3291, 9400, and 17,000 for samples MRCN-1K, MRCN-2K, MRCN-3K, and MRCN-4K, respectively. Lower moduli are ascribed to the plasticizing effect of the dangling chains, and the material behaves as swollen in dangling chains. For swollen networks, the phantom model with a front factor 1/3 would be more appropriate , giving M_c values of 589, 1100, 3100, and 5800, somewhat closer to the values from the structure.

Loss modulus (E'') curves shown in Figure 8 display a single well-defined glass transition. T_g values determined from the maxima on the E''-temperature curves are about 20°C higher than those from DSC not only because of the effect of frequency, but also because of some thermal lag in thicker samples for DMA. T_g values observed by this method were 7°C, −26°C, −40°C, and −46.5°C, respectively, for networks based on triols from MW 1000 to 4000. It is interesting to compare PU MRCN-1K and castor oil-based polyurethane. Castor oil has exactly three fatty acids per triglyceride whereas MRCN-1K has a distribution, ranging from less than three to more than three. Both have six-carbon dangling chains from ricinoleic acids, but castor oil has about 30% triglycerides with oleic acid or linoleic as additional dangling chains, behaving as a mixture of diols and triols (30 : 70) with an average functionality of 2.7, whereas MRCN-1K should be strictly a triol of somewhat higher MW. One would expect the castor oil polyurethane to have a lower T_g, but that is not the case since lower functionality is compensated by a higher OH number. A higher OH number requires a higher content of aromatic isocyanates, giving higher tensile strength and hardness, and lower elongation. Higher strength was observed with the castor oil-based
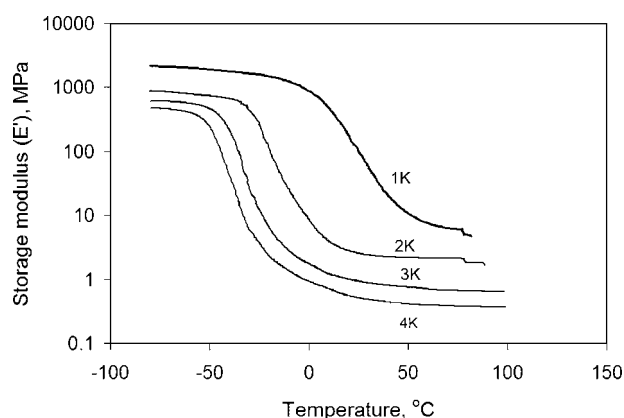
Figure 7 Effect of temperature on storage moduli of four MRCN polyurethanes. Designations 1K, 2K, 3K, and 4K refer to polyurethanes based on polyols MRCN-1K, MRCN-2K, MRCN-3K, and MRCN-4K.
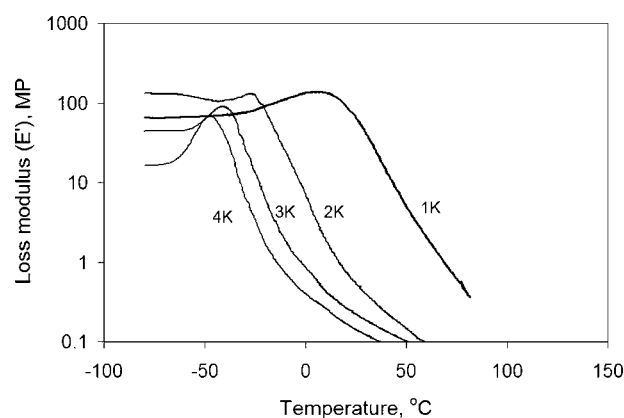
Figure 8 Effect of temperature on loss moduli (E'') of four MRCN polyurethanes. Designations 1K, 2K, 3K, and 4K refer to polyurethanes based on polyols MRCN-1K, MRCN-2K, MRCN-3K, and MRCN-4K.

polyurethane, but it also gave higher elongation and the same hardness. PU Arcol has almost identical properties to PU-MRCN-2K indicating that they have similar cross-linking densities.

Tensile strengths of polyurethanes from the polyricinoleate triols and MDI were relatively low (below 1 MPa), except that from PU-MRCN-1K, presumably because of low intermolecular forces, lack of crystallization during stretching, and the plasticizing effect of dangling chains. It should be emphasized that comparable values were obtained from polyurethanes based on polypropylene oxide triols of comparable MW. Lower elongations at break reflect the same effects. It should be pointed out that mechanical properties of PPO polyurethanes can be improved by addition of fillers, and it is expected that the same effect could be obtained with MRCN polyurethanes. The higher elongation at break for the castor oil polyurethane compared to that of PU-MRCN-1K is due to the more regular structure and considerable diol content in the former, which lowers the cross-linking density. The higher content of MDI in the castor oil polyurethane offsets lower cross-linking density, and brings the modulus to approximately the same level as in PU-MRCN-1K. Shore hardness is a measure of modulus and it scales with the MW of triols the same way as tensile modulus. The low hardness values of MRCN-based polyurethanes may recommend them for cushioning applications as in shoes. Significant benefits of the new polyurethanes stem from their low glass transitions, and retention of elastic properties well below freezing.

Cross-linked MRCN triols were tested as elastomers to get information on their structure from the properties of networks. However, their full potential may be realized in flexible foams, which was not the subject of this work.

CONCLUSIONS

Four triols of nominal MW 1000–4000 were synthesized from TMP and MRCN by transesterification. Obtaining high MW triols is challenging due to increased cyclization, and possibly loss of monomers, resulting in lower OH numbers. Polyurethanes made from these polyols display low glass transitions and mechanical properties comparable with those of petrochemical polyurethanes, except for lower Shore A hardness. They may be new renewable raw materials for flexible foam applications.

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