J Amer Oil Chem Soc (2007) 84:55–63
DOI 10.1007/s11746-006-1006-4

ORIGINAL PAPER

Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: I. Elastomers

Suresh S. Narine · Xiaohua Kong · Laziz Bouzidi · Peter Sporns

Abstract Polyols synthesized by ozonolysis and hydrogenation from canola oil were reacted with aliphatic 1,6-hexamethylene diisocyanates (HDI) to produce polyurethane (PU) elastomers. The properties of the materials were examined by dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), modulated differential scanning calorimetry (MDSC), and thermogravimetric analysis (TGA), and measurements were taken of tensile properties. The effect of dangling chains on network properties was assessed. The formation of hydrogen bonds was observed by FTIR. The measured properties were found to be strongly dependent on processing-dependent factors such as the crosslinking density and the molar ratio of polyols to HDI component. The glass transition temperatures (T_g) of the elastomers were found to increase as the OH/NCO molar ratio decreased. With the same OH/NCO molar ratio, T_g of canola-oil-based PU was higher than that of soybean-oil-based PU. The TGA thermographs showed two well-defined steps of degradation for all the elastomers. In the first step, up to 30% weight loss, the fastest rate of loss was found at 345 °C for canola-oil-based PU while soybean-oil-based PU lost most of the weight in the second step. With the same OH/NCO molar ratio, the elastomers made from canola-oil-based polyol showed slightly higher Young's modulus and tensile strength.

Keywords Canola oil · Soybean oil · Mechanical properties · Polyurethane elastomers · Polyols · Thermal properties

Introduction

Increasing concerns about the environment and sustainability are fueling a growing worldwide research effort devoted to understanding and using renewable resources. The aim is to reduce the dependence on fossil fuels, which are rapidly being exhausted [1, 2], and to develop innovative technologies and competitive industrial products. Vegetable oils are abundant and cheap renewable resources which represent a major potential alternative source of chemicals suitable for developing safe environmentally and consumer-friendly products.

Plant oils mainly consist of triacylglycerols (TAGs), which can be processed into high-value biochemicals for various industries [3]. In polymer applications, the conversion of oilseed crops into bioplastics could be a sustainable alternative which could compete with plastics obtained from petroleum chemicals. Certain grades of vegetable oils and their derivatives, such as polyol products, are already utilized industrially as an alternative feedstock to produce additives or components for composites or polymers [4]. In recent years, naturally functionalized triglyceride oils [5, 6] as well as vegetable oil polyols [7–10] have attracted attention for providing source materials for a multitude of plastic products, including various PUs. It has been already shown that PUs produced using vegetable oils such as soybean oil present some excellent properties such as enhanced hydrolytic and thermal stability [11]. However, the

S. S. Narine (✉) · X. Kong · L. Bouzidi ·
P. Sporns
Alberta Lipid Utilization Program,
Department of Agricultural Food and Nutritional Science,
4–10 Agriculture/Forestry Centre, University of Alberta,
Edmonton, AB T6G 2P5, Canada
e-mail: suresh.narine@ualberta.ca

hydroxyl groups of these commercial polyols are located in the middle of the fatty acid chain. The pendant chains act as dangling chains when these polyols are crosslinked with isocyanate, resulting in significant steric hindrance to further crosslinking. Recently, a method using ozone to cleave and oxidize the double bonds in the vegetable oil and then reduce the ozonides to polyols using various reducing catalysts has been developed [12]. Polyols prepared by this method (Narine SS, Yue J, Kong X, 2006, *Production of polyols from canola oil and their chemical identification and physical properties*, submitted to J Am Oil Chem Soc) have terminal primary hydroxyl groups, which remove part of the plasticizing effect in subsequent PU networks.

This paper reports on the properties of PU elastomers prepared by reacting polyols synthesized using ozonolysis and hydrogenation-based technology from canola oil with aliphatic diisocyanates and compared to elastomers made from commercial soybean-based polyols. The structural differences between the starting materials—canola polyol have terminal functional groups and soybean-based polyols have OH groups in the middle of the chain—allowed us to evaluate the effects of dangling chains on the properties of the elastomers. The physical and thermal properties of the PUs were studied and compared using dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), modulated differential scanning calorimetry (MDSC) and thermogravimetric analysis (TGA) techniques.

Experimental Procedures

Materials

The canola-oil-based polyols used in this study have been 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 as catalyst. The technology and the polyol used in this study have been described in detail elsewhere (Narine SS, Yue J, Kong X, 2006, *Production of polyols from canola oil and their chemical identification and physical properties*, submitted to J Am Oil Chem Soc). The polyol consisted of triol, diol, mono-ol and saturated TAGs. The chemical structures of the polyol components (triol, diol and mono-ol) are shown in Fig. 1. The components of the polyol have been identified by FTIR, ^{1}H-NMR and mass spectrometry, and quantified using an HPLC analysis protocol developed in our laboratory based on the HPLC procedure developed by Elfman-Borjesson and Harrod [13] for the analysis of lipid derivatives. The mass contents of triol, diol and mono-ol of the polyol were about 22, 38 and 26%, respectively. The percent conversion of canola oil into triol, diol and mono-ol mixture was 87%. The soybean-oil-based polyol was sourced from Urethane Soy Systems Company, IL, USA. The aliphatic 1,6-hexamethylene diisocyanate (HDI, Desmodur N-3200) was sourced from Bayer Corporation, Pittsburgh, PA, USA. The hydroxyl number of the polyols was determined according to the ASTM D1957-86 and the acidity values were determined according to the

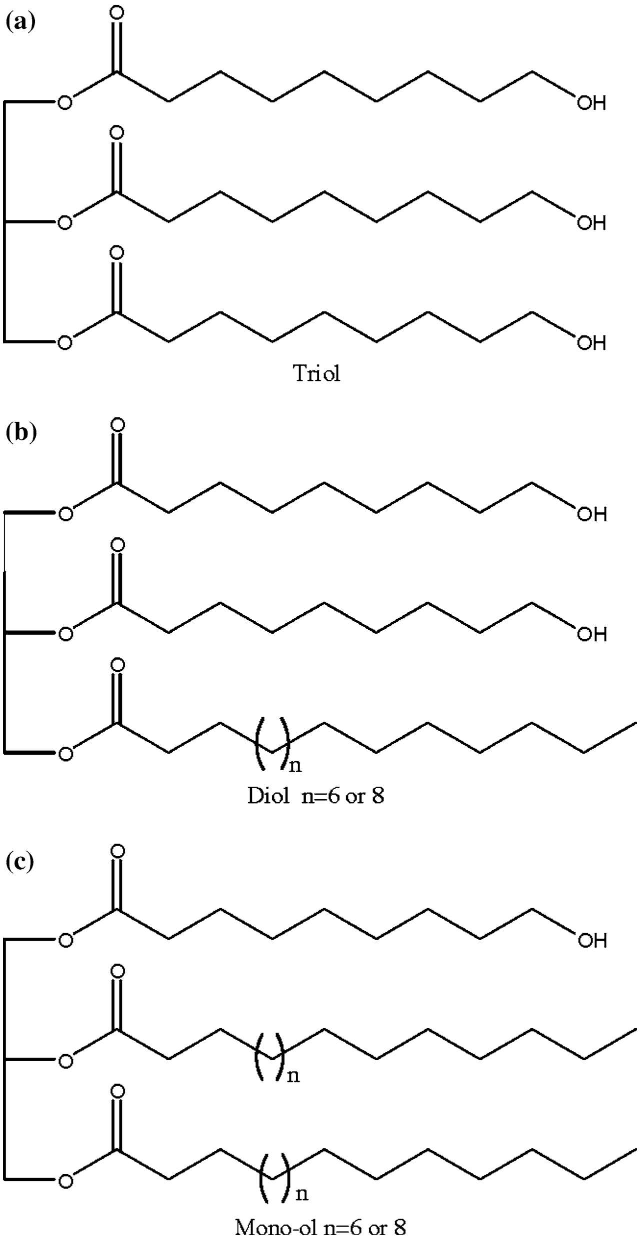

Fig. 1 Representative structure of canola-oil-based polyol. **a** Triol, **b** diol and **c** mono-ol

ASTM D4662-98 standard. The results are listed in Table 1. The equivalent weights of the polyols and of the HDI used in this study are listed in Table 1.

Preparation of the Polyurethanes

The elastomers were prepared using three formulations by fixing the molar ratio of the OH group to the isocyanate (NCO) group (M_{ratio}) to 1.0:0.8, 1.0:1.0 and 1.0:1.2. The desired OH/NCO molar ratio satisfies the equation:

$$M_{\mathrm{ratio}} = \frac{W_{\mathrm{polyol}}/\mathrm{EW}_{\mathrm{polyol}}}{\left(W_{\mathrm{PU}} - W_{\mathrm{polyol}}\right)/\mathrm{EW}_{\mathrm{isocyanate}}} \qquad (1)$$

where W_{polyol} is the weight of the polyol, $\mathrm{EW}_{\mathrm{polyol}}$ is the equivalent weights of polyol, W_{PU} is the total weight of PU to produce and $\mathrm{EW}_{\mathrm{isocyanate}}$ is the equivalent weight of the isocyanate.

The equivalent weight for the isocyanate was provided by the supplier and was $\mathrm{EW}_{\mathrm{isocyanate}} = 183$ g/mol. The equivalent weights of polyol were determined using the equation: $\mathrm{EW}_{\mathrm{polyol}} = \frac{\text{molecular weight of KOH}\times 1000}{\text{OH Number}} = \frac{56110}{\text{OH Number}}$ g per mole of hydroxyl groups.

The weight of the polyol and isocyanate were calculated using the above-calculated equivalent weight.

The elastomers produced are referred to as canola-oil-based PU (COBPU) and soybean-oil-based PU (SOBPU), when prepared using canola- and soybean-oil-based polyols, respectively.

A suitable amount 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. After this time, the sample was very viscous and tacky. Air was then introduced to the oven to avoid the deformation of the sample under vacuum, and the sample was postcured for about 48 h at 40–45 °C. The sample was 2 mm thick and ready for mechanical and thermal mechanical properties tests.

Table 1 Parameters for the polyols and diisocyanate used. *Errors* are standard deviations; $n = 3$

	Equivalent weight (g/mol)	OH number (mg KOH/g)	Acidity number (mg KOH/g)
Canola oil-based polyol	368	152.4 ± 0.3	22.9 ± 0.3
Soybean oil-based polyol	902	62.2 ± 2.7	7.67 ± 0.05
HDI	183		

FTIR

The FTIR spectra were recorded on a Nicolet Magna 750 FTIR (Nicolet Instrument Corp., Madison, WI, USA), equipped with an MCT-A detector and a Nicolet Nic-Plan IR microscope used in transmission mode. The spectra were recorded in the range 650–4,000 cm^{-1} with a nominal resolution of 4 cm^{-1}. A background spectrum was collected before each absorbance spectrum was recorded. 128 interferograms were coadded before Fourier transformation using the Nicolet Omnic software.

Thermal Properties

DSC measurements were carried out on a TA Instruments (New Castle, DE, USA) MDSC Q100, equipped with a refrigerated cooling system. All the DSC measurements were performed following the ASTM E1356-03 standard. About 10 mg of the samples were heated at a rate of 10 °C/min from –90 to +100 °C under a dry nitrogen gas atmosphere. MDSC measurements were performed with a modulation amplitude of 0.5 °C and a modulation period of 60 s at a rate of 2 °C/min for COBPU.

DMA measurements were carried out on a TA Instruments DMA Q800 equipped with a liquid nitrogen cooling apparatus, in the single cantilever mode, with a constant heating rate of 1 °C/min from –120 to +50 °C. The size of the samples was 18 × 7 × 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 measurements were performed every 5 and 30 °C below and above the glass transition temperature.

A TA Instruments TMA 2940 was used to measure the change in dimensions of the PU elastomers while the material was subjected to a constant heating rate of 5 °C/min through the glass transition from –120 to +150 °C. The measurements were performed according to the ASTM E1545–00 standard. The size of the samples was 5 × 5 × 2 mm. The probe was kept in close contact with the specimen surface. The applied force on the specimen was 0.05 N.

TGA was carried out on a Dupont (Wilmington, DE, USA) 951 Thermogravimetric Analyzer following the ASTM D3850-94 standard. The sample was ground to a powder after chilling with liquid nitrogen and approximately 20 mg of the specimen was loaded into an open platinum pan. The samples were heated from 25 to 600 °C under dry nitrogen at a constant heating rate of 5 °C/min.

Mechanical Properties

The tensile properties of the PU elastomers were measured on an Instron (Norwood, MA, USA) 4202 according to the ASTM D882–97 standard. Dumbbell-shaped specimens were cut out from the PU elastomers using an ASTM D638 Type V cutter. The cross-head speed was 50 mm/min with a load cell of 50 Kgf. At least five identical specimens prepared by cutting the material from a polymer sheet were tested and the results averaged.

All the samples were run in duplicate for thermal property measurements and in sextuplicate for the tensile tests. The reported errors are the subsequent standard deviations.

Results and Discussion

As listed in Table 1, the hydroxyl value (152.4 mg KOH/g) is relatively lower than the maximum value of 251 mg KOH/g theoretically obtainable when producing polyols assuming that all the double bonds in canola oil are cleaved [14]. The content of triol was also not optimal (22% instead of the 75% theoretically possible) and the amounts of mono-ol (26%) and saturated fatty acid (14%) were relatively high. The production of mono-ol and diol is unavoidable since the starting oil contains TAGs (6%) [14] that have a mixture of saturated and unsaturated fatty acids. The abnormally high mono-ol and diol contents could be explained by the difficulty involved in completely converting the reactant in the presence of a medium for ozonolysis such as water which is not miscible with the oil or with the ozonide. Despite the relatively high content of saturated fatty acids, which act as dangling chains when the polyol is crosslinked with isocyanate, the canola-oil-based polyol was still capable of producing PU elastomers with better properties than those prepared from commercial soybean-oil-based polyol. This is attributed to the difference in quantity and nature of the dangling chains present in the polyols. The amount of dangling chains in the COBPU is lower than in SOBPU which lessened the plasticizing effect in subsequent PU networks. On the other hand, the dangling chains in SOBPU, which are located in the middle of the fatty acid chains, resulted in significantly higher steric hindrance to further crosslinking than the dangling chains present in the COBPU.

The FTIR spectra for the two elastomers (COBPU and SOBPU) with an OH/NCO molar ratio of 1.0 are shown in Fig. 2. The –NCO group absorption band centered at 2,270 cm^{-1} is clearly missing, and a strong 3,340 cm^{-1} absorption band characteristic of the N–H group and an absorption band characteristic of the C=O group centered around 1,700 cm^{-1} are present in all the FTIR spectra. FTIR spectra confirmed that almost all of the diisocyanate groups reacted during polymerization and formed urethane linkages and amide groups.

The existence of hydrogen bonds, a very important feature of polyurethanes which has significant effect on material properties, was directly observed in the FTIR spectra, as seen in Fig. 2. The band centered around 1,700 cm^{-1} split into two resolved branched peaks (1,690 and 1,740 cm^{-1}), indicating the presence of hydrogen-bonded urethane carbonyl (C=O) groups [15]. Based on the fact that the wavenumber of the hydrogen-bonded urethane C=O groups is usually lower than that of non-hydrogen-bonded C=O groups [16], the position of the hydrogen-bonded C=O groups was assigned to the 1,690 cm^{-1} wavenumber, and that of non-hydrogen-bonded C=O groups to the 1,740 cm^{-1} wavenumber. Even if rigorous quantitative FTIR analysis is lacking, a comparison of the intensity ratio of the hydrogen-bonded to the non-hydrogen-bonded peaks in COBPU to that of SOBPU elastomers (the

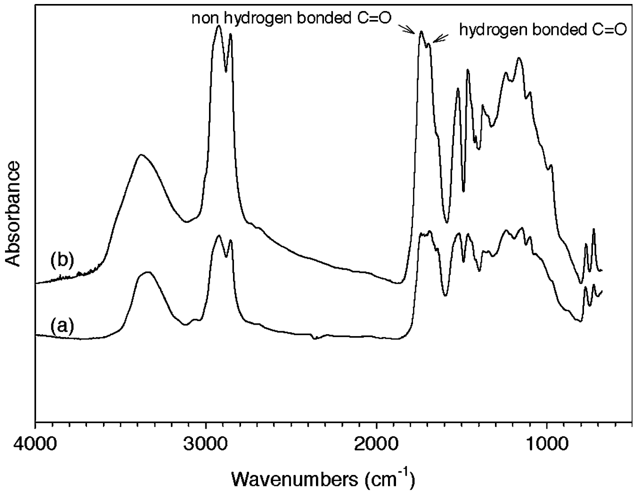

Fig. 2 FTIR spectra of polyurethane elastomers with OH/NCO molar ratio 1.0 (*a*) canola-oil-based polyurethane (COBPU), (*b*) soybean-oil-based polyurethane (*SOBPU*)

ratio was higher for COBPU than for SOBPU elastomer) suggested that more hydrogen bonds may have been formed for COBPU than for SOBPU. The N–H group, another strong proton donor which can form hydrogen bonds, was hard to resolve because its vibration region overlapped with the O–H vibration region (around 3,300 cm^{-1}). In the case of COBPU elastomers, the appearance of a single N–H band at 3,340 cm^{-1} suggested that most of its N–H groups were hydrogen bonded. In the case of SOBPU, a N–H absorption band at 3,400 cm^{-1} with a weak shoulder at even higher wavenumbers (3,500 cm^{-1}) was found, indicating the existence of non-hydrogen-bonded N–H groups. This is due to a steric hindrance effect caused by the large amount of dangling chains in SOBPU, which blocked the formation of hydrogen bonds.

PUs usually undergo phase separation, which results in a hard-segment domain, a soft-segment matrix and an interphase. This is due to the immiscibility between the two components and the strong intermolecular interaction of hydrogen bonding between the hard–hard segments of urethane linkages. It is well-known that hydrogen bonding in PU mixtures is related to phase separation [17]. Qualitatively, a high degree of phase mixing should be expected if hydrogen bonds could be formed between two phases. In the PU networks studied here, the degree of phase mixing is high, as indicated by the observation of only one glass transition (T_g). This will be discussed in detail later. The T_g of the COBPU samples with different molar ratios were measured using three methods: TMA, MDSC and DMA. The results are reported in Table 2. Figure 3 shows the reversing heat flow versus temperature curves obtained for COBPU with different molar ratios. The T_g values were determined from the shift of heat capacity with temperature. Typical TMA curves of COBPU elastomers with different molar ratios are shown in Fig. 4. The T_g values were determined from the intersect of the tangent to the low-temperature thermal expansion side with the tangent to the thermal-expansion side of the curve beyond the transition. Only one T_g was detected in all of the PU elastomers in the case of TMA and MDSC methods. The T_g values determined from TMA were lower than for DMA and MDSC but the trend was the same: T_g increased with decreasing OH/NCO molar ratio.

Table 2 T_g values (°C) for canola-oil-based polyurethane elastomers (COBPU), as obtained by DMA, TMA and MDSC

Molar ratio (OH/NCO)	Canola-oil-based PU elastomers		
	DMA	TMA	MDSC
1:0.8	–11	–26	–20
1:1	–8	–17	–15
1:1.2	–5	–14	–9

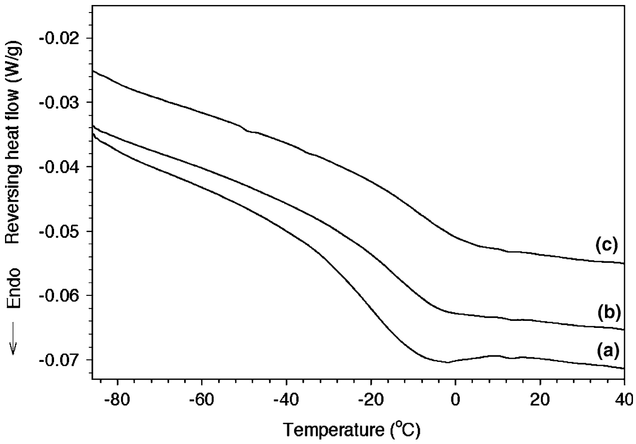

Fig. 3 Reversing heat flow vs. temperature for canola-oil-based polyurethane (*COBPU*) elastomers with different OH/NCO molar ratios. (*a*) OH/NCO = 1.0/0.8, (*b*) OH/NCO = 1.0/1.0, (*c*) OH/NCO = 1.0/1.2

The determination of the glass transition is not unique because it is both thermodynamic and kinetic in nature [18]. The measured glass transition temperature is dependent upon the physical property measured, the type of measuring apparatus and the experimental parameters used. Changes in heat capacity, viscosity, dielectric relaxation, or thermal expansion coefficients used to probe the shift from the glassy to the rubbery states could yield very different T_g values [19]. DSC is very sensitive to any additional phenomenon that occurs near the T_g process, and its evaluation is affected [20]. The temperature variation rate also has a direct

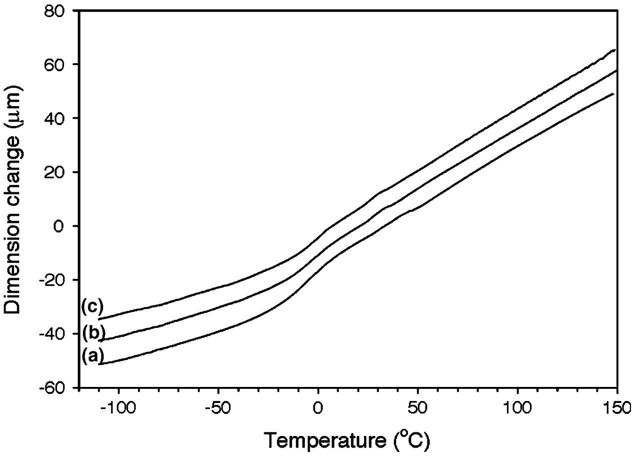

Fig. 4 Thermomechanical analysis curves of canola-oil-based polyurethane (*COBPU*) elastomers with different OH/NCO molar ratios. (*a*) OH/NCO = 1.0/0.8, (*b*) OH/NCO = 1.0/1.0, (*c*) OH/NCO = 1.0/1.2

influence on the heat capacity, especially at T_g, with heat transfer effects complicating the process [21]. Standard DSC often provides only a weak indication of T_g and sometimes does not reveal its existence at all, as our measurements have shown (data not provided). MDSC, however, minimizes this problem by providing not only the total heat flow signal but also the heat capacity and its kinetic components. The total heat flow is divided into *reversing heat flow* and *nonreversing heat flow*. Reversing heat flow is the heat capacity component of the total heat flow and is calculated by converting the measured heat capacity into a heat flow signal using the classical heat flow equation as a theoretical basis. As a result, T_g can be determined from the reversing heat flow signal [22]. While TMA does not always show a clear glass transition (as shown in the imprecision in our TMA determination of T_g, mentioned above), it does however yield repeatable measurements associated with T_g [23]. DMA is very sensitive to the glass transition because the mechanical properties (such as modulus and damping) measured by DMA depend strongly on the material's relaxation time, which undergoes large changes during the glass transition [24]. It provides the most credible information on changes that occur during glass transition and therefore is well suited to measuring T_g. The DMA traces are frequency-dependent but yield unambiguous peaks for T_g.

Figure 5 shows the evolution with temperature of the storage moduli (E') of the COBPU and SOBPU elastomers with OH/NCO molar ratios of 1.0 and illustrates typical dynamic mechanical behavior for our samples. At the same temperature, E' of SOBPU is much lower than that of COBPU. The T_g of the SOBPU (–43 °C as determined by DMA) was also lower than that of COBPU. A weak transition at about –80 °C was also observed for all our samples, as illustrated by the first peak in the loss moduli curves (arrows in Fig. 6). The identification of this peak is not clear. Such transitions have usually been identified as the β-transition, which is related to the movements of a chain section containing the urethane group attached to a crosslinker [25] or to the motion of the backbone chain of the short groups in the fatty acid chains [26]. However, due to the existence of hydrogen bonds in all of the studied PU networks as mentioned earlier, the occurrence of phase separation was inevitable and the transition could be related to the T_g of a soft-segment phase caused by a weak phase separation. The weakness of the degree of the phase separation is also evidenced by TMA and MDSC, which detected only one T_g. The T_g values of crosslinked PUs are affected by several factors, including the relative amounts of the soft and hard segments, the crosslinking density, and the amount of hydrogen bonding. The T_g value for the SOBPU was much lower than that for the COBPU sample. This is probably due to a smaller amount of hydrogen bonding in SOBPU compared to COBPU and the presence of a large amount of dangling chains in SOBPU networks resulting from the hydroxyl groups being located in the middle of the chains. The elastic behavior of polymer networks can be described by the following equation [27]:

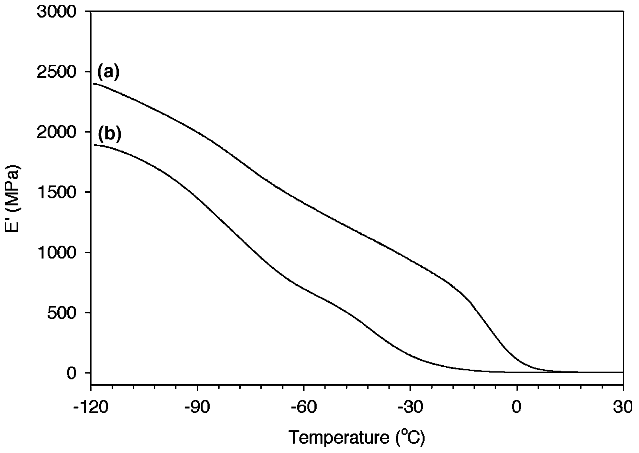

Fig. 5 Storage moduli for polyurethane elastomers with OH/NCO molar ratios of 1.0, (*a*) canola-oil-based polyurethane (*COBPU*), (*b*) soybean-oil-based polyurethane (*SOBPU*)

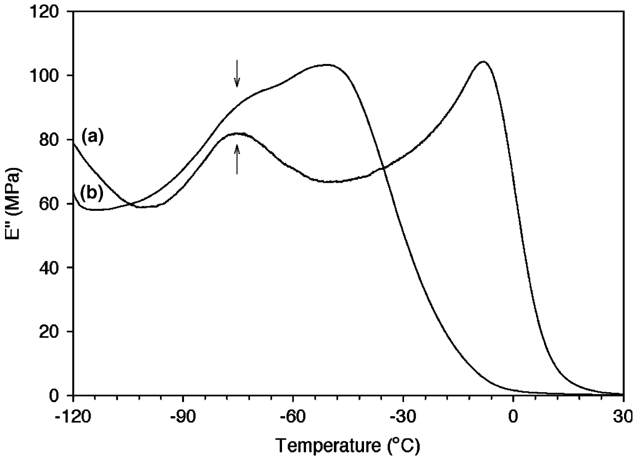

Fig. 6 Loss moduli for polyurethane elastomers with OH/NCO molar ratios of 1.0, (*a*) canola-oil-based polyurethane (*COBPU*), (*b*) soybean-oil-based polyurethane (*SOBPU*)

$$G' = \frac{E'}{3} = v_e RT \tag{2}$$

where G' is the shear storage modulus, R the gas constant, v_e the crosslinking density, and T the absolute temperature. Using the time–temperature superposition principle [28], it is possible to characterize the viscoelastic behavior of a polymer at various temperatures over an experimentally unapproachable time or temperature range. Isothermal oscillation measurements were performed in the T_g region. The isothermal storage moduli (E') were obtained as a function of frequency. The curves obtained at different temperatures were superposed in the standard manner into respective master curves using the time–temperature superposition principle. The extended frequency range obtained by the superposition was 10^{-5} to 10^9 Hz. The pseudo-equilibrium modulus of the crosslinking network, G', is related to v_e through Eq. 2. The values of v_e obtained for COBPU are 2.7×10^2 M/m^3, 5.9×10^2 M/m^3 and 8.4×10^2 M/m^3, for OH/NCO molar ratios of 1.0/0.8, 1.0/1.0 and 1.0/1.2, respectively. This indicates that the flexibility of the polymer chains was reduced in the higher crosslinked networks, increasing the T_g and thus shifting the rubbery state to higher temperatures. As listed in Table 2, T_g for COBPU increased with decreasing OH/NCO molar ratio. This trend is consistent with what has been reported by Petrovic et al. [29]. At low OH/NCO molar ratio, the PUs exhibit a higher T_g because the excess NCO groups continue to react with the existing urethane groups and form more crosslinked structures, resulting in larger v_e values. On the other hand, when OH/NCO > 1, the excess OH groups may act as a plasticizer and decrease T_g.

TGA curves of the PU elastomers with OH/NCO molar ratios of 1.0 and their derivatives (DTGA) are shown in Fig. 7a and b, respectively. All the decompositions started at approximately 160 °C. Weight loss was very gradual until 300 °C, where a rapid drop followed and ended at approximately 490 °C. The shapes of the weight loss curves of both PUs were similar in the temperature range of 160–300 °C and different in the 300–400 °C temperature range. DTGA data (Fig. 7b) reveal two main degradation processes, one correlated with the first 25–30% of the weight loss, and the second with the remaining weight loss. COBPU had its fastest rate of loss at 345 °C, and SOBPU had its fastest rate of loss at 430 °C. SOBPU lost most of the weight in the second step, while COBPU lost around 25% of the weight in the first step.

It is known that the first stage of degradation is dominated by urethane bond decomposition and that the amount of residue is correlated with the amount of unreacted isocyanate in polymers [30]. Javni et al. [31] have found that although the early stage of degradation is dominated by urethane bond decomposition, the

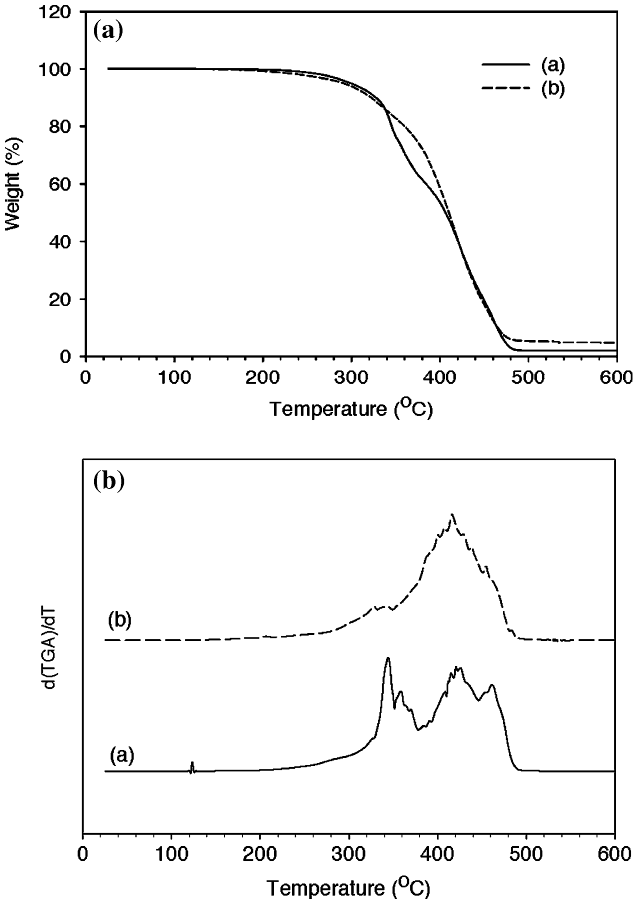

Fig. 7a–b **a** TGA curves for polyurethane elastomers with OH/NCO molar ratios of 1.0, (*a*) canola-oil-based polyurethane (*COBPU*), (*b*) soybean-oil-based polyurethane (*SOBPU*). **b** Derivative TGA curves for polyurethane elastomers with OH/NCO molar ratios of 1.0 (*a*) COBPU, (*b*) SOBPU

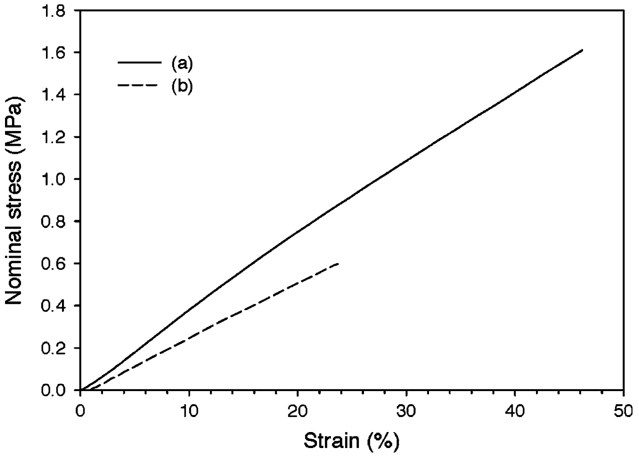

Fig. 8 Nominal stress–strain of polyurethane elastomers with OH/NCO molar ratios of 1.0, (*a*) canola-oil-based polyurethane (*COBPU*), (*b*) soybean-oil-based polyurethane (*SOBPU*)

Table 3 Mechanical properties of polyurethane elastomers at various OH/NCO molar ratios. *Errors* are standard deviations, $n = 5$

	Molar ratio (OH/NCO)	Young's modulus (MPa)	Strength at break (MPa)	Strain at break (%)
Canola-based polyol/HDI	1:0.8	3.08 ± 0.07	1.00 ± 0.05	41.6 ± 3.9
	1:1	4.82 ± 0.15	1.58 ± 0.13	43.1 ± 3.2
	1:1.2	5.71 ± 0.18	2.09 ± 0.17	44.3 ± 3.3
Soybean-based polyol/HDI	1:0.8	1.51 ± 0.04	0.29 ± 0.06	26.4 ± 0.8
	1:1	2.80 ± 0.23	0.55 ± 0.04	22.9 ± 2.3
	1:1.2	3.32 ± 0.26	0.63 ± 0.04	22.4 ± 0.6

polyol component may contribute to the weight loss at higher conversions, causing an increase in activation energy. This suggests that the first step in the COBPU loss is likely due to a higher conversion of –NCO groups to urethane bonds compared to that in SOBPU samples.

The stress versus strain curves for the PU elastomers with an OH/NCO molar ratio of 1.0:1.0 are shown in Fig. 8. Mechanical properties of PU elastomers obtained for the three OH/NCO molar ratios are summarized in Table 3. Young's modulus and tensile strength at break increased with increasing diisocyanate content, which are well-known features in urethanes. With the same OH/NCO molar ratio, COBPU has a higher Young's modulus and tensile strength at break and a larger elongation. The higher strength and modulus of COBPU are due to its high hydrogen bond content and its high density of crosslinks, which hinder molecular motion, while the lower strength and modulus of SOBPU is a result of the large amount of dangling chains present, which are imperfections in the final polymer network, and do not support stress when the network is under load.

The poor performances of the polyurethane elastomers can mainly be explained by the structures of the polyols and the type of diisocyanate used. The low triol and high mono-ol and saturated fatty acid contents of the canola-oil-based polyols resulted in relatively low crosslinking densities. Mono-ol in the polyols acts as a chain terminator when polyols are crosslinked with diisocyanate. Furthermore, 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 crosslinks of their subsequent polyurethane. The use of the aliphatic diisocyanate (HDI), which is weaker than aromatic diisocyanates such as MDI, also limits the strength and elongation at break.

Acknowledgements The authors acknowledge the technical contributions of Mr. Ereddad Kharraz. The financial support of NSERC, Bunge Corp., AVAC Ltd. and Archer Daniels Midland are gratefully acknowledged.

References

1. Sperling LH, Manson JA (1983) Interpenetrating polymer networks from triglyceride oils containing special functional groups—a brief review. J Am Oil Chem Soc 60:1887–1892
2. Sperling HL, Manson JA, Linne MA (1984) Simultaneous interpenetrating networks prepared from special functional group triglyceride oils: castor oil, *Lesquerella palmeri* and other wild plant oils. J Polym Mater 1:54–67
3. Pryde EH, Princen LH, Mukherjee KD (eds) (1981) New sources of fats and oils (American Oil Chemists Society Monograph no. 9). American Oil Chemists Society, Champaign, IL
4. Nayak PL (2000) Natural oil-based polymers: opportunities and challenges. J Macromol Sci Rev Macromol Chem Phys C 40:1–21
5. Barrett LW, Sperling LH, Murphy CJ (1993) Naturally functionalized triglyceride oils in interpenetrating polymer networks. J Am Oil Chem Soc 70: 523–534
6. Carlson KD, Chang SP (1985) Chemical epoxidation of a natural unsaturated epoxy seed oil from *Vernonia galamensis* and a look at epoxy oil markets. J Am Oil Chem Soc 62:934–939
7. Khoe TH, Otey FH, Frankel EN (1972) Rigid urethane foams from hydroxymethylated linseed oil and polyol esters. J Am Oil Chem Soc 49:615–618
8. Hu YH, Gao Y, Wang DN, Hu CP, Zu S, Vanoverloop L, Randall D (2002) Rigid polyurethane foam prepared from a rape seed oil based polyol. J Appl Polym Sci 84:591–597
9. Dwan'Isa LJP, Mohanty AK, Misra M, Drzal LT, Kazemizadeh M (2003) Novel biobased polyurethanes synthesized from soybean phosphate ester polyols: thermomechanical properties evaluations. J Polym Environ 11:161–168
10. Guo A, Demydov D, Zhang W, Petrovic ZS (2002) Polyols and polyurethanes from hydroformylation of soybean oil. J Polym Environ 10:49–52
11. Zlatanic A, Petrovic ZS (2002) Viscoelastic properties of polyurethanes based on model triglycerides. Abstr Pap Am Chem Soc 223:D77–D77
12. Petrovic ZS, Zhang W, Javni I (2005) Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. Biomacromolecules 6:713–719
13. Elfman-Borjesson I, Harrod M (1997) Analysis of non-polar lipids by HPLC on a diol column. J High Res Chromatog 20:516–518
14. Neff WE, Mounts TL, Rinsch WM, Konishi H, Elagaimy MA (1994) Oxidative stability of purified canola oil triacylglycerols with altered fatty-acid compositions as affected by triacylglycerol composition and structure. J Am Oil Chem Soc 71:1101–1109
15. Yu TL, Lin TL, Tsai YM, Liu WJ (1999) Morphology of polyurethanes with triol monomer crosslinked on hard segments. J Polym Sci Pol Phys 37:2673–2681

16. Coleman MM, Lee KH, Skrovanek DJ, Painter PC (1986) Hydrogen bonding in polymers: 4. Infrared temperature studies of a simple polyurethane. Macromolecules 19:2149–2157
17. Hepburn C (1982) Polyurethane elastomers. Applied Science, London
18. McKenna GS (1989) In: Booth C, Price C (eds) Comprehensive polymer science: the synthesis, characterization, reactions, and applications of polymers. Vol 2: Polymer properties. Pergamon, Oxford, pp 311–362
19. Eisenberg A (1993) Physical properties of polymers. American Chemical Society, Washington, DC, pp 61–96
20. Hutchinson JM (1998) Characterising the glass transition and relaxation kinetics by conventional and temperature-modulated differential scanning calorimetry. Thermochim Acta 324:165–174
21. Hutchinson JM (2003) Studying the glass transition by DSC and TMDSC. J Therm Anal Calorim 72:619–629
22. Wunderlich B (2004) The tribulations and successes on the road from DSC to TMDSC in the 20th century and the prospects for the 21st century. J Therm Anal Calorim 78:7–31
23. Khandare PM, Zondlo JW, Pavlovic AS (1996) The measurement of the glass transition temperature of mesophase pitches using a thermomechanical device. Carbon 34: 663–669
24. Williams RJ (1994) Methods for determination of glass transitions in seeds. Ann Bot 74:525–530
25. Czech P, Okrasa L, Boiteux G, Mechin F, Ulanski J (2005) Polyurethane networks based on hyperbranched polyesters: synthesis and molecular relaxations. J Non-Cryst Solids 351:2735–2741
26. Nielsen LE, Landel RF (1994) Mechanical properties of polymers and composites, 2nd edn. Marcel Dekker, New York, Ch 4
27. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca, NY
28. Ferry JD (1980) Viscoelastic properties of polymers. Wiley, New York, Ch 11
29. Petrovic ZS, Zhang W, Zlatanic A, Lava CC, Ilavsky M (2002) Effect of OH/NCO molar ratio on properties of soy-based polyurethane networks. J Polym Environ 10:5–12
30. Petrovic ZS, Zavargo Z, Flynn JH, Macknight WJ (1994) Thermal degradation of segmented polyurethanes. J Appl Polym Sci 51:1087–1095
31. Javni I, Petrovic ZS, Guo A, Fuller R (2000) Thermal stability of polyurethanes based on vegetable oils. J Appl Polym Sci 77:1723–1734