

# Physical Properties of New Polyurethanes Foams from Benzene Polyols Synthesized from Erucic Acid

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**ABSTRACT:** High density triol-based polyurethane (PU) foams were developed from aromatic triol isomers prepared from erucic acid. The triol monomers were cross-linked with 4,4'-diphenylmethane diisocyanate (MDI) into PU foams. The foam's properties were studied by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The foams

were analyzed for closed cell content and compression strength. The effect of the benzene ring in the polyol structure on the physical properties of these new PU foams was compared with high density foams made from aliphatic polyols originating from canola oil. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3211–3217, 2010

**Key words:** polyurethane foams; aromatic triol monomers; erucic acid; physical properties

## INTRODUCTION

Research on vegetable oil-based polyurethanes (VOBP) foams is heavily focused on the development of rigid<sup>1–13</sup> and flexible foams,<sup>14–19</sup> since these foams constitute the major uses of PU in the market.<sup>20</sup> To obtain flexible foams, polyols should have molecular weights ranging between 3000 and 6000 and a functionality of  $\sim 3$ .<sup>20</sup> Since most vegetable oil-based polyols have molecular weights below 1000, petroleum based polyols are usually added to the formulation to attain the molecular weight requirements for this type of foam. Recently, it was found that the addition of 20–30% vegetable oil-based polyols into a foam formulation can achieve similar mechanical, insulating, and other physical properties as those foams containing solely 100% petroleum based polyols.<sup>15,19,13</sup>

Rigid foam formulation requires a polyol molecular weight below 1000 and a functionality ranging from 3 to 6. Conveniently, polyols with this functionality and molecular weight requirement can be robustly and effectively synthesized from vegetable

oils sources through several types of chemical reactions.<sup>7,21–33</sup> It was even found that VOBP foams can afford similar or superior physical properties compared to petroleum based foams.<sup>6</sup> VOBP foams presented in the literature are exclusively synthesized from aliphatic polyols. The rigidity of these foams is imparted to a significant extent through the use of an aromatic isocyanate as the crosslinker. However, a new potential avenue for imparting rigidity is now offered and investigated here since Yue et al.<sup>34</sup> and Lligadas et al.<sup>35</sup> have recently developed a new benzene polyol having a functionality of 3 with primary hydroxyl groups (triol monomers). This work therefore seeks to investigate the preferential potential for creation of rigid foams using both aromatic polyol (Fig. 1) as well as aromatic diisocyanate in the production of PU foams. The synthesis of foams from vegetable oil-based aromatic polyol containing benzene ring within the monomer structure is susceptible to re-enforce the matrices comparatively to foams made of aliphatic monomers; especially if the crosslinker also contains aromatic structures. However, the production cost of triol monomers is higher than most of the vegetable oil-based monomers due to the utilization of palladium on carbon catalyst and therefore, is less likely to be synthesized for commodity applications. Hence, the physical properties of these new aromatic triols foams were compared with canola polyol-based PU foams (Fig. 2) investigated by Narine et al.<sup>8</sup> to verify if the difference in physical properties of the matrices could justify their

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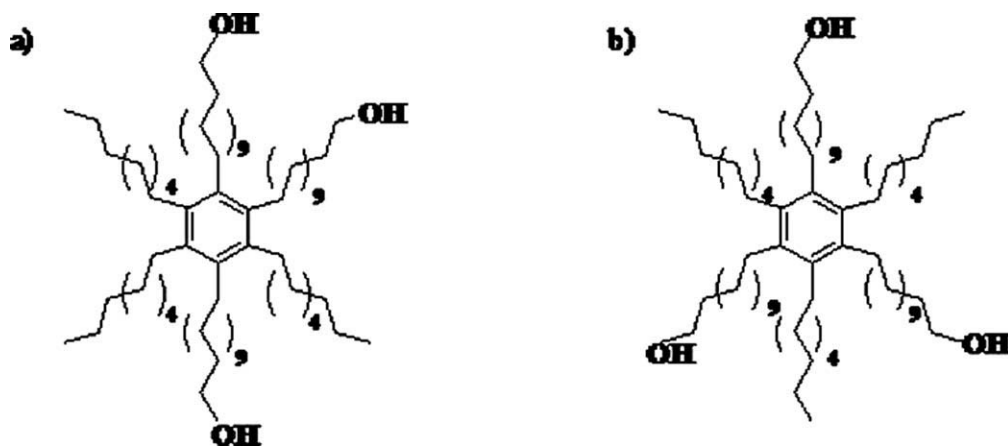


Figure 1 Chemical structures of the triol monomers: (a) A-PU and (b) S-PU.

difference in costs. The choice of the canola polyol-based PU foams as a comparison material is justified because both types of matrices were synthesized within the same research group using the same laboratory facilities. Also, both systems had polyols containing only terminal primary hydroxyl groups. Finally, to ensure similar densities for both matrices, the triol-based PU foams and the canola polyol-based PU foams<sup>8</sup> were allowed to rise in a closed mold container.

## EXPERIMENTAL SECTION

### Materials and monomer synthesis

The reagents, synthesis pathway, and characterization methods used for the synthesis of the tri-substituted benzene polyols are detailed elsewhere.<sup>34</sup> Both types of triols had a functionality of 3 and an equivalent weight of 323 g/mol. The foams formulation

required dilbutin dilaurate (DBTDL) 95% catalyst and 1,4-diazabicyclo[2.2.2]octane (DABCO) 95% catalyst from Sigma-Aldrich. The surfactant chosen was Tegostab B-8404 (100%) from Goldschmidt Chemical, Canada. The aromatic diphenylmethane diisocyanate (MDI, Mondur MRS) having a functionality of 2.6 and a NCO content of 31.5 wt % was donated by the Bayer Corporation (Pittsburg, PA).

### Preparation of polyurethane foams

Benzene triol-based polyurethane foams were prepared following the formulation in Table I. The polyol, water (blowing agent), DABCO, DBTDL, and surfactant were vigorously stirred by hand in a polystyrene container for 3 min to ensure homogeneity. MDI was then added and the mixture was vigorously stirred by hand for 40 seconds. The viscous mixture was then poured into a cylindrical Teflon

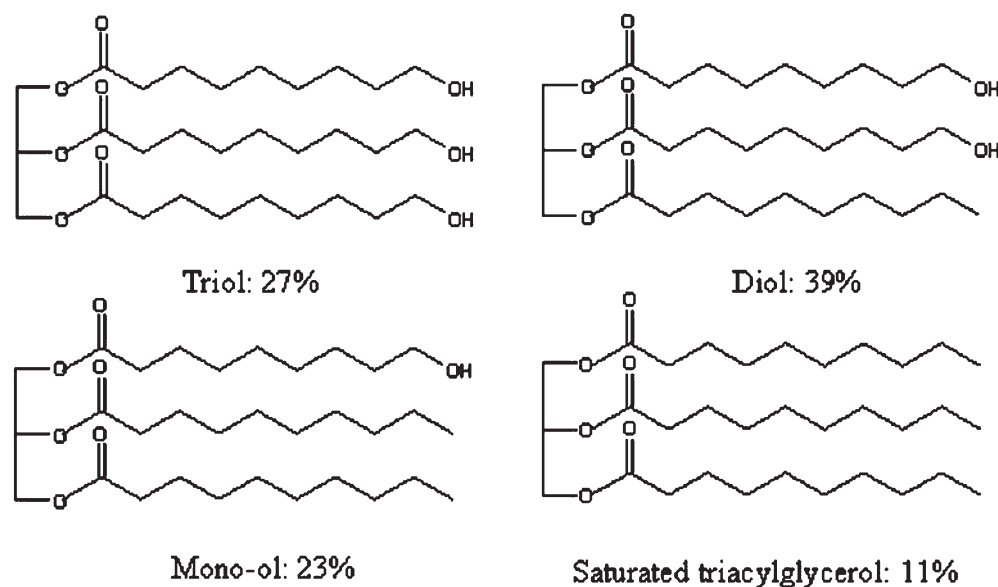


Figure 2 Chemical structure of canola polyols.

**TABLE I**  
**Triol Polyol and Canola Polyol<sup>8</sup>-Based PU**  
**Foam Formulations**

	Parts	
	Triol polyol-based PU foam	Canola polyol-based PU foam <sup>8</sup>
Polyols	100.00	100.00
Glycerin	–	12.00
Water	4.00	3.00
Surfactant	2.00	2.00
DBDTL	0.15	1.00
DABCO	0.15	1.00
Crude MDI index	1.05	1.20

mold, 60 mm diameter and 36 mm long, which was previously greased with silicon release agent, and sealed. The foams were then cured at room temperature for 5 days and post-cured at 60°C for 24 h. The foams were stored at room temperature for at least 5 days after post-curing before any measurements were taken.

#### Rheometric measurements

The viscosity of the triol monomers was measured with an AR 2000 Rheometer (TA Instrument, Delaware) in a shearing mode with a shearing rate of 50.0 s<sup>-1</sup>.

#### XRD

The XRD apparatus used was a Bruker AXS D8 advance diffractometer. The detection limit of the instrument was ranging from 0.5% to 2%. The test conditions were the following: 2θ range of 6–82°, regular scanning of 0.02° per step with 0.2 s per step time and co-radiation of 40 kV and 35 mA. The DF2/PDF4 powder diffraction databases issued by the International Center for Diffraction Data (ICDD) and the DiffracPlus Eva were used for data analysis.

#### FTIR

The FTIR equipment used was a Nicolet Magna 750 coupled with a MCT-A detector and a Nicolet NicPlan IR in transmission mode. The Fourier transformation, using 32 scans, was calculated using the Nicolet Omnic software version 7.1. Spectra were recorded within a range of 4000–650 cm<sup>-1</sup>. The nominal resolution was 4 cm<sup>-1</sup>. Before each sample spectrum, a background spectrum was recorded.

#### Closed cell content

The closed cell content was determined using the ASTM D6226-05 standard. The Pycnometer used

was an AccuPyc 1330 (Micrometrics, GA) with a standard sample holder of 10 cm<sup>3</sup>.

#### Density properties

The density of the PUs was calculated averaging the mass of the foams over the volume following the procedure of the D-1622-98 ASTM standard. The measurements were done on 3 separate samples.

#### Thermal properties

MDSC measurements were performed following the ASTM E-1359-08 standard and were carried out on a DSC Q100 from TA Instruments (DE). This apparatus is equipped with a refrigerated cooling system, and the measurements were performed under a dry nitrogen gas atmosphere. The measurements were divided into 2 cycles. Cycle one, used to erase the thermal history, consisted of heating the sample at a rate of 20°C/min up to 150°C, holding the temperature for 5 min, then cooling the samples down to -120°C at a rate of 5°C/min and holding for 5 min. MDSC measurements were then performed with a modulation amplitude of 1°C and a modulation oscillation period of 60 s at a rate of 3°C/min up to 150°C. The second heating cycle was selected for the analysis of heating data. The measurements were done in triplicate.

The dynamic mechanical analysis measurements were done according to the ASTM E 1640-99 standard method. The dynamic mechanical analyzer (DMA) used for this study was a DMA Q800 TA instrument (DE) equipped with a liquid nitrogen cooling system. The foams' dimensions were 17.2 mm × 11.2 mm × 3.3 mm and were analyzed in single cantilever mode. The oscillation displacement and frequency were fixed at 0.015 mm and 1 Hz, respectively. The tests were performed over a temperature range of -120°C to 155°C with a constant heating rate of 2°C/min. The measurements were done in triplicate.

The thermogravimetric analysis (TGA) measurements were carried out following the ASTM standard procedure D3850-94. The apparatus used was a TGA Q50 TA instrument, and the experiments were performed under a nitrogen gas atmosphere. The samples were ground into a fine powder prior to measurement. The samples were heated from room temperature to 1000°C at a rate of 10°C/min. The measurements were done in triplicate.

#### Mechanical properties

The mechanical properties of the foams samples were carried out following the ASTM D 1621-00 procedure. The instrument used was a hydraulic

**TABLE II**  
Physical Properties of Triol Polyol and Canola Polyol<sup>8</sup>-Based PU Foam Formulations

	Triol polyols-based PU foam	Canola polyols-based PU foam <sup>8</sup>
Cream time (s)	11	10
Gel time (s)	42	40
Rise Time (s)	35	15
Density (Kg/m <sup>3</sup> )	147 ± 3	159 ± 3
Closed-cell Content (%)	52 ± 3	68 ± 4
T <sub>g</sub> (°C)	51	58
Compressive strength (KPa)	700 ± 88	770 ± 145
Young Modulus (MPa)	19 ± 2	22 ± 8

Material Test System (MTS model 810). The cross-head speed was 2.5 mm/min. The deformation and the corresponding load were recorded until each of the 3 specimens was compressed to ~ 15% of their thickness. Each sample was tested at room temperature.

### Scanning electron microscopy

A SEM (Phillips XL30 ESEM LaB<sub>6</sub> from FEI Company, OR) was used to study the microstructure of the PU foams. The apparatus was equipped with a gaseous secondary electron detector and the samples were analyzed under a partial vapor pressure of 1.2 mbar. The vacuum pressure of the chamber was ~ 9.4 × 10<sup>-5</sup> mbar. The foams were fractured by hand before analysis. A layer of gold was coated to the samples prior to investigation to ensure a sufficient contrast image.

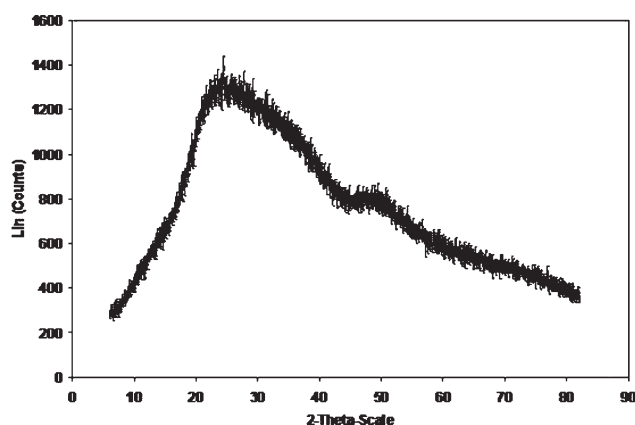
## RESULTS AND DISCUSSION

The synthesis of triols monomers from erucic acid through a tricyclomerization reaction yielded a mixture of asymmetrical and symmetrical molecules (Fig. 1). An increase in reactivity of the triol monomers has been observed due to the presence of three primary hydroxyl groups at the end of the carbon chain (terminal position). Thus, an amount of catalyst as low as 0.15 parts was used to allow a sufficient delay between the cream time and the rising time to permit the foam mixture to be poured in the mold. The aromatic structure of the monomers used in this study was sufficient to ensure the rigidity of the foams. Aliphatic polyols synthesized through the ozonolysis and hydrogenation of vegetable oils<sup>22</sup> also have a high content of primary hydroxyl group in terminal position. However, the mixtures also contain mono-ols and saturated triacylglycerols, which act as chain terminators and dangling chains, respectively (Fig. 2). Because of these side-reactions, glycerol had to be added to the canola polyol-based

PU foam formulation to increase the hydroxyl number and thus increase the rigidity of the final foam, which otherwise, would have been much lower than what is normally found in the literature for VOBP foams.<sup>5,8</sup> Unlike the foams produced from canola-based polyols using ozonolysis and hydrogenation technology,<sup>8</sup> there was no need to add glycerol to increase the hydroxyl content. Table I presents the triol-based PU foam formulation used in this study and the canola-polyol<sup>8</sup> foam formulation.

The viscosity of the triol monomers was 11.6 Pa s at 25°C, a value which required 4 parts of water to generate a sufficient concentration of CO<sub>2(g)</sub> for the necessary foaming activity. Note that the viscosity of the triol monomers is significantly higher than the canola-polyols (0.90 Pa s).<sup>22</sup> The reactivity of the foaming reaction was monitored through the cream time, gel time, and rising time (Table II). More specifically, the cream time was monitored from the beginning of the mixing to the beginning of the foam rise. At this time, a change in color from a dark to a lighter color was observed due to the evolution of the blowing agent. The gel time (or string time) was observed by touching the surface of the mixture with a stick when it produces a string which will form and break easily, this was taken as the gel time. The rising time was monitored as the period between the gel time and the end of the rising foam.<sup>36</sup> As can be seen, the cream time and the gel time of the triol-based PU foams compared to that of the canola polyol-based foams<sup>8</sup> are similar (Table II). This is anticipated as both structures contain primary hydroxyl groups. However, the rise time of the triol-based foams was longer than the canola polyol-based foams. The higher viscosity of the triol polyols, might have slowed down the diffusion of CO<sub>2(g)</sub> into the matrix.

The triol-based PU foams were analyzed by XRD (Fig. 3). The peak at 2θ = 20° is characteristic of the amorphous structure of the polymers. Also, the FTIR confirmed the urethane linkage formation (Fig. 4).



**Figure 3** WAXD data of triol-based PU foams.



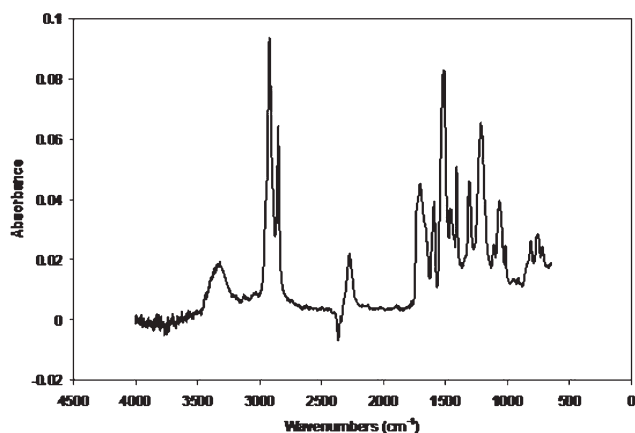


Figure 4 FTIR spectra of triol-based PU foam.

The peak centered at  $2277\text{ cm}^{-1}$  is characteristic of free NCO content which is due to the use of excess isocyanate.<sup>37</sup> The C=O and N–H vibrational regions present are characteristic of urethane linkages.<sup>38</sup> The bands centered at  $1710\text{ cm}^{-1}$  and  $1725\text{ cm}^{-1}$  indicate the presence of bonded and free C=O groups, respectively, and the bands centered at  $3333\text{ cm}^{-1}$  and  $3441\text{ cm}^{-1}$  correspond to the H-bonded and free N–H groups, respectively.<sup>39,40</sup> The presence of urea was not clearly detected. This can be due to the carbonyl urea C=O stretching region from the free urea to the bidentate area spread from  $1640\text{ cm}^{-1}$  to  $1700\text{ cm}^{-1}$ , which could be overlapping with the urethane C=O region ( $1699\text{ cm}^{-1}$ – $1733\text{ cm}^{-1}$ )<sup>39–41</sup> or to an incomplete foaming reaction. It is now known that VOBP foams have similar foaming reactions to petroleum based PUs,<sup>42</sup> where the third phase of foam development involves urea microphase separation and cell opening.

The  $T_g$  measured by DSC (Fig. 5) and DMA (Fig. 6) are  $47 \pm 2^\circ\text{C}$  and  $51 \pm 2^\circ\text{C}$ , respectively. As expected, these  $T_g$  results are superior (about  $20^\circ\text{C}$  higher) than the corresponding plastic sheets made

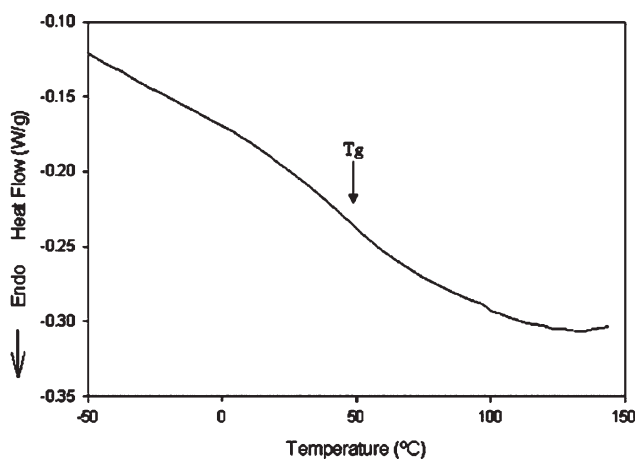


Figure 5 MDSC curve of triol-based PU foam.

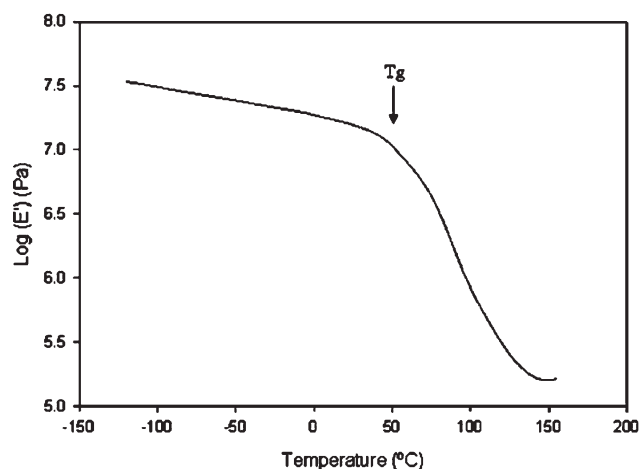
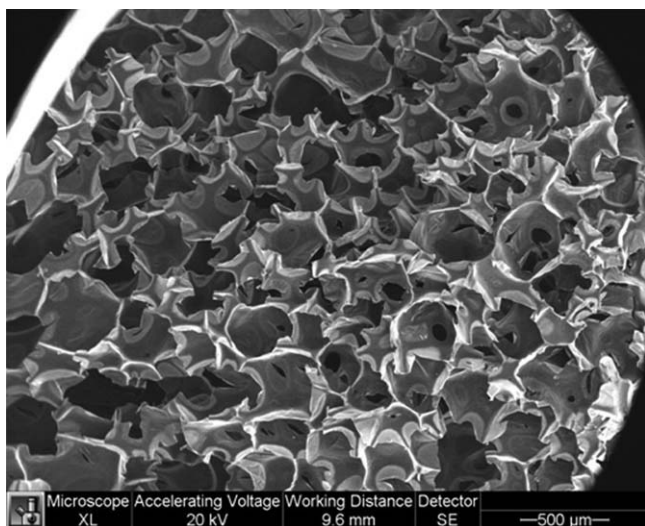


Figure 6 Triol-based PU foam storage modulus as a function of temperature.

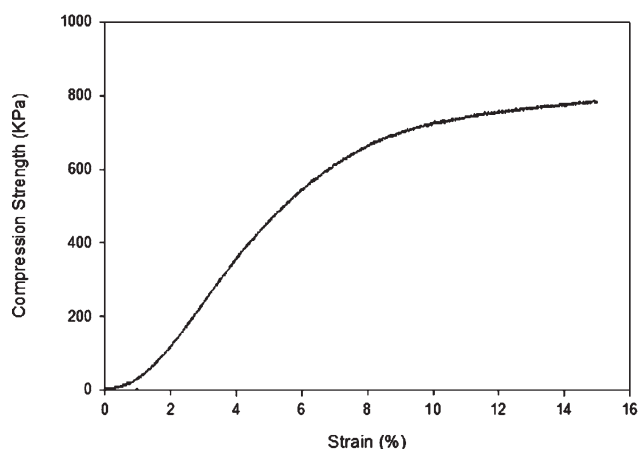
from the same polyols<sup>43</sup> due to the reaction between water and isocyanate which result in the formation of hard urea domains.<sup>16,36</sup> Foam matrices prepared by Narine et al.<sup>8</sup> were composed of primary hydroxyl group canola oil-polyols. These matrices had higher  $T_g$  values (Table II) than the triol-based foams presented here. Possible explanation for these values is the use of glycerol which is known to be an excellent crosslinker.<sup>5</sup> It has been shown that the addition of two parts of glycerin in a VOBP system containing primary hydroxyl groups results in a lower crosslinking density than a system containing secondary hydroxyl groups and three parts of glycerin.<sup>8</sup> Furthermore, by adding glycerin into the PU formulation, the polyol equivalent weight decreases, which requires a greater amount of MDI following the OH/NCO stoichiometry.<sup>4</sup> In addition, the canola polyol mixture<sup>8</sup> had non-negligible amount of carboxylic acid within due to ozonolysis. Carboxylic acid reacts with isocyanate to form amide<sup>36</sup> and to balance the effect of the acid, an excess amount of isocyanate has to be incorporated to the foam formulation. The triol-based PU has an excess of 5% in NCO whereas the canola polyol foam had an excess of 20%. It is well-known that an increase in MDI index increases the  $T_g$  value.<sup>6</sup>

The microstructure and the closed cell content greatly affect the overall mechanical properties of foams. The percentage of closed cell content is affected by the water content, the viscosity of the polyol matrix, the amount of surfactant and organometallic catalyst (dibutyltin dilaurate) used in the formulation.<sup>42,44</sup> An increase in water content and a diminution in organometallic catalyst diminish the closed cell content, whereas an increase in polyol viscosity increases the close cell content.<sup>42,44</sup> The triol-based PU foams have a lower closed cell content (52%) and larger cell size (0.26–0.50 mm) (Fig. 7)

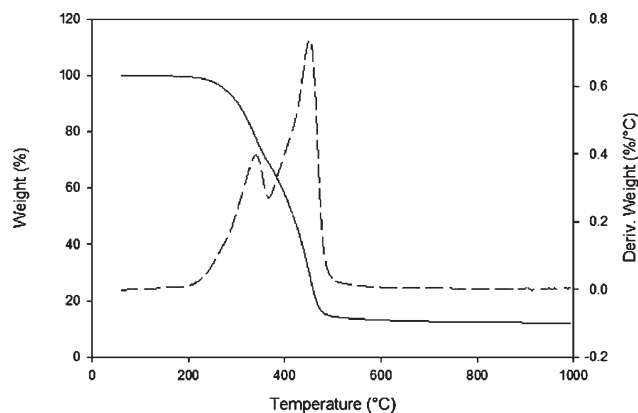


**Figure 7** Scanning electron microscopy of triol-based PU foam.

compared to the canola polyol-based PU foam (68%, 0.25 mm) (Table II). This can be explained by the higher water content and lower dibutyltin dilaurate catalyst concentration in the triol-based PU foams formulation compared to the canola polyol-based PU foam. Furthermore, the addition of glycerol in canola polyol-based PU foam increased the closed cell content of the PU foam matrices as well.<sup>4</sup> These factors seemed to have overcome the effect of viscosity on the close cell content, as the higher viscosity of triol polyols should have resulted in the triol-based PU foams having a higher closed cell content. Since both foams matrices have similar densities (Table II), it was suspected that the cell walls of the triol-based PU foams are thinner than the canola polyol-based PU foam, because cell size of the former foam is bigger than the latter one. These factors have contributed to the lower mechanical properties of the triol-based PU foams. The compressive strength of the triol-



**Figure 8** Compression strength versus strain of triol-based PU foam.



**Figure 9** TGA and derivative TGA curves of triol-based PU foam.

based PU foams ( $700 \pm 88$  KPa) and the Young modulus ( $19 \pm 2$  MPa) (Fig. 8 and Table II) are lower than the reported values from Narine et al.<sup>8</sup> (Table II). As mentioned, this was attributed to the different cellular structure of the foams but it could also be attributed to the addition of glycerol, which increases the hard segment content of PU matrices due to its participation in the microphase separation.<sup>45</sup> The fact that the carbon chain to which the hydroxyl groups were attached to the benzene ring contained 12 carbons may also have played a role in lowering the expected rigidity of the triol-based PU foams.

Figure 9 shows the TGA and derivative TGA curves of the triol-based PU foams. From this figure, the thermodegradation started at around  $210^\circ\text{C}$ , which is characteristic of urethane linkage degradation. The derivative TGA reveals two degradation stages, where the first stage appears at  $340^\circ\text{C}$  with a rate of degradation of  $0.4\%/^\circ\text{C}$  and the second stage appears at  $451^\circ\text{C}$  with a degradation rate of  $0.74\%/^\circ\text{C}$ . These results are similar to those found for other vegetable oil-based PU foam systems.<sup>5,8</sup> The first degradation stage may be attributed to the degradation of the dangling chains as discussed in the case of plastic sheets made from triol monomers.<sup>43</sup> The last degradation stage is attributed to the breakdown of the polyol backbone.

## CONCLUSIONS

Novel vegetable oil-based polyurethanes foams containing a benzene ring within the monomer structure have been synthesized and characterized. The formation of the urethane linkage and the amorphous structure of the resulting foams were verified through FTIR and XRD, respectively. The physical properties of the novel high density triol-based PU foams were then compared to canola polyol-based PU foams<sup>8</sup> reinforced with glycerin.<sup>8</sup> The addition of glycerol may have increased the crosslinking density

of these matrices over the high density triol-based PU foams. Furthermore, the addition of an aromatic structure within the triol-based polyol did not improve upon the advantageous physical effects of glycerol on the mechanical properties of the foam matrices of linear polyols. The 12-carbon chain to which the hydroxyl groups were attached to the benzene ring may also have mitigated the expected increase in rigidity of the PU foams produced using the aromatic polyols.

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