

Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: II. Foams

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

Received: 8 February 2006 / Accepted: 26 October 2006 / Published online: 12 December 2006
© AOCS 2006

Abstract Rigid polyurethane (PU) foams were prepared using three North American seed oil starting materials. Polyol with terminal primary hydroxyl groups synthesized from canola oil by ozonolysis and hydrogenation based technology, commercially available soybean based polyol and crude castor oil were reacted with aromatic diphenylmethane diisocyanate to prepare the foams. Their physical and thermal properties were studied and compared using dynamic mechanical analysis and thermogravimetric analysis techniques, and their cellular structures were investigated by scanning electron microscope. The chemical diversity of the starting materials allowed the evaluation of the effect of dangling chain on the properties of the foams. The reactivity of soybean oil-derived polyols and of unrefined crude castor oil were found to be lower than that of the canola based polyol as shown by their processing parameters (cream, rising and gel times) and FTIR. Canola-PU foam demonstrated better compressive properties than Soybean-PU foam but less than Castor-PU foam. The differences in performance were found to be related to the differences in the number and position of OH-groups and dangling chains in the starting materials, and to the differences in cellular structure.

Keywords Canola oil · Castor oil · Mechanical and thermal properties · Polyurethanes · Polyols · Rigid foams from plant oils · Soybean oil

Introduction

Rigid polyurethane (PU) foams are used for many engineering applications, such as insulation materials, automotive parts, and structural materials [1, 2]. The production of PU foams is based on the reaction of organic isocyanates with polyols. Currently, both starting materials are mostly derived from petrochemical resources. As natural resources become scarce, many researchers and industries are beginning to investigate and utilize various renewable resources [3–8] such as the abundant and cheap vegetable oils.

In polymer industry, vegetable oils which represent a major potential source of chemicals have been utilized as an alternative feedstock for monomers. PU foams made from castor oil have existed for many years [4]. Other oils such as soybean oil- and rapeseed oil-based polyols have been used to make PU foams as well [7, 9]. Due to the hydrophobic nature of the triacylglycerols (TAG), the predominant component in vegetable oils, the produced polymers have some excellent chemical and physical properties such as enhanced hydrolytic and thermal stability [10]. However, most vegetable oil-based polyols currently utilized to produce PU foams have their hydroxyl groups located in the middle of the TAG's alkyl chains. Upon crosslinking these polyols, the pendant, or dangling chains, are unsupported which significantly limits the rigidity of the PU polymers [9]. Significant steric hindrance to cross-

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,
T6G 2P5 Edmonton, AB, Canada
e-mail: Suresh.narine@ualberta.ca

linking (especially by bulky aromatic diisocyanates) is introduced by the –OH groups when located in the middle of the fatty-acid moieties. Moreover, these dangling chains which are imperfections in the final polymer network, do not support stress if the network is under load and can act as a plasticizer thereby reducing polymer rigidity while increasing its flexibility.

In the present work, we report on rigid PU foam prepared using polyol from North American vegetable oils and on their properties. Polyol with terminal primary hydroxyl groups synthesized from canola oil by ozonolysis and hydrogenation based technology was used as a model system to prepare such materials. It was compared to rigid foams made from commercially available soybean based polyol and from unrefined crude castor oil. The chemical diversity of the starting materials allowed the evaluation of the effect of dangling chains on the properties of the foams. The physical and thermal properties of the foams were studied and compared using dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) techniques, and their cellular structures were investigated by scanning electron microscope (SEM).

Experimental Procedures

Materials

Polyol with terminal primary functional groups at position nine of each fatty acid ester in the original TAG has been successfully synthesized from canola oil using a technology based on ozonolysis and hydrogenation. Its composition was determined by an HPLC analysis protocol developed in our laboratory based on the HPLC procedure developed by Elfman-Borjesson and Harrod [11] for analysis of lipid derivatives. The polyol contained about 27, 39, and 23% (on a molar basis) of triol, diol, and mono-ol, respectively. The remaining 11% (mol) were saturated TAGs. The total saturated fatty acid content, considering an average molecular weight, was approximately 40% (mol). For a detailed characterization of the canola polyol used for this study, the reader is referred to S.S. Narine et al., *Production of Polyols from Canola Oil and their Chemical Identification and Physical properties*, submitted to JAOCS, (2006). Soybean based polyol produced by epoxidation and hydroxylation based technology, was sourced from Urethane Soy Systems Co. Inc., Princeton, IL. (USA) and unrefined crude castor oil was obtained from

CasChem Company, NJ. (USA). The chemical structures of canola and soybean based polyols [12] and castor oil are shown in Fig. 1. The aromatic diphenylmethane diisocyanate (MDI, Mondur MRS) was sourced from Bayer Corporation, Pittsburgh, PA, USA. Its NCO content was 31.5 Wt % and its functionality was 2.6 as provided by the supplier. The hydroxyl number of the polyols was determined according to the ASTM D1957-86 and the acidity values were determined according to the ASTM D4662-98 standard. The crude MDI index was fixed to 1.2. The equivalent weight, OH number and acidity number of the polyols and the equivalent weight of MDI are listed in Table 1. Dibutyl Dilaurate (DBTDL), 95%, from Aldrich Chemical (USA) was used as the main catalyst, *N,N*-Dimethylethanolamine (DMEA), 99.5%, from Aldrich Chemical (USA) as the co-catalyst, glycerin (99.5%) from Fisher Chemicals (USA) as crosslinker agents and distilled water as blowing agent. The surfactant was Tegostab B-8404 (100%) from Goldschmidt Chemical, Canada.

Preparation of the Polyurethane Foams

The formulation to prepare the foams was chosen so that the final hydroxyl number is between 450 and 500 mg KOH/g in order to obtain a rigidity that is close to what was commonly used for foams prepared from vegetable oils based polyols and found in the literature [9]. Because the hydroxyl number of our starting materials was too low, glycerin, a hydroxyl containing crosslinker, and water were added to attain the desired hydroxyl number. In Soybean oil based PU system, 15 parts of glycerin and 2 parts of water were added while 12 parts of glycerin and 3 parts of water were added in Canola and Castor oil based PU foams.

The detailed foam formulation is shown in Table 2. The polyol was first mixed during 2 min in a plastic container with suitable amounts of crosslinkers, catalyst, and surfactant. MDI was added and the mixture was stirred vigorously at 1,500 rpm for 40 s in the case of Canola and Castor oil based PU foams and for 90 s in the case of Soybean oil based PU foams. The mixture was then poured into a home-made Teflon mold which was previously greased with silicon release agent and sealed with a hand-tightened clamp. After the completion of the reaction, the sample was post cured at room temperature for 4 days. Cream time, rising time and gel time are reported in Table 3.

The produced PU foams are referred to as Canola-PU, Castor-PU and Soybean-PU for the Canola oil based PUs, Castor oil based PUs and Soybean oil based PUs, respectively.

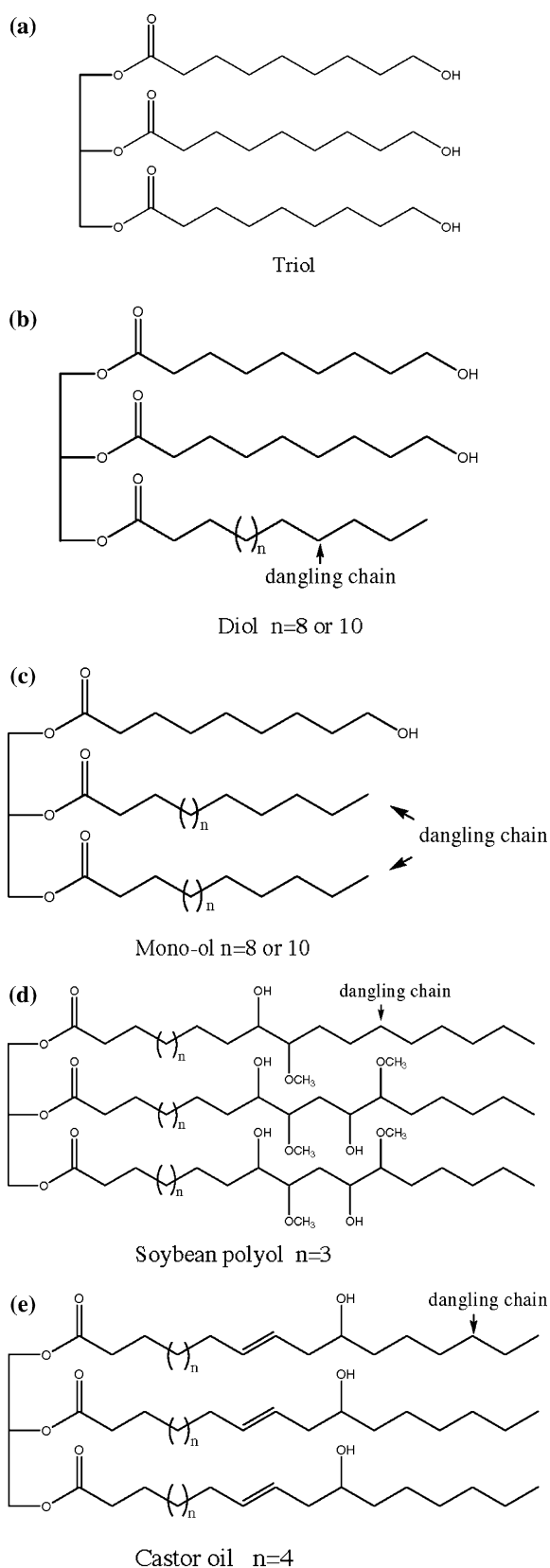


Fig. 1 Representative structures of the components of canola based polyol (**a** triol, **b** diol, **c** mono-ol), **d** representative structure of soybean based polyol and **e** castor oil structure

Table 1 Parameters of the used polyols and diisocyanate

	Equivalent weight (g/mole)	OH number (mg KOH/g)	Acidity number (mg KOH/g)
Canola based polyol	368	152.4 ± 0.3	22.9 ± 0.3
Castor oil	340	165.2 ± 3.8	1.8 ± 0.1
Soybean based polyol	302	185.5 ± 3.0	7.6 ± 0.4
MDI	133		

Errors are standard deviations; $n = 3$

Table 2 Typical foam formulation

Polyol	100.0 part
Glycerin	12.0 or 15.0
Water	2.0 or 3.0
Surfactant	2.0
DBTDL T-12	1.0
DABCO DMEA	1.0
Crude MDI index	1.2

Table 3 Processing parameters, density, closed-cell content and glass transition temperatures of PU foams

	Canola-PU	Soybean-PU	Castor-PU
Cream time (s)	10	30	15
Rising time (s)	15	35	20
Gel time (s)	40	90	50
Density (kg/m^3)	159 ± 3	163 ± 3	158 ± 1
Closed-cell content (%)	68 ± 4	9 ± 1	9 ± 1
T_g ($^{\circ}\text{C}$)	58	67	56

Closed-cell Content Test

The closed-cell content was determined using AccuPyc 1330 pycnometer (Micromeritics, GA, USA) with a standard sample holder of 10 cm^3 following ASTM D2856-94 (Reapproved 1998) standard.

FTIR

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

Dynamic Mechanical Analysis

Dynamic mechanical analysis measurements were carried out on a TA Instrument DMA Q800 equipped

with a liquid nitrogen cooling apparatus, in the single cantilever clamp mode, with a constant heating rate of 2°C/min from –120 to +150°C. Rectangular samples were prepared by polymerizing the reactants in (18 mm × 13 mm × 4 mm) Teflon molds. DMA measurements were performed following ASTM E1640-99 standard at a fixed frequency of 1Hz and a fixed oscillation displacement of 0.015 mm.

Thermogravimetric Analysis

TGA was carried out on a Dupont Instruments Thermogravimetric Analyzer (951) 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 in the open platinum pan. The samples were heated from 25 to 600°C under dry nitrogen at a constant heating rate of 5°C/min. The samples were run in duplicate for thermal property measurements.

Mechanical Properties

The compressive properties of the foams were measured on an Instron universal testing machine (model 4202) according to the ASTM D1621–00 standard. Samples were prepared in cylindrical Teflon molds of 60-mm diameter and 36-mm long. The cross-head speed was 3.54 mm/min with a load cell of 500 kgf. The load was applied until the foam was compressed to approximately 15% of its original thickness and the compressive strengths were calculated based on the “10% deformation” method according to the standard. The strengths of five identical specimens per sample were tested and the results averaged.

Scanning Electron Microscopy

The microstructure of the obtained PU foams was examined using a SEM (Philips XL30 ESEM LaB₆ manufactured by FEI Company, Oregon, USA). Samples were examined uncoated and without processing, with a Gaseous Secondary electron Detector (GSED), within a gaseous environment and a partial vapor pressure of 1.2 mbar. The sample chamber vacuum was around 9.4×10^{-5} mbar. The circular sample was cut into small strips and then snapped by hand to reveal a fracture surface for subsequent microscopy observation.

Density Test

The density of the PU foam was determined by averaging the mass/volume measurement results of five

specimens per sample following ASTM D1622–98 standard. The results are listed in Table 3.

All the reported errors are the subsequent standard deviations of the different runs.

Results and Discussion

The ozonolysis and hydrogenation based technology has produced polyol from canola oil which contained about 60% of triol and diol that have only primary functional hydroxyl groups located at the end of the chains. Because ozonide, a product of ozonolysis, tends to hydrolyze and produce carboxylic acid [13] that cannot be hydrogenated, canola oil based polyol ended up with relatively high acid number, as listed in Table 1. The formulation of the PU foams (listed in Table 2) was designed with a relatively high level of catalyst (1 part) and higher isocyanate content (Crude MDI Index was fixed to 1.2) to compensate for the detrimental effect of the acid which is a killer of catalyst.

The processing parameters (cream time, rising time and gel time) measured with an uncertainty lower than 1 s and listed in Table 3 illustrate the reactivity of the different PU foams. Canola-PU was the most reactive system with the shortest cream, rising and gel times and Soybean-PU the least reactive one with the longest times. Glycerin played a major role in the reaction but its presence does not explain the differences in reactivity. Because the amount of glycerin used in Canola- and Castor- PU formulations was the same, its contribution was expected to be the same. However, significantly different reactivity was observed between the two PU networks. Castor oil PU has a cream time 50% larger, a rising time 35% larger and a gel time 25% larger than those of Canola PU. This was therefore attributed to the difference in polyol structure, particularly the dangling chains content and their location. Canola based polyol contained only primary terminal hydroxyl groups located at carbon 9 whereas soybean polyol and castor oil contained secondary functional hydroxyl groups all located in the middle of the fatty acid chains which resulted in significantly higher steric hindrance to further crosslinking. Note that even if canola polyol was constituted of 30% (on a molar basis) pendant chains, that in the soybean polyol and in the castor oil, every molecule with hydroxyl functionality provided a portion of the fatty acid chain as a dangling chain. Soybean based polyol had the lowest reactivity because it has not only secondary hydroxyl groups but also (–OCH₃) nonfunctional groups which are all located in the middle of the chains (see Fig. 1d) causing significant additional steric hindrance.

The FTIR spectra of Canola-PU, Soybean-PU and Castor-PU foams are shown in Fig. 2. A broad absorption band at $3,340\text{ cm}^{-1}$ characteristic of the N-H group and an absorbance band centered around $1,720\text{ cm}^{-1}$ characteristic of the C = O group are present in all the FTIR spectra [1]. However, both bands are not symmetrical. The asymmetrical shape of the band around $1,720\text{ cm}^{-1}$ shows that the hydrogen bonded C = O group vibration region is overlapping with the free C = O group vibration region. In addition, the band centered at $2,270\text{ cm}^{-1}$ characteristic of the –NCO group observed in all spectra indicated that the isocyanate has not completely reacted. For the same OH/NCO molar ratio, its relative intensity in Soybean-PU and Castor-PU was higher than that in Canola-PU foams. Furthermore, Canola-PU foams had a relatively higher N-H peak than the other two foams. These clear differences, even if precise quantitative analyses of the FTIR results are lacking, shows that the –NCO amount left after the reaction was lower and the urethane linkages amount was higher in the case of Canola-PU foams. It evidences the strong effect of the dangling chains on the reaction and on the degree of its completion. In the case of soybean based polyols and crude castor oil, the presence of large amount of dangling chains caused significant steric hindrance to crosslinking and resulted in less complete reactions with the isocyanate than that of canola based polyol, and yielded a smaller amount of hard segment in the PU.

Dynamic mechanical behavior of Canola-PU, Soybean-PU and Castor-PU foams with plots of the storage modulus (E'), loss modulus (E'') and tangent δ ($\tan \delta$) as a function of temperature are shown in

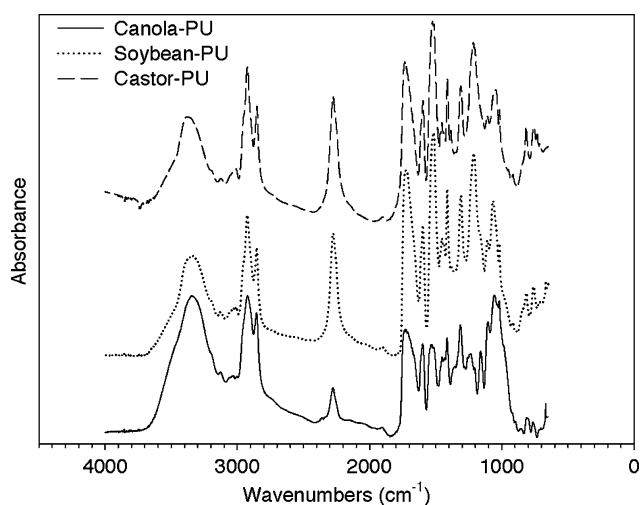


Fig. 2 FTIR spectra of polyurethane foams. *Solid line*: canola oil based polyurethane (Canola-PU); *dotted line*: soybean oil based polyurethane (Soybean-PU), and *dashed line*: castor oil based polyurethane (Castor-PU)

Fig. 3a, b and c, respectively. The storage modulus, E' , as highlighted by its first derivative (insert in Fig. 3a) drops first gradually then exhibits a relatively rapid drop around -90°C and another large drop around 50°C during the transition from glassy to rubbery states. The first rapid drop is attributed to the β -transition and the second to the glass transition. The β -transition may be related to the rotation [14] or backbone chain motion of the short groups [15] in the fatty acid chains. The E' for Soybean-PU foams decreases at a slower rate and plateaus at a higher level than Canola-PU and Castor-PU foams. Generally, with the increase of crosslinking density, the transition region broadens, and the modulus drops at a lower rate and plateaus at a higher level. Since 15 parts of glycerin (12 parts in the other two PU foams) with primary hydroxyl groups were added in Soybean-PU system, it is expected to have higher crosslinking density. Furthermore, the presence of ($-\text{OCH}_3$) nonfunctional groups in the middle of fatty acid chains of soybean based polyol resulted in heterogeneities in the molecular weight giving rise to the broadening of the transition region.

The T_g s listed in Table 3 were determined with a very good accuracy from Fig. 3a following ASTM E1640-99 standard. Soybean-PU has a higher T_g because more glycerin with primary hydroxyl groups was added which increased crosslinking density. Crosslinks hinder the polymer segmental motion by introducing restrictions on the molecule motion of a chain therefore increasing T_g .

A weak transition at about 0°C was observed for all the PU foams as clearly revealed by the first derivative of E' (arrow in the insert of Fig. 3a). This weak transition was also observed in the loss modulus curves shown in Fig. 3b. In the case of Canola-PU, it appeared as a broad shoulder between -50 and 10°C . Petrovic et al. [14] reported the same phenomena for similar PU systems. In addition, it was found that the two main loss modulus peaks of Soybean-PU foams were much broader than for the other two foams, indicating a broader distribution in crosslinking density. Similar behavior was observed for the $\tan \delta$ curves shown in Fig. 3c.

TGA curves and their calculated derivatives (DTGA) (Fig. 4a, b, respectively) show that the decompositions of the PU foams started at approximately 200°C . The DTGA curves show two separate main features which are associated with two distinct degradation stages. The first feature which ends at around 400°C has well-resolved peaks specific to each structure (three peaks for Soybean-PU and Castor-PU, and two peaks for Canola-PU). The second feature is a relatively broad signal which ends abruptly and is

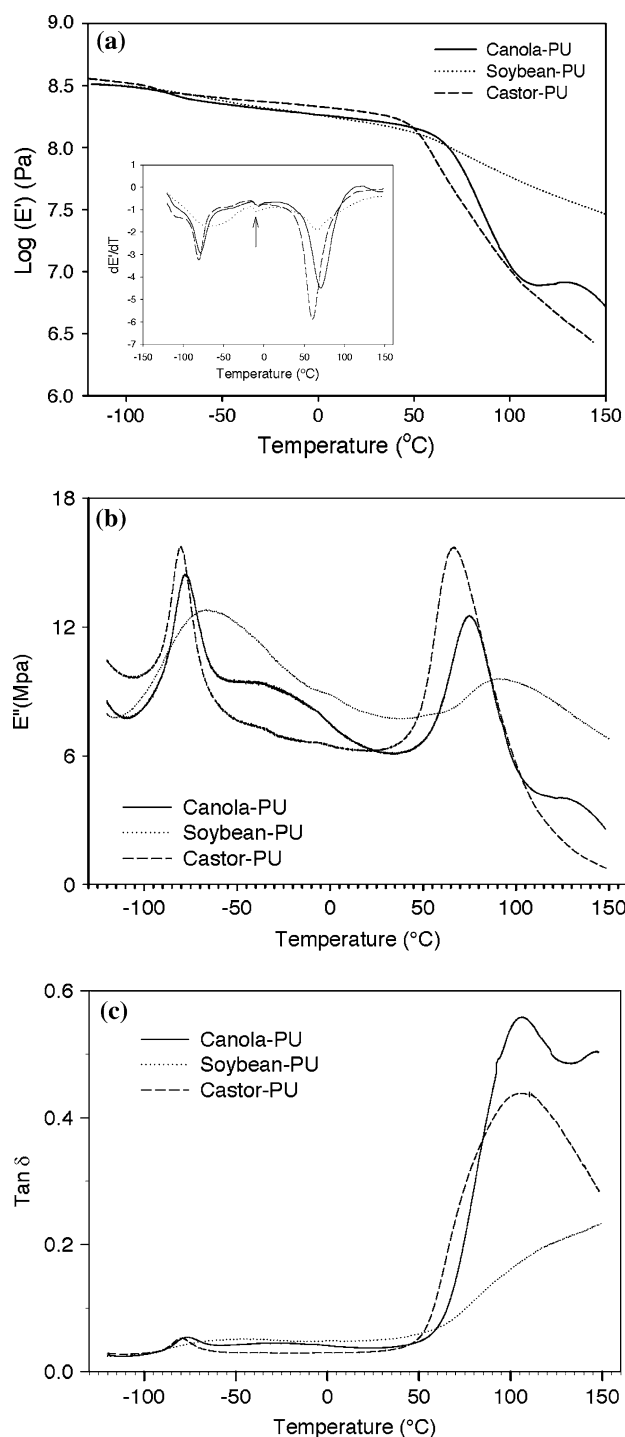


Fig. 3 **a** Storage moduli of polyurethane foams. *Insert:* plot the first derivatives of the storage moduli. **b** Loss moduli of polyurethane foams. **c** Tan δ of polyurethane foams. *Solid line:* canola oil based polyurethane (Canola-PU); *dotted line:* soybean oil based polyurethane (Soybean-PU), and *dashed line:* castor oil based polyurethane (Castor-PU)

practically the same for all specimens. In the first stage, the fastest rate of loss was at 335°C for Canola-PU, and at 380°C for Soybean-PU and Castor-PU. The second

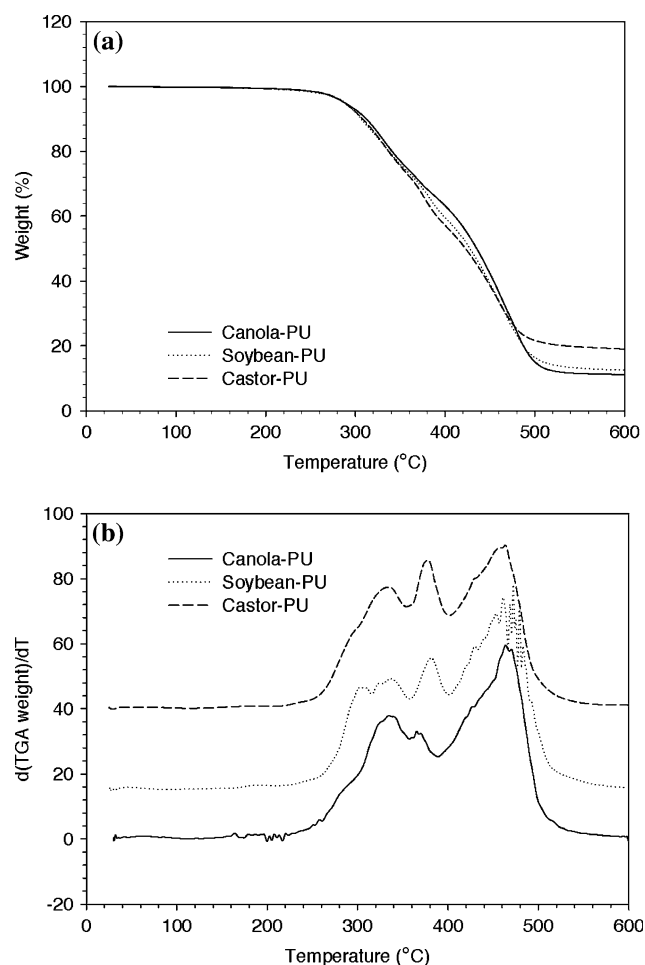


Fig. 4 **a** TGA curves of polyurethane foams in nitrogen. **b** Derivative TGA curves polyurethane foams. *Solid line:* canola oil based polyurethane (Canola-PU); *dotted line:* soybean oil based polyurethane (Soybean-PU), and *dashed line:* castor oil based polyurethane (Castor-PU)

stage involved an estimated weight loss of 70% with the fastest rate of loss situated at 470°C for all samples.

The degrading process is complex and depends on several factors such as urethane bonds, polyol type, dangling chains and unreacted isocyanate. In the first stage, the similarity of all the samples degradation processes could be explained by similar conversion of $-NCO$ groups to urethane bonds and the differences in the fine structure and shifts of maximum loss rate peaks could be explained by the differences in the activation energies introduced by the dangling chains present in the soybean polyol and castor oil. About 60% (mol) of dangling chains in canola based polyol was replaced by hydroxyl groups after ozonolysis and hydrogenation reaction whereas all the dangling chains remained in the soybean based polyol and castor oil. Activation energy reflects the mobility of the chains, which is higher for samples with lower activation en-

ergy. The highest mobility would be expected in the oil-based PUs free of dangling chains and the lowest in the oil-based ones which have dangling chains. A direct relationship between activation energy and cross-linking density would be expected as found in similar systems [12]. This may be explained by the fact that an increase in temperature induces breakage of physical cross-links between long branches which are characterized by relatively low activation energies. As a result of thermally induced destruction of “weak” junctions, only relatively strong knots between backbones survive [16]. The second stage where most of the weight loss occurred could be correlated to a similar decomposition process of the polyols’ backbone.

The mechanical properties of the foams were characterized by compressive stress-strain measurements and the results are shown in Fig. 5. After an initial near-linearity of stress to strain up to about 3%, the specimens exhibited relatively abrupt yielding, followed by a sustained plateau region over which there was a little increase in stress with increasing strain. The initial linear region determines the modulus of the foam. The broad plateau region results from a plastic collapse or cell wall buckling of the foams, which is referred to as the collapse stress.

Young’s modulus was calculated according to the ASTM D1621-00 standard. With a density of 160 kg/m^3 , the Canola-PU foam has a compressive strength of $770 \pm 145 \text{ kPa}$ and a modulus of $22 \pm 8 \text{ MPa}$. The Castor-PU foam yields the highest compressive strength ($1,170 \pm 140 \text{ kPa}$) and modulus ($30 \pm 3 \text{ MPa}$). With the same density, the modulus and compressive strength of the Soybean-PU foam are substantially lower ($14 \pm 1 \text{ MPa}$ and $415 \pm 50 \text{ kPa}$, respectively).

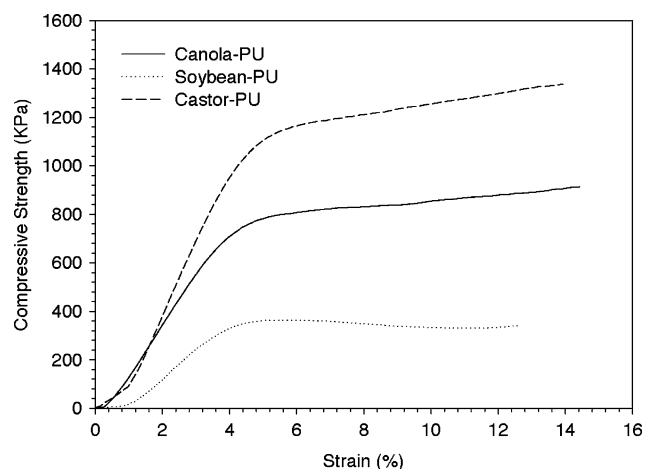


Fig. 5 Compressive strength versus strain of polyurethane foams. *Solid line*: canola oil based polyurethane (Canola-PU); *dotted line*: soybean oil based polyurethane (Soybean-PU), and *dashed line*: castor oil based polyurethane (Castor-PU)

The compressive strength and modulus depend not only on the cellular structure of the foam, i.e. the material of the cell walls (strut) and the size and shape of the cells but also on the type of the cells (which could be closed or open). The results of closed-cell content of all the PU foams are listed in Table 3. As can be seen the closed-cell content of Canola-PU foams is much higher than those of Soybean-PU and Castor-PU foams. It is known [17] that the strength of open cell foam is greater than that of a closed-cell material which has had its walls ruptured, because the broken walls are unable to contribute any reinforcement to support stress when the network is under load. Also, open cell material will naturally have thicker cell walls because not so much material is required to form the walls. The compressive strength and modulus of Castor-PU foams were the highest mainly because it had the lowest closed-cell content and the thickest cell walls. This will be discussed in detail later. The lowest compressive strength of Soybean-PU samples was the result of the plasticizing effect of the dangling chains combined with a smaller amount of hard segment even with less closed-cell content. The plasticizer weakens the network under load and lowers the compressive strength and Young’s modulus. The hard segments confer to the PU foams high modulus, especially when they are of non-uniform size and therefore more difficult to disrupt.

The cross-sectional surfaces of the foams observed with SEM are shown in Fig. 6. Canola-PU foams have small pores of approximately 0.25-mm diameter, uniformly distributed with relatively thin walls (Fig. 6a). Soybean-PU foams have a less uniform structure composed of larger elongated strips-like pores interconnected by smaller pores of different sizes (Fig. 6b). In the case of Castor-PU foams, the cells are very coarse even observed by naked eye and have the thickest walls (Fig. 6c). Combined with the lower closed-cell content, this resulted in the highest compressive strength and modulus. The relatively poor quality of the Castor-PU foam microstructure might be attributed to its inadequate optimization of the catalyst and surfactant used in its formulation. When the amounts of catalysts are reduced to 0.5 parts, finer cells with narrow distribution were obtained. (Data not reported). It is known [1] that the role of the surfactant is to stabilize the cell walls by lowering the surface tension between the cells and prevent their coalescence, resulting in smaller cells uniformly distributed over the network. Meanwhile, catalysts are added to accelerate reactions according to the requirement. The final cellular structure is a balance between the network formation and the blowing reaction.

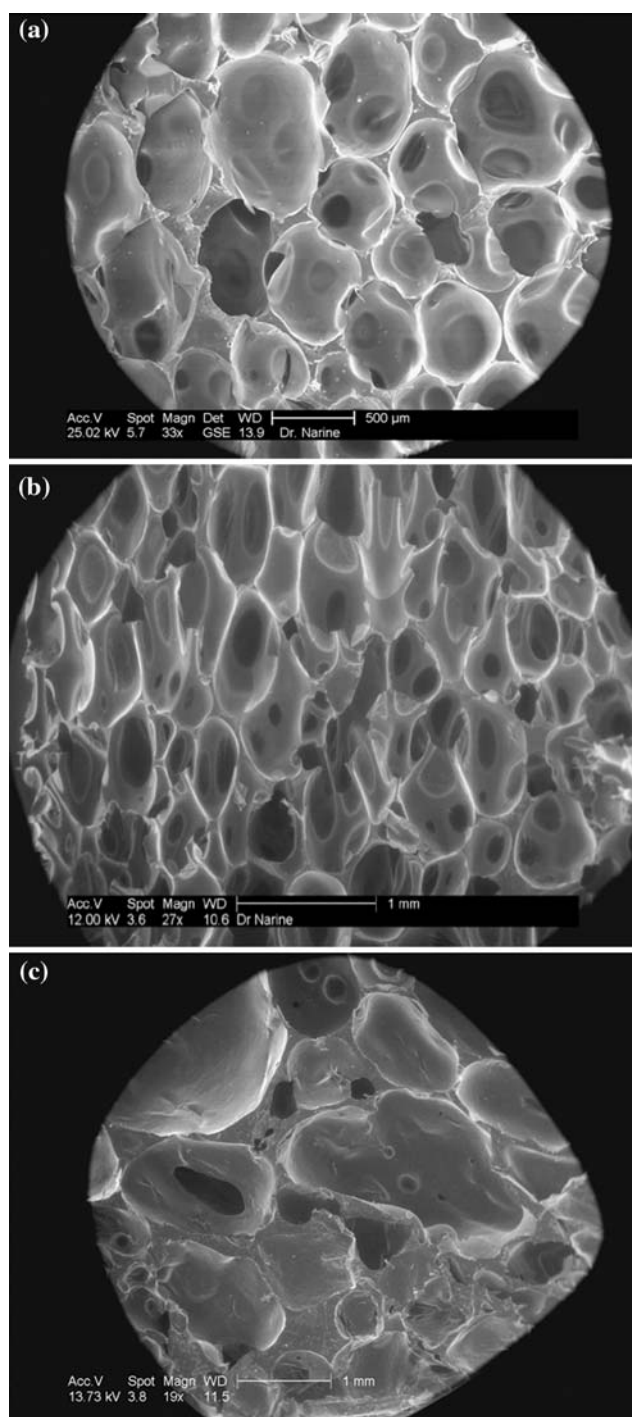


Fig. 6 Scanning electron micrograph of the polyurethane foams. **a** Canola oil based polyurethane, **b** soybean oil based polyurethane, and **c** castor oil based polyurethane

Acknowledgments 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. Szycher M (1999) Szycher's handbook of polyurethanes. CRC Press, Boca Raton
2. Melzer YL (1971) Urethane foams technology and applications, Chap 5. Noyes Data Corporation, Park Ridge
3. 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
4. Lyon CK, Garrett VH, Frankel EN (1974) Rigid urethane foams from hydroxymethylated castor oil, safflower oil, oleic safflower oil, and polyol esters of castor acids. *J Am Oil Chem Soc* 51:331–334
5. Guo A, Cho YJ, Petrovic ZS (2000) Structure and properties of halogenated and nonhalogenated soy-based polyols. *J Polym Sci Pol Chem* 38:3900–3910
6. Guo A, Demydov D, Zhang W, Petrovic ZS (2002) Polyols and polyurethanes from hydroformylation of soybean oil. *J Polym Environ* 10:49–52
7. 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
8. Dwan'Isa JPL, 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
9. Guo A, Javni I, Petrovic Z (2000) Rigid polyurethane foams based on soybean oil. *J Appl Polym Sci* 77:467–473
10. Zlatanic A, Petrovic ZS, Dusek K (2002) Structure and properties of triolein-based polyurethane networks. *Biomacromolecules* 3:1048–1056
11. Elfman-Borjesson I, Harrod M (1997) Analysis of non-polar lipids by HPLC on a diol column. *HRC-J High Resolut Chromatogr* 20:516–518
12. 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
13. Bailey PS (1958) The reactions of ozone with organic compounds. *Chem Rev* 58:925–1010
14. Petrovic ZS, Zhang W, Javni I (2005) Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. *Biomacromolecules* 6:713–719
15. Nielsen LE, Landel RF (1994) Mechanical properties of polymers and composites, 2nd edn, Chap 4. Marcel Dekker, New York
16. Drozdov AD, Agarwal S, Gupta RK (2003) Linear viscoelasticity of polyolefin melts: the effects of temperature and chain branching condensed matter. *Abstract cond-mat/0311322:1–20*
17. Meinecke EA, Clark RC (1973) Mechanical properties of polymeric foams, Chap 3. Technomic Publishing, Westport