Physical Properties of Canola Oil Based Polyurethane Networks

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Received April 11, 2007; Revised Manuscript Received June 22, 2007

A new generation polyol (generation-II) with significantly higher triol content and higher hydroxyl value was synthesized from canola oil by introducing a mild solvent (ethyl acetate) and a more efficient reductive reagent (zinc) to the previous synthetic procedure (Narine, S. S.; Yue, J.; Kong, X. *J. Am. Oil Chem. Soc.* **2007**, *84*, 173−179). Polyurethane (PUR) elastomers were prepared by reacting this type of polyol with aliphatic diisocyanates. The physical and thermal properties of the PUR elastomers were studied using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) and compared to the elastomers made from the old generation polyol (generation-I). The concentration of elastically active network chains (ν_e) of the polymer networks was calculated based on rubber elasticity theory. Larger ν_e and narrower distribution of ν_e was observed in the case of the PURs prepared from the generation-II polyol. The relatively faster relaxation at higher temperature for this type of PUR elastomer, suggests a tighter cross-linked network structure by reducing the dangling chains effect. With the same OH/NCO molar ratio, the PURs prepared from the generation-II polyol showed higher glass transition temperatures (T_g), higher Young's modulus and tensile strength, and longer elongation at break.

Introduction

Polyurethanes (PURs) form a large family of polymeric materials with versatile chemical compositions and properties. They have wide applications: automotive parts, furnishing, construction, paints and coatings for appliances, etc.[1] In general, PURs are industrially produced by reacting petroleum-based polyols with isocyanates. The traditional process to produce suitable polyols from petroleum is costly, and the resulting products may cause serious environmental issues. In order to reduce the dependence on petroleum which is being exhausted at a fast rate, it is necessary to find more versatile, renewable, and more environmentally friendly resources. Vegetable oils, an abundant renewable resource, can be used to produce PURs through the introduction of hydroxyl functional groups into their structures. This process involves a number of approaches and has been extensively investigated by several researchers.[2−14]

One of the methods developed to prepare polyols from vegetable oils is to introduce epoxides onto the double bonds which later can be opened in various ways to produce polyols with secondary hydroxyl groups.[3,4,6] Another method is based on hydroformylating fatty acid double bonds to form aldehyde first, which is then hydrogenated to produce polyols.[3,5,8,10] However, both technologies yield heterogeneous polyols with hydroxyl functionality situated in the middle of the fatty acid chains, causing significant steric hindrance during cross-linking reactions in the production of polymers. Recently, an alternative method using ozone to cleave and oxidize the double bonds in the vegetable oil and then using various reducing catalysts to reduce the ozonides to polyols has been developed. Polyols prepared by this method have terminal primary hydroxyl groups, which reduce the plasticizing effect in the subsequent PUR networks.[2,9,11−14]

Ozonolysis technology was first industrially established and used to produce azelaic acid and pelargonic acid from commercial-grade oleic acid.[15] In our previous work, this technology was applied to vegetable oil to produce polyols (generation I) with primary alcohol functional groups at position 9 of the fatty acid ester.[2] This type of polyol is capable of producing high-quality PUR elastomers and foams which had very good thermomechanical and mechanical properties.[11,12] However, the procedure to synthesize polyol involved toxic solvent, high temperatures, and high pressure which would limit performance at an industrial scale. The yield of triols was 22% (mass content) which is also relatively low.[2]

In this paper, generation-II polyol with higher hydroxyl value was synthesized from canola oil by introducing a mild solvent (ethyl acetate) and a more efficient reductive reagent (zinc) to the polyol preparation procedure. Generation-II PUR elastomers were prepared by reacting this polyol with aliphatic diisocyanates. The physical and thermal properties of the PUR elastomers were studied using dynamic mechanical analysis (DMA) and modulated differential scanning calorimetry (MDSC) and compared to the elastomers made from generation-I polyols. The difference in structure of the starting materials (polyol), i.e., higher triol and less mono-ol content in generation-II polyol, provided the opportunity to evaluate the effect of dangling chain on the properties of the elastomers.

Materials and Methods

Materials. The canola vegetable oil used in this study was a "100% pure Canola" supplied by Canbra Foods Limited, Lethbridge, AB, Canada. Raney nickel 2800 (slurry in water) catalyst was obtained from Sigma-Aldrich Co. Ethyl acetate (reagent grade) and zinc (30 mesh, granular) were obtained from Fisher Scientific. Aliphatic 1,6-hexamethylene diisocyanate (HDI, Desmodur N-3200) was sourced from Bayer Corporation, Pittsburgh, PA. The relevant parameters of the polyols and diisocyanates used in this study are listed in Table 1.

Synthesis of Polyol. Generation-I polyol used in this study was synthesized in our laboratory using ozonolysis and hydrogenation-based technology. Canola oil was reacted with ozone in water to produce ozonide, then hydrogenated in tetrahydrofuran (THF) with Raney nickel

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10.1021/bm0704018 CCC: $37.00

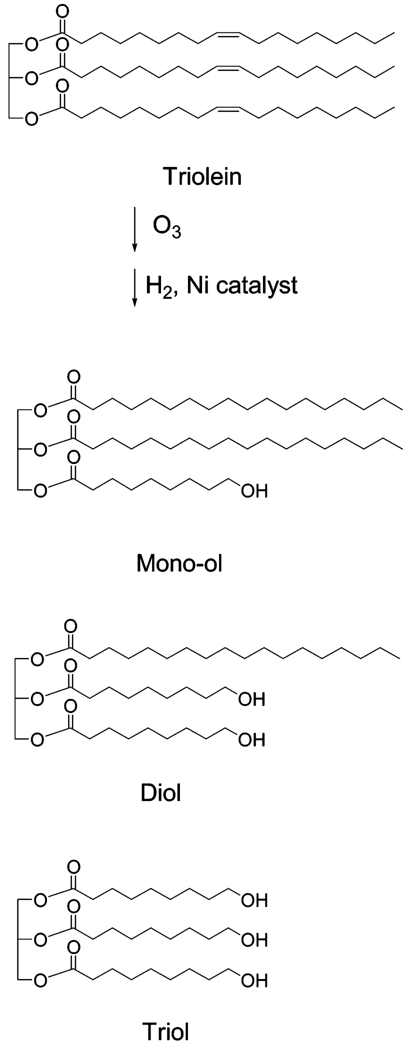

Figure 1. Reaction scheme using triolein as an example and representative structure of main component in polyol.

Table 1. Parameters of the Polyols and Diisocyanate Used in the Formulations to Prepare Polyurethanes[a]

	equivalent weight (g/mol)	OH number (mg KOH/g)	acidity number (mg KOH/g)	viscosity at 25 °C (Pa•s) ± 5 × 10^{-4}
polyol-I	368	152.4 ± 0.3	22.9 ± 0.3	0.4527
polyol-II	239	235.2 ± 4.6	15.8 ± 2.1	0.9860
HDI	183			

[a] Errors are standard deviations; $n = 3$.

as catalyst. The detailed procedures have been described elsewhere.[2] This grade of polyol is referred to as polyol-I.

Generation-II polyol was synthesized by the following procedure: Canola oil in the ethyl acetate (volume of 1:4) was ozonized (20% volume solution) at 10 °C, 5 L/min O_2 flow rate (with the concentration of ozone of 62 g/m^3) for 1 h. The ozonolysis product was reduced by zinc (molar ratio of 1:1.2 of equivalent weight) at room temperature, followed by hydrogenation at 70 °C, 100 psi with Raney nickel as catalyst. Finally, the solvent was removed by rotary evaporation and the low molecular weight byproducts were removed by wiped blade molecular distillation. This grade of polyol is referred to as polyol-II. Figure 1 illustrates the reaction scheme using triolein as an example and the representative structure of the main component in polyol.

Preparation of the Polyurethane Elastomers. PUR elastomers were prepared by reacting polyols with diisocyanates, and the detailed procedures have been described elsewhere.[11] The OH/NCO molar ratio was controlled as 1.0/1.2. Suitable amounts of polyol mixture and HDI were weighed in a plastic container, mixed thoroughly, poured in a metallic mold previously greased with silicone release agent, and placed in a vacuum oven at 45 °C for 10−20 min to degas the CO_2 released during the side reaction of isocyanate with moisture or carboxylic acids and the air trapped during mixing. Air was then introduced to the oven to avoid the deformation of the sample under vacuum, and the sample was postcured at 40−45 °C for about 48 h. The sample was 2 mm thick and ready for mechanical and thermal mechanical properties tests. On the basis of the different polyol used, i.e., polyol-I or polyol-II, the PUR samples are referred as PUR-I and PUR-II, respectively.

Hydroxyl and Acidity Values. Hydroxyl and acidity values of the polyols were determined according to ASTM titration method D1957-86 and ASTM D4662-98, respectively. All the samples were run in triplicate. The average values and standard deviations are reported.

Rheometeric Measurements. Viscosity of the polyols was measured in shearing mode with the TA advanced rheometer AR 2000 using a constant shearing rate of 51.6 s^{-1} at 25 °C.

Density Tests. The density of the PUR elastomers was determined according to ASTM D 792-00 standards.

Thermal Properties. Differential scanning calorimetry (DSC) measurements were carried out on a DSC Q100 (TA Instruments), equipped with a refrigerated cooling system. All the DSC measurements were performed following the ASTM E1356-03 standard. About 10 mg of sample was heated at a rate of 10 °C/min from +25 to +100 °C to eliminate the thermal history, cooled down to −50 °C at a cooling rate of 5 °C/min, and then heated again to +100 °C at a rate of 10 °C/min. Only the second heating step was selected for data analysis. All the procedures were performed under a dry nitrogen gas atmosphere.

DMA measurements were carried out on a DMA Q800 (TA Instruments) equipped with a liquid nitrogen cooling apparatus in the single cantilever clamp with a constant heating rate of 1 °C/min from −120 to 100 °C. The size of the samples was 18 mm × 7 mm × 2 mm. The measurements were performed following ASTM E1640-99 standard at a fixed frequency of 1 Hz and a fixed oscillation displacement of 0.015 mm. In the case of multiple isothermal oscillation experiments, the isothermal evolution of rheological parameters was recorded as a function of frequency ranging from 0.1 to 100 Hz. The isothermal oscillation was made, every 5 °C, 30 °C below and above the glass transition temperature (T_g).

Stress relaxation experiment was performed at 50 °C above the T_g with a shear clamp. A 0.2% strain was applied to each sample immediately prior to the collection of the relaxation spectrum. The relaxation modulus was monitored for approximately 10 min.

All the samples were run in triplicate for thermal property measurements. The reported errors are the subsequent standard deviations.

Mechanical Properties. Specimens for tensile measurements were cut out from the PUR samples using an ASTM D638 type V cutter. The tests were performed at room temperature using an Instron (MA) tensile testing machine (model 4202) equipped with a 50 Kgf load cell and activated grips which prevented slippage of the sample before break. The cross-head speed was 50 mm/min as suggested by the above-mentioned ASTM standard. At least five identical dumbbell-shaped specimens for each sample were tested, and their average mechanical properties are reported. The reported errors are the subsequent standard deviations.

Results and Discussion

Characterization of Polyols. The average values and standard deviations of hydroxyl and acidity of the polyols are reported in Table 1. The hydroxyl number of polyol-II (235 mg KOH/g) is very close to the theoretical maximum value (251 mg KOH/g) which was calculated based on the data of triacylglycerols (TAGs) composition and structure of canola oil.[16] It is much higher than that of polyol-I (152 mg KOH/g). The composition of the polyols was determined by an analysis protocol developed in our laboratory based on the HPLC procedure developed by Elfman-Borjesson and Harrod[17] for the analysis of lipid derivatives. The mass content of triol, diol, mono-ol, and saturated TAGs of polyol-II was 60%, 26%, 5%, and 9%, respectively, whereas that of polyol-I was 22%, 38%, 26%, and 14%, respectively. The saturated fatty acid chains in diol and mono-ol would act as dangling chains in the PUR networks. The lower hydroxyl value and amount of triol of the polyol-I could be explained by the difficulty to completely convert the reactant in the presence of a medium for ozonolysis such as water which is immiscible with the oil or with the ozonide. With the introduction of ethyl acetate as a solvent for ozonolysis and reduction, it can efficiently dissolve the starting material, the intermediate product, and the final product to increase the reaction and conversion rate.

It is noticed that both generations of polyol ended up with relatively high acid number, which resulted from oxidation, either during or after ozonolysis. Part of the ozonide was oxidized to carboxylic acid which could not be hydrogenated.[18] In order to compensate for the detrimental effect of the acid, a relatively higher isocyanate content was used in the formulation to produce PUR elastomers. To minimize the acid content, the following precautions could be taken: (1) dry the solvent (ethyl acetate) by using, for example, molecular sieve to get rid of the moisture; (2) perform the ozonolysis reaction at lower temperature.

Characterization of PUR Networks. The concentration of elastically active network chains (EANCs), ν_e, were determined by measuring equilibrium modulus of networks based on rubber elasticity theory by the following equation:[19]

$$G' = \frac{E'}{3} = a\nu_e RT = \frac{a\rho RT}{M_c} \tag{1}$$

where a is a prefactor that depends on the assumptions of the model, R is the gas constant, T is the absolute temperature, M_c is the number-average molecule weight between cross-links, and ρ is the density of the PUR networks.

Generally, the elastic behavior of polymer networks is described by either the phantom or the affine network model. For the phantom model, a depends on the functionality of the cross-links (f): $a = 1 - (2/f)$, whereas for affinely deforming networks $a = 1$. Phantom networks[20] are defined as perfect networks; no interactions between network chains exist and the cross-links are fully mobile. However, in real networks, the network chains do interact. The molecular chains will also interact with each other and reduce the junction fluctuations. For example, nonidealities in the networks, such as dangling chains, will decrease ν_e, and entrapped entanglements will increase it, inversely. Because of the strong interactions between molecular chains in the PUR network, the junctions are assumed to be immobile, and the storage modulus G' of the PUR network could be related to ν_e using the affine network model.

The equilibrium modulus of networks were investigated by creating master curves of the storage modulus versus frequency following the time–temperature superposition principle[21] using $T_g + 5$ °C as the reference temperature. Figure 2 shows the master curve of E' at a reference temperature of 20 °C for PUR-II elastomers as an example. The extended frequency range obtained by the superposition is 10^{-7} to 10^{8} Hz. The pseudoequilibrium modulus of the cross-linking network, G' ($G' = E'/3$), is related to ν_e through eq 1. ρ was determined according to ASTM D 792-00 standards and assumed to be a constant when the M_c was calculated. The results are listed in Table 2.

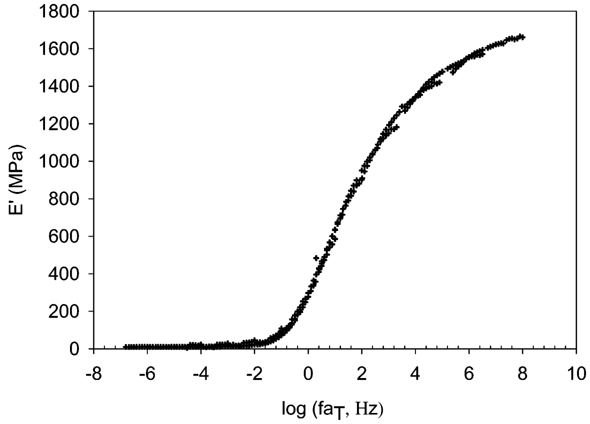

Figure 2. Master curve of E' at a reference temperature of $T_g + 5$ °C for PUR-II elastomers.

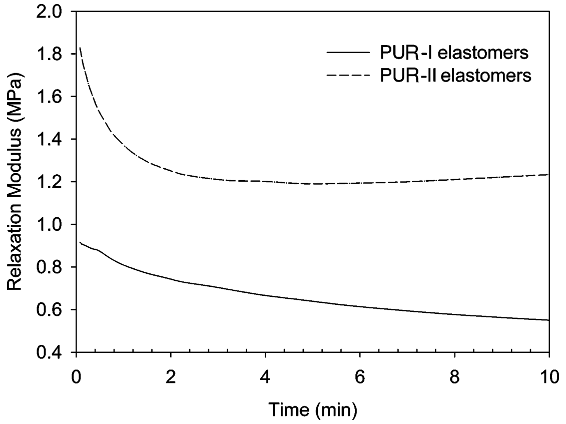

Figure 3. Response of the relaxation modulus during the stress relaxation experiments performed at 50 °C above T_g.

Table 2. T_g (°C) Obtained by DSC and DMA, Density, and Parameters of Cross-Linking Networks of the Polyurethane Elastomers

	T_g (°C) from DSC	T_g (°C) from DMA	E' (MPa)[a]	ρ at 23 °C (g/cm^3)	ν_e (mol/cm^3)	M_c (g/mol)
PUR-I elastomers	−9.6 ± 1.0	−5.3 ± 0.6	8.0	1.112	1.0×10^{-3}	1066
PUR-II elastomers	8.3 ± 0.6	15.0 ± 0	10.1	1.110	1.4×10^{-3}	803

[a] E' at rubbery plateau from master curve.

PUR-II elastomers have larger ν_e and smaller M_c confirming that polyols with higher functionality are more efficient at building network structure than those with lower functionality. Furthermore, the large amount of saturated fatty acids in polyol-I act as dangling chains, causing significant steric hindrance to cross-linking which resulted in lower ν_e in the produced PUR. As will be discussed later, the concentrations of EANCs play an important role in the physical and mechanical properties of the PUR networks.

Note that the ν_e measured using the above-mentioned procedure is composed of contributions from both chemical cross-links and trapped entanglements. In order to evaluate the amount of trapped entanglements in the PUR networks, relaxation of the shear modulus was measured as a function of time for each polymer in its rubbery state. To ensure that each material was in its rubbery region, each sample was tested at a temperature 50 °C above its T_g. It is evident from the relaxation spectra presented in Figure 3 that PUR-II elastomers appeared to have an initial equilibrium value of the relaxation modulus at 2 min, while PUR-I elastomers underwent a relaxation process at longer times. As known, PUR-I elastomers have a much higher fraction of "inert" material (dangling chains and saturated TAGs), which disrupt the network formation and therefore "dilute" the EANCs backbones. Alternatively, one can say that the dangling chains make the EANCs more bulky and the network structure loose. It is hypothesized that PUR-I elastomers may contain very loose networks of chemical cross-links augmented by physical cross-links that are caused by those "inert" materials. Thus, on a short time scale these materials behave as though they are well cross-linked. But as the physical interactions are overcome on larger time scales, they begin to display the flow characteristics and long-range relaxation ability of a loose network. This trend is consistent with what has been reported for lightly cross-linked natural rubber which can take hundreds of hours to equilibrate in a stress relaxation or creep experiment.[22]

Sol Fraction and Concentration of PUR Networks. The swelling of PUR-I elastomers in toluene at room temperature is 66%, which is higher than that of PUR-II elastomers (39%). The sol fraction for each sample was determined by multiple extractions with toluene. The content of the soluble part of PUR-I elastomers is 8.6% and that of PUR-II elastomers is only 0.8%. By considering the mono-ol and saturated TAGs contents in the polyols, it was expected that PUR-I elastomers would have considerable sol fractions, whereas PUR-II elastomers would have low sol fractions. The existence of sol in these materials might have a substantial impact on various properties.

ν_e and M_c of the PUR networks were also determined by applying the equilibrium degree of swelling to eq 2 according to Flory−Rehner theory.[19]

$$1/\nu_e = M_c/\rho_2 = \frac{[-V_1(A\phi_2^{1/3} - 2B\phi_2/f)]}{[\ln(1-\phi_2) + \phi_2 + \chi_{12}\phi_2^{2}]} \qquad (2)$$

where ρ_2 is the density of the dry polymer, V_1 is the molar volume of the solvent, ϕ_2 is the volume fraction of the polymer in the swollen sample, f is the functionality of the network branch points, and χ_{12} is the polymer−solvent interaction parameter. A and B within the junction−fluctuation theory of Flory (JFF theory)[19] have the following limits: $A = (f - 2)/f$, $B = 0$ (phantom model); $A = 1$, $B = 1$ (affine model).

The polymer−solvent interaction parameter, χ_{12}, was calculated from the solubility parameters of the solvent, δ_1, and the polymer network, δ_2:

$$\chi_{12} = \frac{(\delta_1 - \delta_2)^2 V_1}{RT} \qquad (3)$$

The solubility parameter of toluene, $\delta_1 = 18.2\ (\mathrm{J/cm^3})^{1/2}$, was obtained from a polymer handbook;[23] the solubility parameter of PUR, δ_2, can be calculated from cohesive energy densities and the volume contribution of atomic groups using group contributions theory.[24]

Notice that M_c calculated from eq 2 is 210 g/mol for PUR-I elastomers and 150 g/mol for PUR-II elastomers by applying affine model. These values are unrealistically low which can be due to the contribution of trapped entanglements. It might be also due to the inaccurate calculation of δ_2 which was obtained by assuming a perfect network structure. In reality, impurity of the starting products, the presence of material with lower functionality, and competing side reactions can all lead to an influence of the network structure. It is therefore difficult to evaluate the exact network parameters calculated from swelling experiments. However, by comparing with the results described previously from the equilibrium modulus, the trends are the same: PUR-II elastomers have larger ν_e and smaller M_c than PUR-I elastomers.

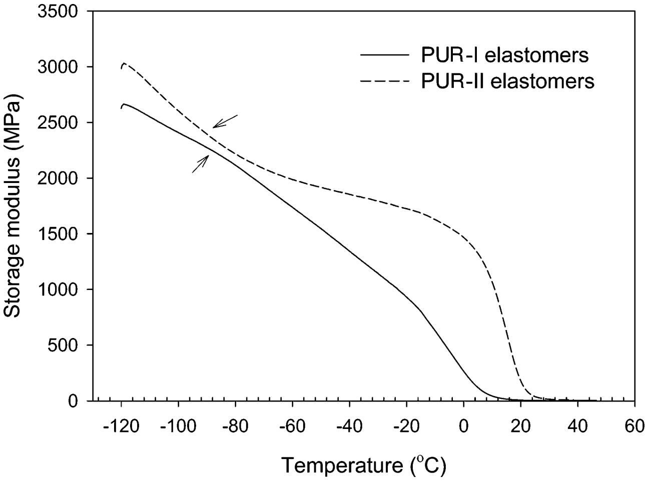

Figure 4. Storage moduli vs temperature, obtained from DMA carried out at a frequency of 1 Hz.

Thermal Mechanical Properties of PUR Networks. The dynamic mechanical properties of both PUR elastomers were investigated as a function of temperature starting in the glassy state, through glass transition, and well into the rubbery plateau of each material. The storage modulus measured at a frequency of 1 Hz for PUR elastomers with different polyols is shown in Figure 4. For both elastomers, the storage modulus drops first gradually, then exhibits a relatively rapid drop around −90 to −70 °C (β-transition) as indicated by the arrows in the figure, followed by another large drop during the transition from glassy to rubbery states (glass transition). The storage moduli of the PUR-I elastomers decrease slightly with increasing temperature, whereas that of PUR-II elastomers drops abruptly in the glass transition region. In the glassy state, stiffness is related to changes in the stored elastic energy upon small deformation as the molecular segments resist motion. The PUR-I elastomers with lower ν_e appear less able to resist segmental motion and thus are not capable of storing elastic energy, resulting in a lower glass modulus than those of PUR-II elastomers.

T_g values for both elastomers determined from the inflection point of E' versus temperature from DMA measurements are listed in Table 2. The T_g's of the PUR elastomers were also determined from the shift of heat capacity with temperature of the DSC curves (see Figure 5) and are listed in Table 2 as well. The T_g values determined by DSC and DMA showed the same trend: the T_g's of PUR-II elastomers are about 20 °C higher than those of PUR-I elastomers. However, the values obtained from DMA are somewhat higher than those obtained by DSC which is due to the frequency effect.[7]

The glass transition of a polymer network is affected by cross-linking density and chemical structure as well. The increase of T_g (~20 °C) indicated that the flexibility of the polymer chains was reduced for the higher cross-linked networks shifting the rubbery state to higher temperatures. This could be explained by the high ν_e value for the PUR-II sample as mentioned earlier. In addition, the large amount of dangling chains in PUR-I sample act as plasticizers which reduce the polymer rigidity and increase the flexibility, resulting in lower T_g as well.

Plots of loss modulus (E'') versus temperature for both PUR elastomers are given in Figure 6. A weak β-transition in the range of −90 to −70 °C was observed for both samples, which may be related to the movements of a chain part containing the

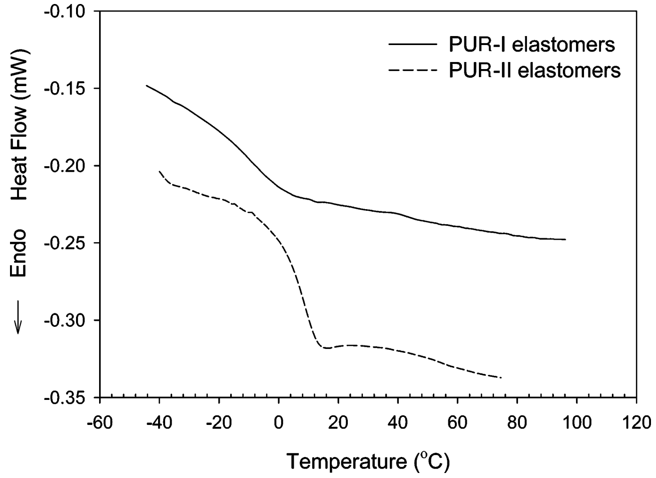

Figure 5. DSC curves of the PUR elastomers.

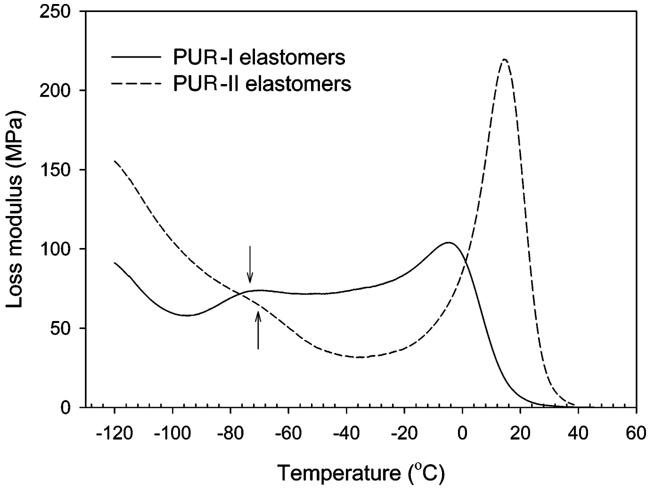

Figure 6. Changes in the loss (E'') moduli with temperature, obtained from DMA carried out at frequency of 1 Hz.

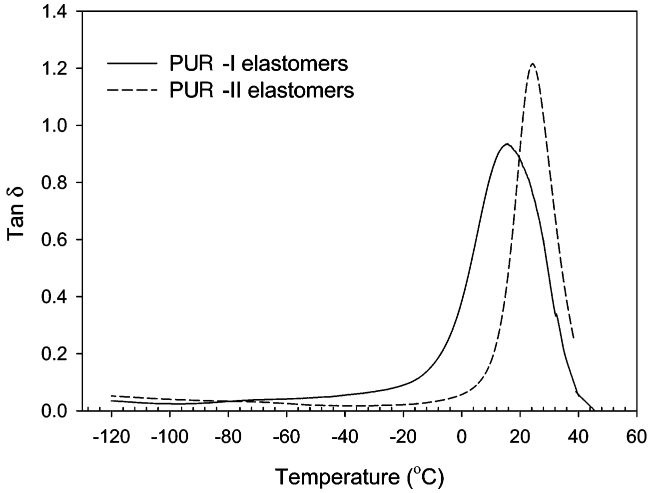

Figure 7. Temperature dependence of tangent δ (tan δ) of PUR elastomers measured by DMA.

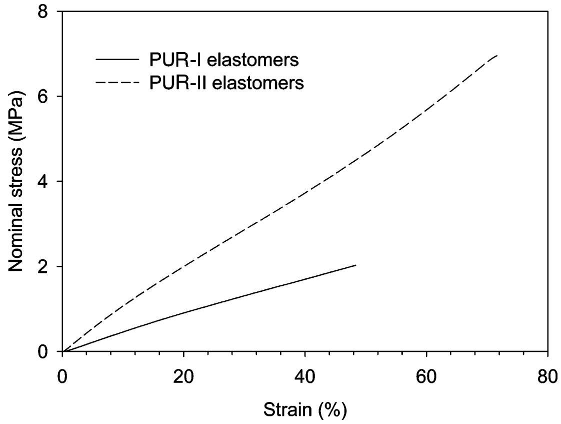

Figure 8. Stress vs strain curves for the PUR elastomers.

urethane group attached to cross-linker[25] or to the motion of the backbone chain of the short groups in the fatty acid chains.[26] The β-transition has also been detected in other PURs[11−13] as well. In the case of PUR-II elastomers, the strong peak in the loss modulus curve, which is associated with glass transition, appears to be narrower, indicating a narrower distribution of network structures.

The network homogeneity for each PUR may also be analyzed from the width of glass transition peaks in tangent δ (tan δ) curves.[27] The temperature dependence of tan δ from DMA for PUR elastomers is shown in Figure 7. The full width at half-maximum (fwhm) of the tan δ peak for PUR-II elastomers, around 16 °C, is much less than that of PUR-I elastomers, around 28 °C. The broader peak width at half-height of the tan δ peak for PUR-I elastomers indicates a wider distribution of network structures, which is due to the heterogeneities in the molecular weight between cross-link joints resulting from the heterogeneous nature of polyol-I as described previously.

Mechanical Properties of PUR Networks. The stress versus strain curves for PUR elastomers are shown in Figure 8. PUR-II elastomers displayed a higher Young's modulus, higher tensile strength, and larger elongation at break (9.9 ± 0.3 MPa, 6.9 ± 0.1 MPa, and 69 ± 4%, respectively) than those of PUR-I elastomers (5.7 ± 0.2 MPa, 2.1 ± 0.2 MPa, and 44 ± 3%, respectively). Both impurity of the starting products and the presence of material with lower functionality can affect the network structure and, thus, the mechanical properties. PUR-II elastomers exhibited better mechanical properties, which is due to the relatively homogeneous nature of PUR-II polyols and, therefore, the higher ν_e and narrower distribution of the polymer network. Whereas the poorer mechanical properties of PUR-I elastomers are a result of higher sol fraction, the loose network structure and large amount of dangling chains, which are imperfections in the final polymer network, do not support stress when the network is under load.

It is worth pointing out that the strength and strain values of the vegetable oil based PUR elastomers are lower than those of the commercial PUR elastomers currently used in the market.[28] The poor performances of the vegetable oil based PUR elastomers can be attributed mainly to the structure of the polyols and the type of diisocyanate used. Vegetable oils offer sites for functionality mainly located at carbon 9 and hence produce polyols with functional groups (i.e., hydroxyl groups) located at carbon 9 which limits the length of the chain between two cross-links of their subsequent polyurethane. The use of the aliphatic diisocyanate (HDI), which is weaker than aromatic diisocyanates such as diphenylmethane diisocyanate, also limits the strength and elongation at break. However, the properties could be enhanced with addition of various ingredients in the formulation such as chain extenders or the use of specific types of isocyanate. In addition, it should be indicated that the present study focuses on the development of green PUR based on the proposed novel synthesis method, which could be a potential candidate to replace or partially replace petroleum-based PUR in the market. To this end, further studies on their various properties and functionalities, in particular, comparing them with those of petroleum-based PUR, are underway in our laboratory.

Conclusions

Generation-II polyol with higher hydroxyl value and triol content was synthesized, and the corresponding PUR elastomers were prepared by reacting this type of polyol with HDI. By comparing with the PUR elastomers prepared from generation-I polyol, this PUR elastomers displayed a higher T_g, a larger ν_e, a smaller M_c, a higher tensile strength, and a longer elongation at break. The relatively faster relaxation at higher temperature for the generation-II PUR elastomers suggests a tighter cross-linked network structure with narrower distribution by lowering the dangling chains effect.

Acknowledgment. The authors acknowledge the technical contributions of Mr. Ereddad Kharraz. The financial support of Bunge Oils, NSERC, Alberta Canola Producers Commission, Alberta Agricultural Research Institute, and Alberta Crop Industry Development Fund are gratefully acknowledged.

References and Notes

(1) Szycher, M. *Szycher's Handbook of Polyurethanes*; CRC Press: Boca Raton, FL, 1999.
(2) Narine, S. S.; Yue, J.; Kong, X. Production of polyols from canola oil and their chemical identification and physical properties. *J. Am. Oil Chem. Soc.* **2007**, *84*, 173−179.
(3) Erhan, S. Z. *Industrial Uses of Vegetable Oils*; AOCS Press: Champaign, IL, 2005; Chapter 6.
(4) Javni, I.; Petrovic, Z. S.; Guo, A.; Fuller, R. Thermal stability of polyurethanes based on vegetable oils. *J. Appl. Polym. Sci.* **2000**, *77*, 1723−1734.
(5) Guo, A.; Demydov, D.; Zhang, W.; Petrovic, Z. S. Polyols and polyurethanes from hydroformylation of soybean oil. *J. Polym. Environ.* **2002**, *10*, 49−52.
(6) Hu, Y. H.; Gao, Y.; Wang, D. N.; Hu, C. P.; Zu, S.; Vanoverloop, L.; Randall, D. Rigid polyurethane foam prepared from a rape seed oil based polyol. *J. Appl. Polym. Sci.* **2002**, *84*, 591−597.
(7) Javni, I.; Zhang, W.; Petrovic, Z. S. Soybean oil based polyisocyanurate cast resins. *J. Appl. Polym. Sci.* **2003**, *90*, 3333−3337.
(8) Khoe, T. H.; Otey, F. H.; Frankel, E. N. Rigid urethane foams from hydroxymethylated linseed oil and polyol esters. *J. Am. Oil Chem. Soc.* **1972**, *49*, 615−618.
(9) Kong, X.; Narine, S. S. Physical properties of polyurethanes plastic sheets produced from polyols from canola oil. *Biomacromolecules* **2007**, *8*, 2203−2209.
(10) Lyon, C. K.; Garrett, V. H.; Frankel, E. N. Rigid urethane foams from hydroxymethylated castor oil, safflower oil, oleic safflower oil, and polyol esters of castor acids. *J. Am. Oil Chem. Soc.* **1974**, *51*, 331−334.
(11) Narine, S. S.; Kong, X.; Bouzidi, L.; Sporns, P. Physical properties of polyurethanes produced from polyols from seed oils. I−elastomers. *J. Am. Oil Chem. Soc.* **2007**, *84*, 55−63.
(12) Narine, S. S.; Kong, X.; Bouzidi, L.; Sporns, P. Physical properties of polyurethanes produced from polyols from seed oils. II−foams. *J. Am. Oil Chem. Soc.* **2007**, *84*, 65−72.
(13) Petrovic, Z. S.; Zhang, W.; Javni, I. Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. *Biomacromolecules* **2005**, *6*, 713−719.
(14) Tran, P.; Graiver, D.; Narayan, R. Ozone-mediated polyol synthesis from soybean oil. *J. Am. Oil Chem. Soc.* **2005**, *82*, 653−659.
(15) Goebel, C. G.; Brown, A. C.; Oehlschlaeger, H. F.; Rolfes, R. P. U.S. Patent 2,813,113, 1957.
(16) Neff, W. E.; Mounts, T. L.; Rinsch, W. M.; Konishi, H.; Elagaimy, M. A. Oxidative stability of purified canola oil triacylglycerols with altered fatty-acid compositions as affected by triacylglycerol composition and structure. *J. Am. Oil Chem. Soc.* **1994**, *71*, 1101−1109.
(17) Elfman-Borjesson, I.; Harrod, M. Analysis of non-polar lipids by HPLC on a diol column. *HRC, J. High Resolut. Chromatogr.* **1997**, *20*, 516−518.
(18) Bailey, P. S. The reactions of ozone with organic compounds. *Chem. Rev.* **1958**, *58*, 925−1010.
(19) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(20) James, H. M.; Guth, E. Theory of the increase in rigidity of rubber during cure. *J. Chem. Phys.* **1947**, *15*, 669−683.
(21) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980; Chapter 11.
(22) Plazek, D. J. Effect of crosslink density on creep behavior of natural rubber vulcanizates. *J. Polym. Sci., Part A−2* **1966**, *4*, 745−763.
(23) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Wiley: New York, 1999; Chapter VII.
(24) Krevelen, D. W. V. *Properties of Polymers*; Elsevier: Amsterdam and New York, 1997; Chapter 7.
(25) Czech, P.; Okrasa, L.; Boiteux, G.; Mechin, F.; Ulanski, J. Polyurethane networks based on hyperbranched polyesters: Synthesis and molecular relaxations. *J. Non-Cryst. Solids* **2005**, *351*, 2735−2741.
(26) Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*, 2nd ed.; Marcel Dekker: New York, 1994; Chapter 4.
(27) Son, T. W.; Lee, D. W.; Lim, S. K. Thermal and phase behavior of polyurethane based on chain extender, 2,2-bis-[4-(2-hydroxyethoxy)-phenyl]propane. *Polym. J.* **1999**, *31*, 563−568.
(28) Vermette, P.; Griesser, H. J.; Laroche, G.; Guidoin, a. R. *Biomedical Applications of Polyurethanes*; Landes Bioscience: Georgetown, TX, 2001; Chapter 1.

BM0704018