**University of Alberta**

# Polyurethanes Plastic Sheets and Foams Synthesized from Aromatic Triols

By

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# ABSTRACT

Novel plastic sheets and foams from vegetable oil-based monomers were produced. These new polyurethanes were synthesized from aromatic polyols, with erucic acid as the starting material. These monomers have the unique feature of containing an aromatic ring which was hypothesized to improve the rigidity of the polyurethane matrices and the overall physical properties of the plastics and foams. The benefits of the aromatic ring were proposed to be enhanced due to three terminal primary hydroxyl groups within the structure of the polyols.

Reactions to produce hexasubstituted benzene derivatives containing alcohol groups in positions 1,2,4- and 1,3,5- around the benzene ring were suitably scaled up to provide amounts necessary for polyurethane production and characterization. These isomers (asymmetric and symmetric triols) were separated using chromatography. The pure triols were crosslinked with 4,4'-methylenebis(phenyl isocyanate) into polyurethanes sheets (asymmetric and symmetric polyurethane respectively). The physico-chemical properties of these PUs were studied by Fourier transform infrared spectroscopy, x-ray diffraction,, differential scanning calorimetry dynamic mechanical analysis, thermogravimetric analysis coupled with Fourier transform infrared spectroscopy, and tensile analysis. The asymmetric polyurethane sheet and the symmetric polyurethane sheet differed in their glass transition temperatures and crosslinking densities. This variation could be explained by the differences in crosslinking densities, related to the increase in steric hindrance between adjacent hydroxyl groups of the asymmetric triol monomers. It was found that both polyurethanes had similar mechanical and thermal properties.

Due to the similar properties of the asymmetric polyurethane and symmetric polyurethane sheets, the monomers were combined together in order to synthesize PU foams. The physical properties of these foams were studied by Fourier transform infrared spectroscopy, differential scanning calorimetry, dynamic mechanical analysis, scanning electron microscopy, thermogravimetric analysis and were analyzed for close cell content and compression strength. The effect of the benzene ring in the monomer structure on the physical properties of these new polyurethane foams was mainly compared with high density canola polyurethane foams previously investigated. It was demonstrated that the physical properties of polyurethane foams made with aromatic monomers are comparable to those made with aliphatic monomers when enhanced with glycerol.

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| | |
|---|---|
| $a$ | Affine or phantom model pre-factor |
| A-PU | Asymmetric polyurethane |
| ASTM | American Society for Testing and Materials |
| BDMAEE | 2,2’-bis-(dimethylaminoethylether) |
| $CO_2$ | Carbon dioxide |
| DABCO | 1,4-diazabicyclo (2,2,2) octane |
| DBDTL | dibutyltin dilaurate |
| DMA | Dynamic mechanical analysis |
| DMTA | Dynamic mechanical thermal analysis |
| DSC | Differential scanning calorimetry |
| E’ | Storage modulus |
| ELSD | Evaporative light scattering detector |
| EW | Equivalent weight |
| $f$ | Functionality |
| $fa_t$ | Reduced frequency |
| FTIR | Fourier transform infrared spectroscopy |
| G’ | Storage modulus |
| G” | Loss modulus |
| HDI | Hexamethylene diisocyanate |
| HPLC | High pressure liquid chromatography |
| HSC | Hard segment content |

| | |
|---|---|
| kPa | Kilopascal |
| M-PU | Mixture polyurethane |
| $M_c$ | Average molecular weight between crosslinks |
| MDI | 4,4’-methylenebis(phenyl isocyanate) |
| MPa | Mega Pascal |
| MTS | Material Test System |
| $\rho$ | Density |
| pphp | parts per hundreds parts |
| PPO | Polypropylene oxide |
| PU | Polyurethane |
| PVC | Polyvinyl chloride |
| RMDI | Hydrogenated MDI |
| S-PU | Symmetric polyurethane |
| SBO | Soybean oil |
| SEM | Scanning electron microscopy |
| $\tau$ | Stress |
| T | Temperature |
| TAG | Triacylglycerol |
| Tan $\delta$ | Tangent delta |
| TDI | Toluene diisocyanate |
| Tg | Glass transition temperature |
| TGA-FTIR | Thermogravimetric analysis coupled with Fourier transform infrared |

| | |
|---|---|
| Tm | Melting temperature |
| $v_e$ | Concentration of elastically active network chains |
| VOBP | Vegetable oil-based polyurethanes |
| x | Elongation |
| XRD | X-ray diffraction |
| $Y$ | Young modulus |

# GLOSSARY

**Acid value**: Measure of the acidity of a substance measured in mg KOH/g needed to neutralize the acidity.

**Aliphatic**: Chain-like molecule characterized by its content in carbons and hydrogen atoms and the nonexistence of aromatic structure.

**Amorphous**: Molecular structure which does not confers crystallinity, stratification or interchain orientation.

**Aromatic**: Molecular structure characterized by the presence of at least one benzene ring.

**ASTM**: Abbreviation for American Society for Testing and Materials.

**Blowing reaction**: Chemical reaction characterized by the release of gas occurring during the blowing period.

**Blowing agent**: Chemical ingredient which allows the gas that creates the expansion of the foam.

**Closed cells**: Structural characteristic of foams where the cell confers a complete closed structure.

**Cream time**: Period characterized by the evolution of the blowing agent. The cream time is calculated from the moment where the foam ingredients are discharged until the foam starts to rise.

**Crosslinking**: Covalent bonds between adjacent molecular chains.

**Cure time**: Time needed in order to attain a fully cured thermoset polymer or rubber.

**Damping**: Conversion of work energy into heat. Prevent the brittle failure.

**Diisocyanate**: Crosslinker used in polyurethane chemistry.

**Diol**: Molecule containing two alcohols groups.

**Elastomer**: Rubber-like substance which can be stretched up to 1000% of its initial length and return to its initial state.

**Equivalent weight**: Molecular weight of polyol divided by the functionality.

**Functionality**: Number of reactive groups (hydroxyl groups) per polyol molecule available as reaction sites.

**Gel time**: The time it takes for an infinite network to be formed.

**Hydroxyl number**: Amount of reactive hydroxyl groups in the polyol. Measured in mg KOH/g of sample.

**MDI**: Abbreviation for 4,4'-diphenyl-methane diisocyanate.

**Modulus**: Ratio of the stress over the strain.

**Open cells**: Structural characteristic of foams where the cell confers a complete open structure. Characteristic of flexible foams.

**Polyaddition**: Polymerization method characterized by the combination of monomeric units.

**Polyol**: Molecule containing multiple hydroxyl groups.

**Polyurethane**: Polymer formed by polyaddition of polyols and isocyanates.

**Rise time**: Time needed for the foam to fully expand.

# 1 General Introduction

The research on bio-based polyurethanes (PUs) increased in popularity since it has been discovered that the polymerization of castor oil with a source of diisocyanate was leading to a wide range of PU products such as coatings, plastics sheets, elastomers and foams[1-19]. The facile polymerization of castor oil into polyurethane is attributable to its high content in ricinoleic acid, a fatty acid that has the characteristic of containing a natural occurring hydroxyl group within its structure[20]. Since then, numerous vegetable oils have been converted into polyurethane through the transformation of the unsaturation point of fatty acids into alcohol groups. These transformations are normally leading to aliphatic polyols and have been recently reviewed[21].

Recently, Lligadas et al.[22] and Yue and Narine[23] synthesized aromatic polyols from erucic and oleic acid. The presence of a benzene ring within the polyol structure was due to the utilization of palladium on carbon during the synthesis route. Two aromatic triol isomers, asymmetric and symmetric triols monomers, having their alcohol groups around the benzene ring in position 1,2,4 and 1,3,5 respectively, were the result of this innovative synthetic pathway. The purpose of this thesis is then to determine the physical properties of plastic sheets and foams polymerized from the aromatic asymmetric and symmetric triols monomers synthesized from erucic acid.

Because the synthesis of these monomers results in a mixture of both isomers, the primary objective is to separate the isomers through column chromatography. The polymerization of both monomers into PU sheets via the same experimental conditions is essential in order to assess the role of the hydroxyl groups positioning on the physical properties of the different matrices. Hence, hypothesis 1 is introduced as follow: "*Polymerization of symmetric and asymmetric monomers will result in PU sheets having the same physical properties*."

Moreover, as mentioned previously, the synthesis of linear monomers from vegetable oils is the main current trend in the field. The synthesis of foams from vegetable oil-based aromatic polyol has never been explored before. The introduction of a benzene ring within the monomer structure is susceptible to re-enforce the matrices comparatively to foams made of aliphatic monomers; especially if the crosslinker is also composed of an aromatic structures. Hypothesis 2 is then introduced as follow: "*The incorporation of an aromatic ring within the triol monomer will improve the rigidity of the resulting foam matrices as compared to foams prepared from aliphatic monomers.*"

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# 2 Introduction and Background Information

## 2.1 Introduction

Otto Bayer created the first polyurethanes (PUs) in 1937 by the polyaddition of diols to diisocyanates. PUs can be classified, depending on their formulation as millable elastomers[1,2] to rigid foams[2] and are therefore suitable for a wide range of applications in different industrial and manufacturing sectors such as automotive, medical and machinery. Their worldwide utilization is massive, totaling 8.8 billion tones in 2006[3] and they rank 6th in the global production of plastics[4]. PU feedstock currently is sourced mainly from petroleum and due to growing global environmental and supply concerns; researchers are currently investigating the use of renewable resources as a replacement for the petroleum based monomers for the fabrication of PUs. From the plethora of potential renewable resources, vegetable oils (triacylglycerols (TAGs) and fatty acids) have proven to be excellent alternatives, capable of providing a wide range of polyol monomers. These monomers have the advantage of making the resultant PUs resistant to hydrolytic degradation since triacylglycerols are hydrophobic molecules. Production of suitable monomers[5-11], foams[12-18] and plastic sheet or elastomer[19,20] based on vegetable oils have already been witnessed by a large collection of scientific literature and patents. These vegetable oil-based PUs have potential uses in different sectors such as biomedical and tissue engineering[21], biomaterial for drug delivery[22], latex[23] and insulation. Applications of these PUs as carpets[24,25], shoe materials[26], and even blasting cartridges[27] have also been patented.

The purpose of this review chapter is to cover the work done so far on vegetable oil-based thermoset PUs starting from polyol formation to the physical characteristics of the plastic sheets, elastomers, and foams derived from these polyols, as these areas are pertinent to the research being reported in this thesis.

## 2.2 Polyols

Castor oil was the first vegetable oil to be used as a source of polyol monomers and is still currently used as a polyol source for PU production[1,21,28-44]. Castor oil[45] and lesquerella oil[46] are vegetable oils that naturally contain hydroxyl groups within their structure. Vernonia oil does not contain these hydroxyl groups but does contain epoxy groups. Epoxy groups have been proven suitable to undergo polymerization to produce polyurethane foams and plastic sheets[47,48]. Apart from the above mentioned vegetable oils, other vegetable oils must be modified to be considered polyols, in order to be suitable for polymerization into PUs. The literature presents several chemical pathways to introduce hydroxyl functionality into the triacylglycerols of vegetable oils containing unsaturated fatty acids. The definition of functionality applied to urethane chemistry is the number of reactive groups (hydroxyl groups) per polyol molecule available as reaction sites[2].

The amount of double bonds, or degree of unsaturation of the particular fatty acid to be modified, greatly influences the potential for higher functionality of the corresponding polyol, as the double bond sites provide the potential for introduction of hydroxyl functionality. Functionality affects the degree of formation of urethane linkages and therefore the crosslinking density of the PUs[49] which influences the physical properties of the polymeric matrices. The main unsaturated fatty acid content for common vegetable oils are listed in Table 2.1[50].

The following section covers the type of polyols formed by various hydroxylation pathways such as the formation of polyols with secondary and primary hydroxyl groups. It also covers less common routes such as halogenation and cyclotrimerization of vegetable oils.

| Vegetable oil | Oleic acid (18:1) (%) | Linoleic acid (18:2) (%) | α-Linolenic acid (18:3) (%) | Total (%) |
|---|---|---|---|---|
| Corn | 44 | 48 | - | 92 |
| Soybean | 20 | 64 | 3 | 87 |
| Palm | 15 | 1 | - | 16 |
| Coconut | 6 | - | - | 6 |
| Olive | 75 | 10 | - | 85 |
| Cottonseed | 32 | 45 | - | 77 |
| Canola | 55 | 20 | 8 | 83 |
| Sunflower | 31 | 57 | - | 88 |

Table 2.1: Main unsaturated fatty acid composition of common vegetable oils[50].

### 2.2.1 Common synthetic pathways to produce polyols from unsaturated vegetable oils.

In the literature, the most common vegetable oil-based PU monomers are polyols having secondary hydroxyl groups. The epoxidation of TAGs using peracetic acid [51] followed by alcohol-mediated ring-opening reaction of the epoxidized oil (Figure 2.1, Eq.1)[49,52-58] or the hydroxylation of the double bonds with an acid (Figure 2.1, Eq.2)[51] are common examples of chemical reactions leading to polyols having secondary hydroxyl groups. Since the hydroxyl group is not located at the end of the carbon chain, the monomers introduces dangling chains in the resulting PU's. Hydroformylation followed by hydrogenation (Figure 2.1, Eq.3)[59,60] generates primary hydroxyl groups, however their location is in the middle of the main carbon chain, so this also leaves long dangling chains in the resulting PUs.

Although all the methods discussed above increase the hydroxyl content of vegetable oils, some methods are more efficient. Generally, the yield of epoxidation reactions are higher than 90%[49,53,57,58], leading to high conversion into polyols (>75%), although the conversion percentage varies with the vegetable oil used[57]. In the case of the hydroformylation-hydrogenation reaction, the choice of catalyst is of great importance. For example, the use of cobalt as a catalyst decreases the functionality of soybean oil (SBO) by 52% compared to the use of rhodium as a catalyst[60]. Furthermore, the reaction conversion is 95% when using rhodium catalyst as compared to 67%[60] when using cobalt catalyst. However, the rhodium catalyst is very expensive[3].

As mentioned earlier, polyols with secondary hydroxyl groups or groups not at the terminus of the hydrocarbon chain introduces dangling chains into the PU structure (see Figure 2.2) which have the disadvantage of acting as a plasticizer in the PU matrix. Additionally, the presence of the hydroxyl group in the middle of the carbon chain can lead to high steric hindrance, which is an obstacle to crosslinking. Furthermore, reactions such as epoxidation and hydroxylation using an alcohol leave $–OCH_3$ groups within the polyol structure which also increases stearic hindrance (Figure 2.2). Such disadvantages can be avoided through the formation of polyols containing only terminal primary hydroxyl groups located at the end of the main carbon chain.

Polyols from vegetable oils having their hydroxyl groups in terminal primary position can be synthesized by oil based diethanolamide[62]. The amine group cleaves the ester bond in the triglyceride in order to form the amide functional group (Figure 2.3, Eq.1). Terminal primary hydroxyl groups are also generated by ozonolysis followed by hydrogenation (Figure 2.3, Eq.2)[63] or by ozonolysis of a vegetable oil in the presence of a diol (Figure 2.3, Eq.3) [64]. These methods of producing polyols have the advantages of being cost-efficient and having a yield higher than 90%[65].

Ozonolysis alone has the disadvantage of introducing the acid number of the polyols (see Table 2.2). The acid number is defined as the quantity of base needed in order to neutralize the acid present in 1 g of sample. It is known that the product of ozonolysis (ozonide) can hydrolyze into carboxylic acid[63,66]. The acid is an obstacle to the subsequent hydrogenation since the acid formed is unable to convert into alcohols. It is therefore important to optimize the reaction conditions. This will be discussed in more detail in Section 3.

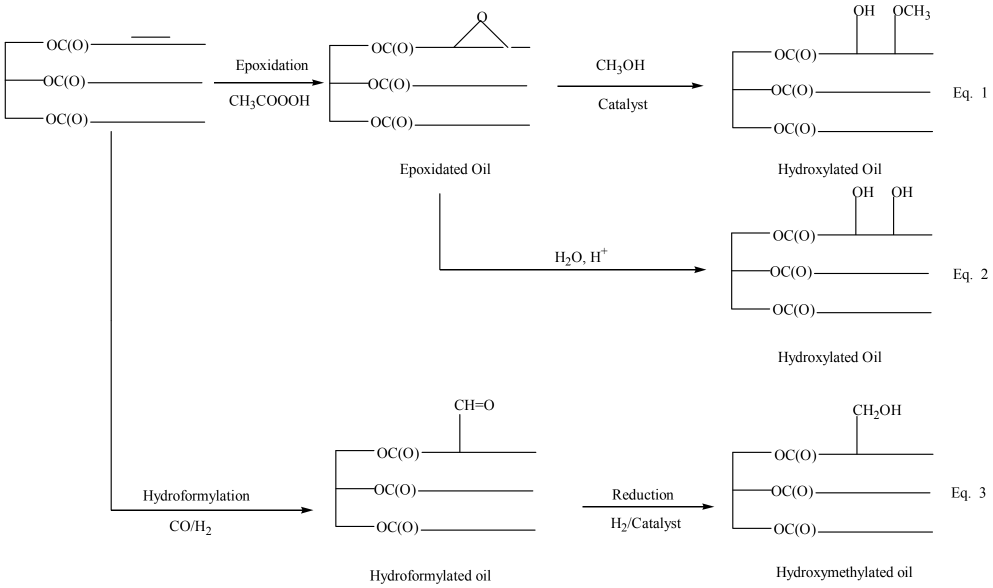

Figure 2.1: Different synthesis pathways in the production of polyols[61].

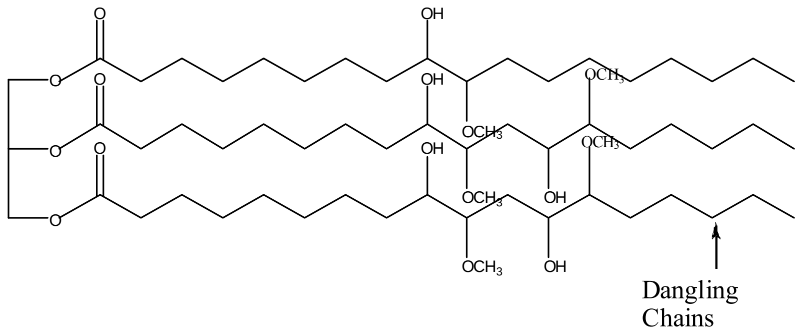

Figure 2.2: TAG treated by epoxidation and hydroxylation

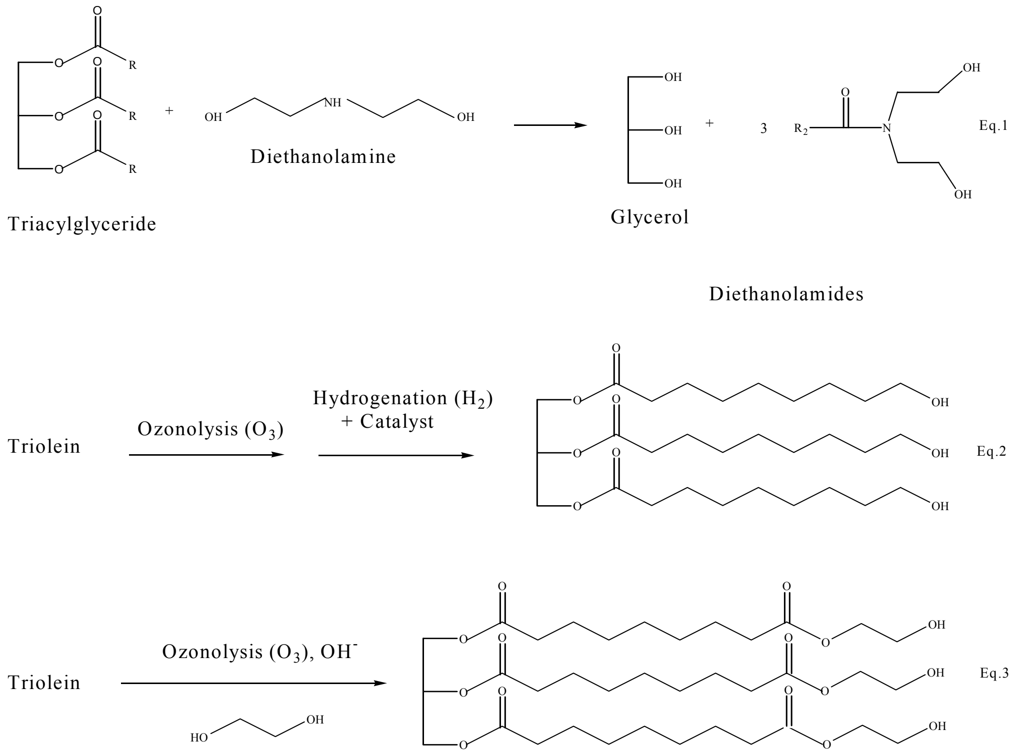

Figure 2.3: Triol formation by 1) reaction of diethanolamides with palm oil[62], 2) ozonolysis and hydrogenation from triolein[63], and 3) ozonolysis of triolein in the presence of a diol[64].

| Starting Material | Chemical Reaction | | Hydroxyl number (mg KOH/g) | Acidity number (mg KOH/g) | Viscosity (Pa.s, 25°C) |
|---|---|---|---|---|---|
| Canola Oil | Ozonolysis | Air | 152.4[63] | 22.9[63] | 0.4527[63] |
| | | $O_2$ | 235.2[63,67] | 15.8[63,67] -2[65] | 0.9860[63,67] - 0.81[65] |
| Soybean Oil | Ozonolysis – $O_2$ | | 228[65] | 2[65] | 0.68[65] |

Table 2.2: Comparison of the properties of polyols produced by ozonolysis (in air or oxygen) of canola oil and soybean oil.

### 2.2.2 Other polyol reactions

The multitude of reactions which can be performed on an epoxy group allow for the formation of many different polyols[53]. As mentioned in section 2.1, the epoxidation of vegetable oil with an alcohol produces polyols with secondary hydroxyl groups. The same result is expected with a catalytic hydrogenation process. It is also possible to convert these epoxy groups into hydroxyl groups using hydrochloric and hydrobormic acids, forming halogenated polyols[53]. The typical products are illustrated in Figure 2.4.

Table 2.3 shows the different characteristics of polyols from epoxidized SBO obtained by methylation, halogenation, and hydrogenation. From this table, it is found that the highest yield (100%) and functionality (4.1) are obtained with hydrogen bromide. The polyols formed using the epoxidation-hydrogenation technique have the lowest hydroxyl number. Both of the brominated and chlorinated soy-polyols have a higher yield and functionality than the methylated and hydrogenated polyols. Furthermore, the addition of the bromine and chlorine atoms to the polyol increases the glass transition temperature and mechanical properties of the resulting PU compared to methoxy and hydrogenated PUs. This might be due to the increase of polarity of the brominated and chlorinated polyols. However, the final thermal stability of the resulting PU is lower[68]. This will be discussed later.

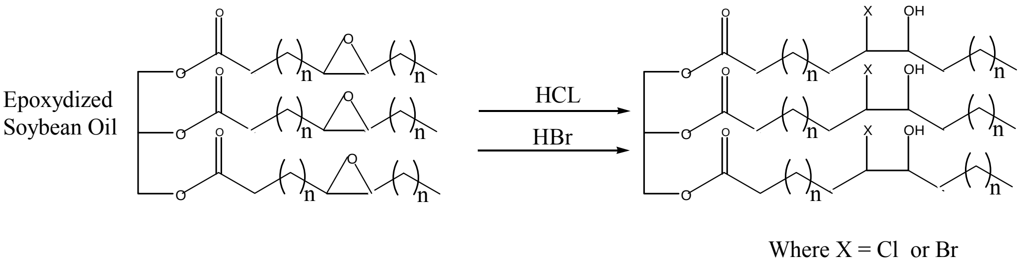

Figure 2.4: Example of halogenation reactions performed on an epoxidized triacylglycerol[53].

| Characteristics | Soy-$CH_3OH$ | Soy-HCL | Soy-HBr | Soy-$H_2$ |
|---|---|---|---|---|
| Yield (%) | 93 | 94 | 100 | 89 |
| Hydroxyl Number | 199 | 197 | 182 | 212 |
| Equivalent Weight (g/Equivalent) | 282 | 285 | 308 | 265 |
| Functionality | 3.7 | 3.8 | 4.1 | 3.5 |
| Molecular Weight (g/mol) | 1053 | 1071 | 1274 | 938 |

Table 2.3: Some characteristics of halogenated and non-halogenated soy-polyols[53]

Transformation of fatty acids into aromatic polyols is also reported in the literature. Lliligadas et al.[69] and Yue and Narine[70] successfully transformed oleic and erucic acid into aromatic triols. The modification of the double bond for the conversion of fatty acids into tricyclomerized polyols is a process that requires several reagents (Figure 2.5). The total yield for the aromatic triol is 70%[69] with the yield for the aromatic symmetric and aromatic asymmetric triols are 17% and 61%, respectively[70]. Similarly, Song and Narine[71] developed hexa-ols from oleic acid with a yield of 94%. The aromatic triols and the aromatic hexa-ols are depicted in Figure 2.6. These highly functional polyols (Figure 2.6) are synthesized through several processing steps. Their production cost is significantly higher than the aliphatic polyols presented previously and they are therefore less likely to be synthesized for commodity applications.

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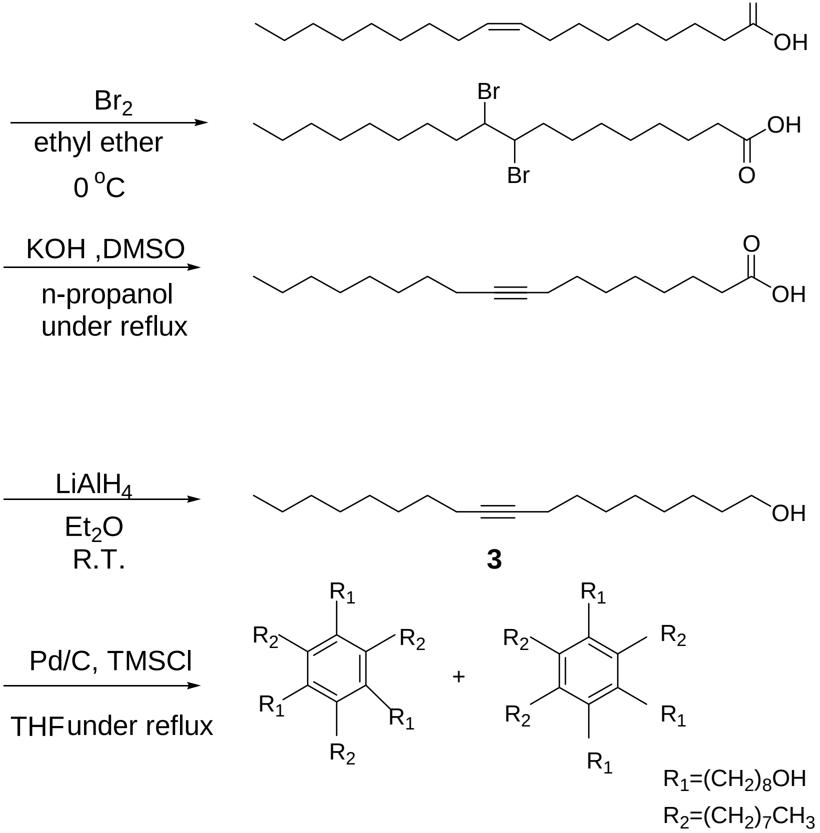
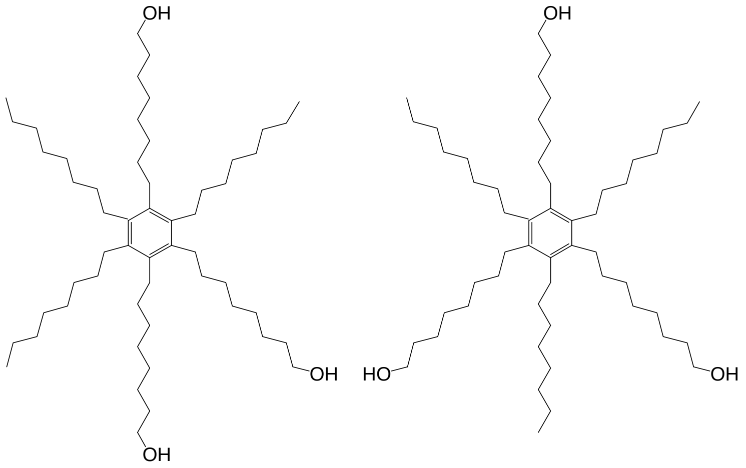
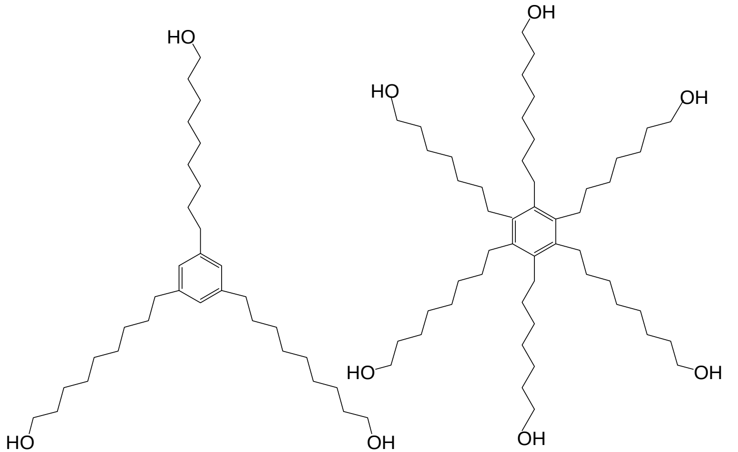


Figure 2.5: Formation of aromatic polyols synthesized from fatty acids[70].



Aromatic asymmetric triol

Aromatic symmetric triol



Aromatic triol

Aromatic hexa-ols

Figure 2.6: Aromatic polyols synthesized from oleic acid[69-71].

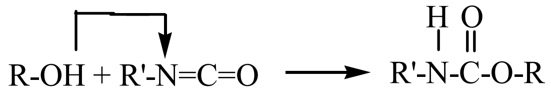
## 2.3 Vegetable oil-based PUs

PU elastomers and foams are the two main types of vegetable oil-based PUs found in the literature. This is most likely because petroleum based elastomers and foams represent 16% and 60% respectively of the PUs global market[72]. This section compares the physical properties of PU elastomers, plastic sheets and foams in relation to the type of polyols used for their polymerization

### 2.3.1 Vegetable-oil based PU plastic sheets and elastomers

Depending on the type and properties of the desired PU plastic sheet or elastomer, their formulation may contain the following chemicals: polyols, chain extenders, isocyanates, and catalysts. The polyols contribute to the so called soft content of PUs[2]. Polyols react with isocyanate to form urethane linkages through the nucleophilc addition of hydrogen from the polyol hydroxyl group across the carbon-nitrogen double bond of the isocyanate (Figure 2.7).

The hard segments, or high melting segments, are formed through the addition of chain extenders which react with the isocyanate. A chain extender is a low molecular weight hydroxyl-terminated or amine-terminated compound. Both the soft and the hard segments play a role in the physical and chemical crosslinking of the PUs. Crosslinking is the result of the formation of a network structure of interconnected branches with a total molecular weight too high to be measured by conventional techniques[73]. One defining characteristic of thermoset polymers is their so-called infinite crosslinking.



$$R\text{-}OH + R'\text{-}N{=}C{=}O \longrightarrow R'\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R$$

Figure 2.7: Formation of the urethane linkage

Several publications about vegetable oil based PUs estimate the crosslinking density of PUs through the rubber elasticity theory which relates the concentration of elastically active network chains ($v_e$) to the number average molecular weight between crosslinks ($M_c$) (Equation 2):

$$G' = \frac{E'}{3} = a v_e RT = \frac{a\rho RT}{M_c} \qquad (2)$$

where G' is the storage modulus and *a* is the pre-factor, whose value depends on either the affine or the phantom model. Both of these models contain a number of assumptions such as: the network deformation is based on the network strand deformation (affine), the junction points of the network do not fluctuate during deformation (affine), the crosslinks can fluctuate around their average position (phantom), and that the strands are ideal (phantom)[74]. It has to be noted that the evaluation of the crosslinking density through the $v_e$ and $M_c$ values generated by the rubber elasticity theory are estimations only and do not represent the true crosslinking density. Among the factors that influence the degree of crosslinking, the polyol average functionality is critical (Table 2.4[75]).

Table 2.4 shows that increasing the functionality increases the crosslinking density for the same type of polyol at the same OH/NCO ratio[67,75,76], as shown by the increase in $v_e$ values and the decrease in $M_c$ values. However, the tendency might not be the same when different vegetable oil-based PUs are characterized via this method (Table 2.5[57]).

| Average functionality of the polyols | $v_e$ (mol/m$^3$) | Mc (g/mol) |
|---|---|---|
| 1.9 | 87 | 12100 |
| 2.5 | 171 | 6300 |
| 2.9 | 424 | 2600 |
| 3.2 | 442 | 2500 |

Table 2.4: Estimation of the crosslinking density through the $\nu$e and Mc values as a function of the average functionality of soy polyol[75].

| Polyol Source | Functionality | Swelling Degree (%) | Sol Fraction (%) | $v_e$* ($10^3$ mol/cm$^3$) | M$_c$* (g/mol) |
|---|---|---|---|---|---|
| Canola | 3.94 | 80.98 | 1.11 | 1.76 | 616 |
| Midoleic sunflower | 3.71 | 96.49 | 1.47 | 1.57 | 685 |
| Soybean | 4.49 | 80.45 | 2.66 | 1.54 | 710 |
| Linseed | 6.44 | 40.40 | 0.68 | N.A. | N.A. |
| Sunflower | 4.63 | 80.16 | 2.52 | 1.53 | 718 |
| Corn | 4.37 | 85.56 | 2.84 | 1.41 | 776 |

*Based on the Affine Model

Table 2.5: Swelling properties, concentration of elastically active network chains ($v_e$ ) and number average molecular weight between crosslinks (M$_c$) [57].

The polyols from Table 2.5 were polymerized with 4,4'-diphenylmethane diisocyanate MDI in a 2% molar excess. Results showed that production of polyols with higher functionalities resulted in lower $v_e$ and a higher $M_c$. Even when polyols were synthesized by the same procedure, the composition of fatty acids changed from one type of vegetable oil to another. This is because the hydroxyl groups' location, the dangling chain content, and the chain length varies from a system to another. It can then be assumed that some vegetable oils, having a higher hydroxyl number, might have a lower crosslinking density due to steric hindrance from the dangling chains due to the hydroxyl groups located in the middle of the carbon chain(s).

One approach to compare the crosslinking density of different systems is to measure the swelling degree. The swelling degree is related to the crosslinking density and is defined as a non-mechanical property that measures a non-negligible change in the PU volume. The increase in volume is due to a chains-stretching effect when the PU is plunged into a desired solvent. After a period of time, the PU network reaches a swelling equilibrium, based on an increase in free energy due to the chains stretching and a contrary decrease in free energy due to the mixing of the solvent with the network[77]. The sol fraction is also an important parameter in the estimation of the crosslinking density since it measures the soluble content of the polymer. This fraction indicates the imperfections of the PU's crosslinking and greatly influences the $v_e$ parameter. Generally, the more crosslinked a matrix is, the less the swelling ratio[28]. The rigidity and the density of PU matrices increase as the crosslinking density increases, which decrease the ability of solvent molecules to penetrate the matrices. In addition, a study on castor oil based PU elastomers showed that, not only does the crosslinking density influence swelling behavior, but the length of the chain extender used affects swelling as well [42]. The diffusion coefficient was found to be higher when the chain length of the chain extender was increased as it increased the flexibility of the polymer matrix.

Chain extenders also play a significant role in the thermal properties of PUs as the glass transition temperature (Tg) is sensitive to the hard segment content (HSC). As an example, PUs from vegetable oil based polyols and L-lysine diisocyanate LDI displayed a Tg value of –17 ºC[78]. The addition of the chain extender, 1,3-propanediol, increasing the hard segment content from 0 % to 42 %, raised the Tg value to 0 ºC[78]. This increase in Tg value is due to the hard segments that disperse into the soft domains. These hard segments are characterized by their marked ability to crystallize, their polar character, and if the HSC is high enough, phase separation (like block copolymers). The phase separation can be verified by a second Tg related to the hard block, or by dynamic mechanical analysis where the tan delta curve is likely to show two maxima. As the content in hard segment increases, the maxima peak height of the tan delta curve decreases due to a decrease in the PU's chain segmental motion as a consequence of a lower loss modulus. In addition, the phase segregation behavior can be confirmed by the storage modulus value, which is found to be higher as the

HSC increases. This is due to an increase in hydrogen bonds which increases the inter-chain interactions and increases the number of urethane connections.

To further illustrate the difference in physical properties upon the addition of chain extenders, Lligadas *et al.*[69] prepared a series of PUs using the triol monomers presented in Figure 2.5 and Figure 2.6, MDI and different content of 1,4-butanediol (chain extender). The aromatic asymmetric and symmetric triols were used as a mixture (A-S-PU) where the aromatic triols without dangling chain (A-PU) were used individually, (Figure 2.6). Table 2.6 shows the effect of the variation of the hard segment content on the thermal properties (Tg and melting temperature (Tm)).

A phase separation was observed for the samples with a hard segment content of 51.9%. In this case, the melting temperature is associated with the hard domain that dissociated from the soft domain[79]. The Tg temperatures increased with increasing hard segment content. The Tg temperatures are also higher for PUs containing no dangling chains in their structure.

| Type of PU | 1,4-butanediol content (g) | HSC (%) | Tg (°C)* | Tm (°C)* |
|---|---|---|---|---|
| A-S-PU | 0 | 0 | 36 | - |
| A-S-PU | 0.077 | 44.0 | 53 | - |
| A-S-PU | 0.15 | 51.9 | 58 | 177 |
| A-PU | 0 | 0 | 48 | - |
| A-PU | 0.015 | 45.2 | 59 | - |
| A-PU | 0.083 | 51.9 | 61 | 183 |

*Values obtained by DSC

Table 2.6: Effect of the variation of the hard segment content on the thermal properties of vegetable-oil based PUs[69].

Petrovic et al.[79] also worked on segmented polyurethanes. The soy polyols used had a functionality of 3.3 and their structure is illustrated in Figure 2.2. Table 2.7 presents different physical properties of soy based PUs in relation to their HSC and the nature of the chain extender used.

As previously discussed, the trends in Table 2.7 show that Tg values increase with increasing HSC. The tensile strength also increased with the augmentation of HSC. However, the HSC is also responsible for an increase of brittleness compared to PU without HSC, and to a diminution in the degree of elongation at break. It was also found that due to the increased crystalline content, the swelling ratios of PUs with chain extenders were diminished compared to PUs without chain extender. Furthermore, the nature of the chain extender also played a role in the physical properties; this was exemplified by a decrease in elongation at break when ethylene glycol was used instead of butanediol[79].

The presence of terminal primary hydroxyl groups versus secondary hydroxyl groups in polyols is another factor that plays an important role in the physical properties of PU matrices as the polymerization reaction rate increases with the presence of primary hydroxyl groups. As an example, PU polymerized from triolein containing only primary hydroxyl groups showed a decrease of 35% in swelling ratio compared with PUs polymerized from triolein containing only

| Nature of the chain extender | HSC (%) | Tg (°C) | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|---|---|
| None | 0 % | 34 | 24 | 74 |
| Ethylene glycol | 40 % | 49.5 | 44 | 3 |
| Butanediol | 40 % | 46 | 36 | 13 |

Table 2.7: Physical properties of soy based PUs as a function of their hard segment content and the nature of the chain extender used[79].

secondary hydroxyl [58]. Therefore primary hydroxyl TAGs would be ideal for PU preparation, however, the synthesis of PUs from pure triacylglycerols is expensive when compared to vegetable oils. As shown in Section 2.1, ozonolysis followed by hydrogenation, or reduction of vegetable oils are recognized to be cheap and efficient methods for producing polyols with primary hydroxyl groups. These polymerization technologies have led to a high content of primary triols, although the presence of diols, mono-ols, and saturated TAGs is inevitable. Furthermore, the optimization of these reactions is important since acid can be present in the mixture in detrimental concentrations[65,67].

In vegetable-based PUs, mono-ols act as chains terminators in the network, and saturated TAGs act as plasticizers. The properties of PUs can be greatly affected by these parameters. Table 2.8 shows two examples of polyols having primary hydroxyl groups : 1) canola-oil based PUs and 2) triolein based PUs which were converted into pure triols[65].

As seen in Table 2.8, the hydroxyl number of triolein polyols is higher than canola polyols. This is a result of the ozonolysis then reduction, upon which every fatty acid chain of the triacylglycerol has a terminal alcohol group. On the contrary, canola polyols have saturated fatty acids where no hydroxyl group may be added. As the hydroxyl number was higher for triolein polyols, the crosslinking density and consequently, the Tg values and tensile strength were higher as well. On the other hand the effect of the dangling chains within the

| | polyol acid number | Polyol OH number | Tg (°C) (DSC) | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|---|---|---|
| Canola-PU 2 | 2.0 | 260 | 36 | 41 | 51 |
| Triolein PU | 2.0 | 298 | 42 | 51 | 25 |

Table 2.8: Effect of the structure of the polyols on the physical properties of PUs

canola polyols resulted into a greater elongation at break and an increase in the damping properties of the network[3]. Not only does the structure of the polyols or the presence of chain extenders change the physical properties of PUs but also the type of isocyanate present[80,81]. Depending on the choice of the isocyanate, vegetable oil based PUs can confer changes in the properties of the resulting elastomers[56], rigid plastics[82], coatings[83] etc. Javni et al. [81] demonstrated a correlation between the isocyanate structure and the physical properties of the vegetable oil-based PUs by polymerizing different isocyanates with soy polyols. Aromatic isocyanates increased the rigidity of the PUs due to their benzene ring. Whereas triisocyanates, such as Desmodur RF-E, increased the crosslinking density of the matrice as it has more reactive sites than diisocyanate, increasing the ratio of elastically active network chains. From these characteristics, it is then understood that the more rigid the PU matrix, the greater the storage modulus, the lower the elongation at break, and the lower the swelling degree (Table 2.9). Similar results were also found for other soybean-oil based PU systems[84].

The crosslinking density can be somewhat controlled by the ratio of OH: NCO content of the PUs. In an ideal case, a ratio of OH: NCO, 1:1, results in a full conversion of polyols into polyurethanes. However, since most of the vegetable oil-based PUs found in literature are synthesized with secondary hydroxyl group polyols and contain dangling chains, an excess of isocyanate is required in order to achieve optimal conversion. It is important to note that the extent of conversion desired will vary depending on the preferred physical

| | Density (Kg/m$^3$) | Tg (°C) (DMA) | Swelling Degree (%) | Flexural modulus (MPa) |
|---|---|---|---|---|
| HDI | 1066 | 22 | 79 | 0 |
| RMDI | 1062 | 69 | 75 | 1190 |
| MDI | 1104 | 74 | 55 | 1380 |
| TDI | 1104 | 62 | 64 | 1180 |
| Desmodur RF-E | 1272 | 84 | 22 | 2480 |

Table 2.9: Effect of the isocyanate structure on the density and swelling degree of soy-based PUs[81].

Note that the acronyms HDI, RMDI and TDI stand for hexamethylene diisocyanate, hydrogenated MDI and toluene diisocyanate respectively.

properties of the final matrix. Petrovic *et al.*[85] found that increasing the OH: MDI ratio of soy-PU from 0.4 to 1.05 increased the Tg from 0°C to 64°C and consequently changed the physical properties of the PU matrices (Table 2.10). However, finding an optimal concentration of isocyanate is important as too large of an excess of isocyanate produces PUs that are very brittle. Kong et al.[82] showed that the stoichiometric excess of isocyanate must be optimized, otherwise the concentration of elastically active network chains and the crosslinking density are not improved. It was also shown that small variations in the isocyanate's NCO content can greatly affect the properties of PUs. For example, the addition of distilled MDI, having a NCO content of 33%, instead of crude MDI, having a NCO content of 32%, increased the Tg value of castor oil-based PUs by 40°C[40].

The literature also presents unconventional routes for increasing the crosslinking density. One study showed that by introducing large halogene atoms in the polyols, such as bromine and chlorine, (Figure 2.4 and Table 2.3)[68] leads to increased crosslinking density due to the increase of polarity introduced by these atoms. Soy-based halogenated PUs have a higher density than hydrogenated and methylated soy-based PUs. They indeed have a higher $M_c$ value and a lower swelling degree as well as higher Young's modulus value and lower elongation at break. However, these PUs were found to be less stable to thermodegradation due to the presence of halogen atoms.

| NCO/OH | Density (g/cm$^3$) | Swelling Degree ($W_1/W_0$) | Sol fraction (%) | $V_e$ (mol/cm$^3$) | $M_c$ (g/mol) |
|---|---|---|---|---|---|
| 1.05 | 1.104 | 1.52 | 0.82 | 0.00273 | 404 |
| 1 | 1.104 | 1.55 | 1.02 | 0.00245 | 451 |
| 0.8 | 1.095 | 1.73 | 2.78 | 0.00148 | 741 |
| 0.4 | 1.064 | 3.06 | 24.78 | 0.000149 | 7118 |

Table 2.10: Influence of the NCO/OH ratio on the physical properties of soy-based PUs[85].

Thermodegradation of polyurethanes starts at about 150-200°C[49] at which point the urethane bond decomposes in three possible ways: 1) the formation of the precursor isocyanate and the precursor alcohol, 2) the formation of a carbamic acid and olefin by cleavage of the oxygen of the alpha $CH_2$ group and association of one hydrogen on the second $CH_2$ group and 3) urethane and secondary amine formation[2,49,76,86,87] (Figure 2.8). The second stage of degradation occurs around 450°C which is associated with the carbon-carbon bond degradation. However, it is not surprising to observe other weight loss stages in the TGA between the degradation of the urethane bond and the carbon-carbon bond. These degradations are proposed to be of the polyol type, the unreacted isocyanate, and the dangling chains[67].

It has been shown that there is a potential for utilizing vegetable oil-based PUs sheets and elastomers as a replacement for petroleum oil-based PUs. These PUs are equally advantageous due to the wide range of potential structural modifications on the polyol backbone, altering the overall physical properties of the sheets and elastomers.

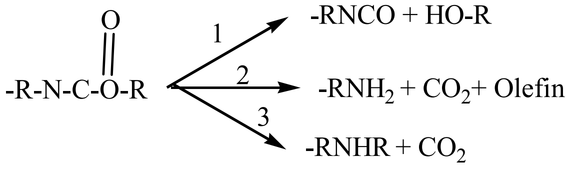


Figure 2.8: Thermodegradation mechanisms of urethane.

### 2.3.2 Vegetable-oil based PU foams

PUs foams can be separated in two main categories: flexible and rigid foams. Flexible foams require polyols having a molecular weight ranging from 3000 to 6000 and having a functionality of about 3. Rigid foams require polyols having a molecular weight below 1000 and having a functionality ranging from 3 to 6. Hence, most of the literature on vegetable oil-based PUs foams is within the category of rigid foams since polyols from vegetable oil have a molecular weight below 1000. Other than the polyols, PUs foams contain isocyanates (mainly MDI or TDI), catalysts, surfactants, and a blowing agent. The blowing agent is involved in producing the cellular structure of the foams. Most of the time, the utilization of water is favored over other types of blowing agents in vegetable oil based PUs. The NCO group of isocyanate reacts with water to release gaseous carbon dioxide (Figure 2.9), which produces the cellular structure.

Other chemical blowing agents such as enolizable compounds will also react with NCO to release gaseous $CO_2$ through complex mechanisms. Blowing agents are low boiling point, inert liquids. These liquids evaporate due to the exothermic nature of PU formation. The addition of a catalyst is not always necessary; however its role is to catalyze the gelation and blowing reactions. Since the reaction of polyols with diisocyanates is often too fast, the use of salt of tertiary amines such as 1,4-diazabicyclo (2,2,2) octane (DABCO) and 2,2'-bis-

$$2\ \mathrm{R\text{-}NCO} + \mathrm{H_2O} \longrightarrow \mathrm{R\text{-}NH\text{-}CO\text{-}NH\text{-}R} + \mathrm{CO_2}\uparrow$$

Figure 2.9: Formation of carbon dioxide from the reaction of isocyanate with alcohol.

(dimethylaminoethylether) (BDMAEE) can delay the action of the catalyst. Tertiary amines catalysts are therefore used as co-catalysts. They improve the $H_2O$-NCO interaction and increase network formation. They also increase the flowability of the mixture by decreasing its viscosity via catalyst dissociation. Other common catalysts such as dibutyltin dilaurate (DBDTL) and tin bis-(2-ethylhexanoate) are organometallic catalysts used for their effectiveness towards gelation activity[88-90]. Organic tin metal salts are used to promote the OH/NCO interaction. Both DABCO and DBDTL are traditionally used in vegetable oil-based PUs.

The foaming reaction of SBO based PU has been monitored with the use of vane geometry in a strain controlled rheometer[91]. The study found that the foaming reaction was similar to synthetic foams[91]. This study highlighted four different steps in the foaming process: 1) bubble nucleation and growth, 2) packed bubble network, 3) urea microphase separation and cell opening and 4) curing[91]. The first step consists of the incorporation of air through mixing which acts as the nucleation site for the release of carbon dioxide. The gel point is then attained when the bubbles become packed in a sufficiently close network for the loss modulus (G") value of the system being equivalent to the storage modulus (G') value. The packed bubble network step is characterized by the continuous expansion of the matrix, which exhibits a solid-like behavior. Formation of urea is also present in this stage due to the reaction of isocyanate with water[2,89]. The urea microphase separation and cell opening step is characterized by an increase in urea formation[91,92] (Figure 2.10).

The hard urea domains are organized into loose hydrogen-bonded structures which increases the PU modulus. This step is responsible for the cell expanding until no further rise in volume is possible. Finally, the modulus increases over several hours during the curing time due to the formation of the material skin[91] and/or the annealing of hard segments[91,93] or covalent bond formation[91,93]. A more common method to determine the reaction rate of PU foam formation is to monitor the cream time, the gel time, and the rise time. The cream time is defined as the time for the polyol and the isocyanate to transition from a clear color to a creamy color, the gel time is the time it takes for an infinite network to be formed, and the rise time is the time needed for the foam to fully expand[2].

The foaming reaction rate is directly influenced by the structure of the polyols. As shown in Table 2.11, rapeseed oil polyols have a slower reaction rate than Daltolac, a commercial polyether polyol. This is due to the structure of rape seed oil polyols which contains secondary hydroxyl groups whereas the Daltolac polyols contain only hydroxyl groups located in primary position. This slower reaction rate is observed even though the hydroxyl value of both polyols is similar, demonstrating the significance of primary versus secondary hydroxylation on reaction rates.

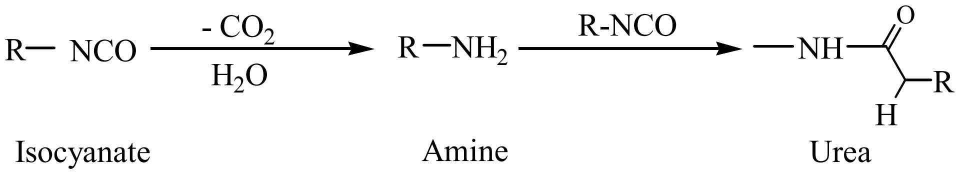


Figure 2.10: Formation of urea in a PUs foam structure.

|  | Cream time (s) | Gel time (s) | Tack free time (s) |
|---|---|---|---|
| Rape seed oil based polyol-PU | 24 | 64 | 122 |
| Daltolac'$^{TM}$ P744 based PU | 25 | 36 | 40 |

Table 2.11: Foaming reaction rate as a function of the polyol type[54].

The optimization of a PU foam formulation can become a rigorous exercise. Not only can the position of the polyols hydroxyl groups influence the reaction time of foaming but also their viscosity[94]. The viscosity of the matrix plays a significant role in the close cell content[91,94]. In comparing two types of soy polyols having the same hydroxyl number but different viscosities (4500 and 1250 cps.), it was found that the polyols with the reduced viscosity had a reduced curing time[94]. However, the uses of higher viscosity polyols slow down the rupture of the cells' walls. As a result, the compressive strength of the foams formulated with the high viscosity polyol was superior than the low viscosity polyols[94] due to the density of the final matrices.

Changes in components other than the polyols can also greatly impact the physical properties the matrices. Experiments conducted on soybean PUs[90,92,95], where the percentage of water content was varied, showed that increased water content increased the foaming reaction rate and amount of $CO_2$ (g) produced, which augmented the cell size and cell rupture, and decreased the density of the foams. The concentration of catalyst also plays an important role[89,94]. The impact of the amount of an organic tin metallic salt catalyst (DABCO T-12) on the physical properties of soy-polyol-based PUs foams was recently studied[94]. It was found that increasing the catalyst from 2 parts per hundreds parts (pphp) of polyols to 5 pphp decreased the blowing time, directly impacting the density of the foams, which dropped from 279 $g/m^3$ to 173 $g/m^3$. Moreover, due to a decrease in blowing time, there was a reduction in the size and the number of cells in the foam matrix. Consequently, the compressive strength of the foams containing 2 php of catalyst was higher (59 KPa) than the foams containing 5 php (28 KPa).

As discussed, the formulation of foams greatly influences the foaming reaction rate, which influences the density and cells morphology and size and therefore, influences the overall mechanical properties of the foam. These statements are true when the foams are formed in a free rise mold. In the case of closed molded systems, the density is controlled by the mass of PU mixture in the mold since the volume is fixed. Consequently, the physical properties of these foams can differ from the properties of free rise foams. Table 2.12 presents some physical properties of vegetable oil-based PUs which have been allowed to rise and cure in a closed mold[37].

In order to obtain a final hydroxyl number ranging between 450 and 500 mg KOH/g[37], which represent the hydroxyl value of most commercial polyols, glycerin have been added into the formulation of canola, castor, and soybean based PUs. More precisely, 12 parts of glycerin and 3 parts of water were added to canola and castor polyols while 15 parts of glycerin and 2 parts of water were added to the SBO polyols. The canola oil was previously treated by ozonolysis and hydrogenation to afford terminal primary hydroxyl groups. With the addition of glycerin, the structure of the canola polyol mixture only contained

|  | Canola-PU | Castor-PU | Soybean-PU |
|---|---|---|---|
| Cream time (s) | 10 | 15 | 30 |
| Rising time (s) | 15 | 20 | 35 |
| Gel time (s) | 40 | 50 | 90 |
| Density (Kg/m$^3$) | 159 | 158 | 163 |
| Closed cell content (%) | 68 | 9 | 9 |
| Compressive Strength (KPa) | 770 | 1170 | 415 |

Table 2.12: Physical properties of high density vegetable oil based-foams[37]

terminal primary hydroxyl groups. The SBO polyols were produced by epoxidation followed by hydrogenation and the castor oil did not undergo any type of oxidative treatment. The quantity of catalyst, surfactant, and MDI were kept constant for each type of foam. As expected, the foaming activity of the canola-PU was the highest due to the primary hydroxyl groups, which reduced the steric hindrance compared to secondary hydroxyl groups[4,37,54]. The foaming activity decreased for castor oil since the hydroxyl groups were in a secondary position. The reactivity of the SBO polyols was the lowest since the structure, not only contained secondary hydroxyl groups, but the presence of $-OCH_3$ groups in the chain led to further steric hindrance. As expected, the close cell content of canola-PU was superior to other foams systems. However, the compressive strength value of canola-PU was not the highest, which is contrary to what would have been expected for free rise foams. Although the plasticizer effect of dangling chains is non-negligible, compressive strength is mainly associated with the close cell content, cell size, cell wall thickness, and foam density[35,37,72,96-98]. Since all the vegetable oil-based foam's densities were similar, Narine et al.[37] explained that castor-PU had the highest compressive strength because of the low closed cell content, which is contrary to what has been discussed previously. This was due to the thickness of the cell walls which had a stronger effect on the compressive strength than the effect of the closed cell content. Castor-PU had the same percentage of closed cells content as soybean-PU, but the presence of non-uniform pores in its structure combined with a smaller content of hard segments decreased its compressive strength dramatically. This was probably due to an imbalance between the glycerol and water concentration in the mixture. It is known that at a constant MDI index, an increase in water content leads to a foam that is less dense due to an increase in the release of $CO_2$. However, this may also result in an increase in the weight percent of polyurea and hard segments within the matrices[89,90]

However, not all primary hydroxyl polyols produce superior foams. Interestingly, Javni et al.[99] found that foams from soypolyol 173 having a hydroxyl number of 173 mg KOH/g with secondary hydroxyl groups had improved physical properties, as described below, than foams made with polypropylene oxide polyols having a hydroxyl number of 168 mg KOH/g (a commercial polyether polyol), which have the hydroxyls groups located in primary position. Foams from the soy polyols and PPO had the same composition.

Table 2.13 also shows that the soy foam matrix, with a MDI index of 200, had the maximum percentage of close cell content without shrinkage. Overall, the Tg values of soy foams having a MDI index greater than 150 were at least 20 ºC above those PPO foams. The authors[99] explained the difference in Tg by the number of carbons present between the crosslinking points, which is significantly lower in the soy foams than PPO foams, resulting in a higher flexibility of PPO foams. This not only explains the difference in Tg but also the difference in compression stress. Javni et al. [99] found that at a MDI index of 200, the compression stress was about 100 MPa superior for soy foams. However,

| | Sample | MDI index | Density (Kg/m$^3$) | Tg by DMA (ºC) | Closed cell content % |
|---|---|---|---|---|---|
| 1 | Soy foam | 110 | 72 | 63 | 86 |
| 2 | Soy foam | 150 | 46 | 65 | 84 |
| 3 | Soy foam | 200 | 34 | 71 | 82 |
| 4 | Soy foam | 250 | 34 | 78 | 74 |
| 5 | Soy foam | 300 | 35 | 84 | 76 |
| 6 | Soy foam | 350 | 29 | 85 | 75 |
| 7 | PPO foam | 110 | 95 | 22 | 17 |
| 8 | PPO foam | 150 | 57 | 42 | 73 |
| 9 | PPO foam | 200 | 35 | 52 | 80 |
| 10 | PPO foam | 250 | 33 | 57 | 75 |
| 11 | PPO foam | 300 | 34 | 58 | 76 |
| 12 | PPO foam | 350 | 31 | 59 | 75 |

Table 2.13: Comparison between the physical properties of soy foams and PPO, a commercial polyol[99].

since the rigidity of the foams increased with the MDI content[100], discrepancies between the stress values were reduced as the concentration of MDI was increased. Discarding samples with a MDI index of 110 and 150 since they underwent shrinkage, Table 2.13 also shows that the close cell content of soy foams and PPO foams is, on average, greater than 75%. Javni et al. [99] also showed that the soy foams had better thermal stability, and lower flammability than PPO-based foams.

Many efforts have been made to incorporate vegetable oil-based polyols into petroleum based PUs foams systems[4,47,48,72,92,101] in order to obtain rigid foams. In these studies, Tu et al.[4] tested 15 types of PUs made from an equal combination of derivatives of SBO polyols and Voranol. In general, thermal conductivity properties of these foams were inferior when compared to foams made with 100% of Voranol. This was due to the secondary hydroxyl position of soybean polyols which decreased the reaction rate of PU foam formation and thus weakened the three-dimensional network structure, leading to higher open cell content. Because of these openings, the cells failed to hold the pressure due to carbon dioxide formation. Open cells in PU foams lose their carbon dioxide content which is then substituted by air. Air being more conductible than $CO_2$, the insulation properties of PU foams diminishes as the ratio of open cell content increases[4,99]. Another study showed that addition of more than 20% of palm, rapeseed, corn, soybean, sunflower or linseed polyols with petroleum based polyols worsened the compressive strength, and closed cell content of the matrices[101]. On the other hand, Tu et al[4] also found that hydroxyl SBO, oxidized epoxidized diglycerides SBO, and epoxidized SBO, when reacted with acetol and Voranol, had similar or better thermal conductibility, density, and compressive strength as compared to 100% Voranol foams. However, no further reasoning was provided to explain these superior properties. Furthermore, a patent[13] described that high load bearing properties was found when 30% of soy base polyols were mixed with petroleum based polyols. Zhang et al.[72] also found that mechanical properties of flexible foams to be improved when vegetable oil based polyols are added to the foams formulation.

## 2.4 Conclusion

Vegetable oil polyols are synthesized by several chemical pathways. When converted to PUs, depending on the structure of these polyols, a wide range of physical properties result. Not only can the structure of polyols change the physical properties of the foams and plastic/elastomer sheets, but also, other chemicals added into the formulation. Some vegetable oil PUs were found to be at least as efficient as petroleum based PUs. With such promising results, it is then not surprising that researchers are now investigating ways of creating diisocyanate from fatty acids[102] in hope to achieve PUs that are 100% derived from vegetable oils.

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# 3 Polyurethanes from benzene polyols synthesized from vegetable oils: dependence of physical properties on structure*

## 3.1 Introduction

The search for suitable mechanical and physical properties of vegetable oil based polyurethanes (PUs) has generated several academic publications and patents which were recently reviewed[1]. One of the approaches to improved properties is to modify the chemical structure of the polyols, either by the addition of reactive groups (functionality), modifying the placement of the functional groups on the polyol molecule, or modifying the structure of the polyol molecule. The literature details several chemical reactions performed on different types of vegetable oils that seeks to serve this purpose[2-19]. Generally, these efforts have led to the formation of aliphatic polyols having their hydroxyl groups in secondary[3,6-8,18,19] and primary positions [4,5,10,14,20].

Recently, Lligadas *et al.*[21] and Yue and Narine[22] synthesized aromatic polyols with a functionality of 3 from erucic and oleic acid, thereby introducing

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another class of vegetable oil derived polyols for research into the effect on physical properties. These monomers are different from the aromatic monomers synthesized by Suresh and Kishanprasad[23] who also developed an aromatic triol from cardanol but where not all of the alcohol groups were located on terminal primary position. Shortly after the work of Lligadas *et al.*[21] and Yue and Narine[22], Song and Narine[24] synthesized an aromatic hexaol from oleic acid. Although this publication focuses on the triols produced by Yue and Narine[22], work continues in the Alberta Lipid Utilization Program to examine the effects of the structure of the hexaols on polyurethane properties.

The chemical route to the synthesis of the aromatic triols produced a mixture of asymmetric and symmetric triols isomers, which have their terminal hydroxyl groups in position 1, 3, 4 and 1, 3, 5 respectively. The presence of the phenyl ring within the polyol structure is of interest due to the potential to increase the rigidity of resulting polyurethane sheets, which was normally achieved through addition of an aromatic isocyanate. Yue and Narine [22] focused their efforts on the synthesis and separation of the symmetric and asymmetric triols, while Lligadas *et al.*[21] synthesized the aromatic triols and polymerized the mixture (M-PU) without further separation of the isomers. The M-PU matrices where synthesized with 4, 4'-methylenebis(phenyl isocyanate) (MDI) and different ratios of chain extenders. The objective of this present study was to polymerize the asymmetric and symmetric triols separately with MDI and to understand the effect of the hydroxyl positioning on the different physical and mechanical properties of the PU matrices. This study also compared the properties of the A-PU and S-PU matrices with the properties found for the M-PU matrix containing no chain extenders unless specified in the text. It also provided additional physical and mechanical information that can be extended to the M-PU matrix.

## 3.2 Materials and Methods

### 3.2.1 Material.

Bromine (99.8%) was purchased from ACROS Organics, (Geel, Belgium) and hydrochloric acid was purchased from Caledon (Canada). The following reagents were purchased from Fisher Scientific, (Canada): diethyl ether anhydrous (ACS grade), sodium thiosulfate anhydrous (certified), hexane (ACS grade), ethyl acetate (ACS grade), sodium sulfate (10-60 mesh, ACS), 1-propanol (certified) and potassium hydroxide (ACS). The following reagents were purchased from Sigma-Aldrich Co. (USA): erucic acid (90%), dimethyl sulfoxide (>99.5%), tetrahydrofuran (>99.9%), lithium aluminum hydride reagent grade (95%), palladium 10 weight % (dry basis) on activated carbon (wet) and chloromethylsilane redistilled (99%). The Bayer Corporation, (Pittsburg, USA), donated the aromatic diphenylmethane diisocyanate (MDI, Mondur MRS) having a functionality of 2.6 and a NCO content of 31.5 wt %.

### 3.2.2 Synthesis, separation and characterization of isomeric triols.

The asymmetric and symmetric triol monomer synthesis procedure and characterization by $^{1}$HNMR and $^{13}$CNMR were described elsewhere[22]. The hexasubstituted benzene derivatives containing three alcohols groups were synthesized from erucic acid derivatives followed by a cyclotrimerization step catalyzed by palladium on activated carbon and chlorotrimethylsilane (TMSCl), such has described by Yue and Narine[22]. Both types of triols had a functionality of 3 and an equivalent weight of 323g/mol. A combi-flash (companion/TS/SMM apparatus) from Teledyne ISCO was used for the separation of the triol isomers. The separation of the isomers was verified with a HPLC model 1200 series from Agilent equipped with an ELSD 2000 detector from Alltech. The polar column used for the separation was a diol 100 from Thermo, USA. The solvent system used was a mixture of isopropanol and heptane in a molar concentration of 1:1 used in a gradient of 0% to 30%, while 100% heptane was used in a gradient of 100% to 70%. The flow rate used was of 1mL/min. The HPLC spectra did not show the presence of impurities for both triols.

### 3.2.3 Preparation of polyurethanes.

Polyurethane sheets were prepared with the asymmetric triols and symmetric triols and were polymerized with MDI with an OH: NCO ratio of 1:1.02. The MDI equivalent weight (EW) was provided by the supplier (133g/mol). The OH:NCO ratio mentioned above was calculated using the following equation:

$$Molar\ \ Ratio = \frac{Weight\ \ Polyol / Equivalent\ Weight\ \ Polyol}{(Weight\, of\ \ isocyanate)/ Equivalent\ \ Weight\ \ Isocyanate} \qquad (1)$$

The plastic sheets were prepared by homogenously mixing MDI with the corresponding triols. The mixtures were then cast into a plastic mold and cured at 75°C for 24 hours, in order to maximize the crosslinking density of the matrices.

### 3.2.4 FTIR.

The FTIR equipment used was a Nicolet Magna 750 coupled with a MCT-A detector and a Nicolet Nic-Plan IR microscope used in a transmission mode. The spectrums were recorded within a range of 4000 to 650 $cm^{-1}$. The nominal resolution was 4 $cm^{-1}$. The Fourier transformation of 32 scans has been calculated using the Nicolet Omnic software version 7.1. Before each absorbance spectrum, a background spectrum was recorded.

### 3.2.5 XRD.

The XRD apparatus used was a Bruker AXS X-ray diffractometer equipped with a 2-D detector and a filtered Cu Kα radiation source ($\lambda$=0.154059 nm). The sample exposure time was 450 seconds. The GADDS V4.1.08 and Topas V 2.1 software were used for data analysis.

### 3.2.6 Density properties.

The densities of PUs were determined using the ASTM standard D-792.

### 3.2.7 Thermal properties.

A DSC Q100 from TA Instruments was used for the DSC measurements. This apparatus was equipped with a refrigerated cooling system. All the measurements were performed under a nitrogen gas atmosphere. The DSC measurements were carried out following the ASTM standard procedure E1356-03. The thermal history was erased by heating the samples from 23°C to 100°C at a rate of 10°C/min after which the samples were cooled to -10°C at a rate of 5°C/min. The analysis was performed using the following procedure: performing a third cycle by heating from -10°C to 300°C at a heating rate of 10°C/min.

The Dynamic mechanical analyzer (DMA) used for this study was a DMA Q800 (TA instruments) equipped with a liquid nitrogen cooling system. The samples were analyzed following the ASTM standard E 1640. The sample dimensions for A-PU and S-PU were 17.3 X 7.7 X 1.4 mm and were analyzed in a 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 -100 °C to 100 °C. The multiple oscillation experiments were recorded as a function of frequency, ranging from 0.01 Hz to 100 Hz. These measurements were made every 5 ºC, over a temperature range of 30 ºC below and above the Tg of the samples. The elastomeric plateau modulus built from the storage modulus master curves to find $M_c$ and $v_e$ using Equation 2[25,26]:

$$G' = \frac{E'}{3} = aVeRT = \frac{a\rho RT}{Mc} \tag{2}$$

Where $a$ has a value of 1 for the affine model and a value of $1-\frac{2}{f}$ for the phantom model, with $f$ being the functionality.

### 3.2.8 TGA-FTIR.

The TGA instrument used was a Perkin Elmer Pyris 1. The purge gas used was nitrogen. The FTIR was a Thermo Nicolet Avatar 360 equipped with a 5 cm gas cell fitted with KBr windows. The cell was operated at room temperature. The FTIR spectra from 4000 to 400 wave numbers were obtained using Omnic software with 32 scans and 4 wave number resolution. The transfer line from the TGA to the FTIR gas cell was a 1 meter length of 3 mm ID Tygon (PVC) tubing at ambient temperature. Before each absorbance spectrum, a background spectrum was recorded.

### 3.2.9 Mechanical properties.

The mechanical properties of the A-PU and S-PU samples were investigated using an Instron (MA) tensile testing machine (model 4202) equipped with a 50KgF load cell and activated grips. Each sample was cut into four identical dumbbell shaped specimens and was cut using a V type cutter at a speed of 100 mm/min as suggested by the ASTM standard D638. Each sample was tested at room temperature.

## 3.3 Results and Discussion

### 3.3.1 Separation of monomers.

The separation of the monomers is shown in the HPLC chromatograph (Figure 3.1). The asymmetric and symmetric monomers had a retention time of 7.4 minutes and 7.8 minutes respectively. The difference in retention time was attributed to the asymmetric triol being less polar than the symmetric triol due to intramolecular hydrogen bonding between the two adjacent alcohol groups[22].

### 3.3.2 Characterization of polymers.

The FTIR spectrum (Figure 3.2) confirmed qualitatively the presence of the urethane linkage of both A-PU and S-PU. The characteristic N-H stretching vibrational region (3200-3500 $cm^{-1}$) and the characteristic C=O vibrational region (1700-1730 $cm^{-1}$) are well represented[27]. The bands in the region below 1600 $cm^{-1}$ represent the fingerprints of the PUs. The unreacted isocyanate (NCO group) is clearly shown by a peak centered at 2273 $cm^{-1}$ [25].

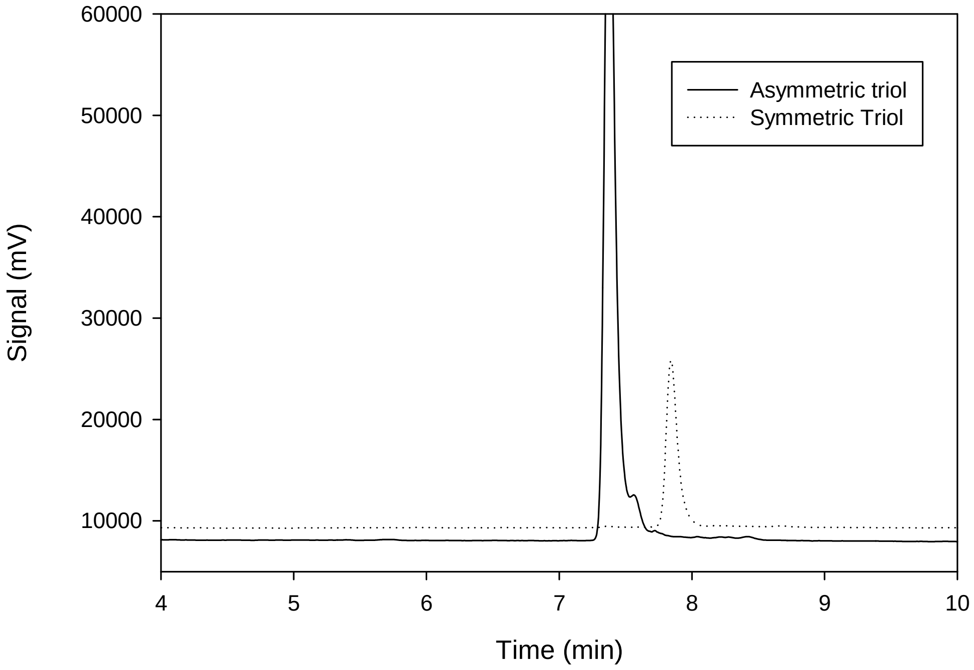

Figure 3.1: HPLC retention times of the asymmetric and symmetric triol monomers. The HPLC system was equipped with a polar column and the mobile phase was a gradient of isopropanol and heptane.

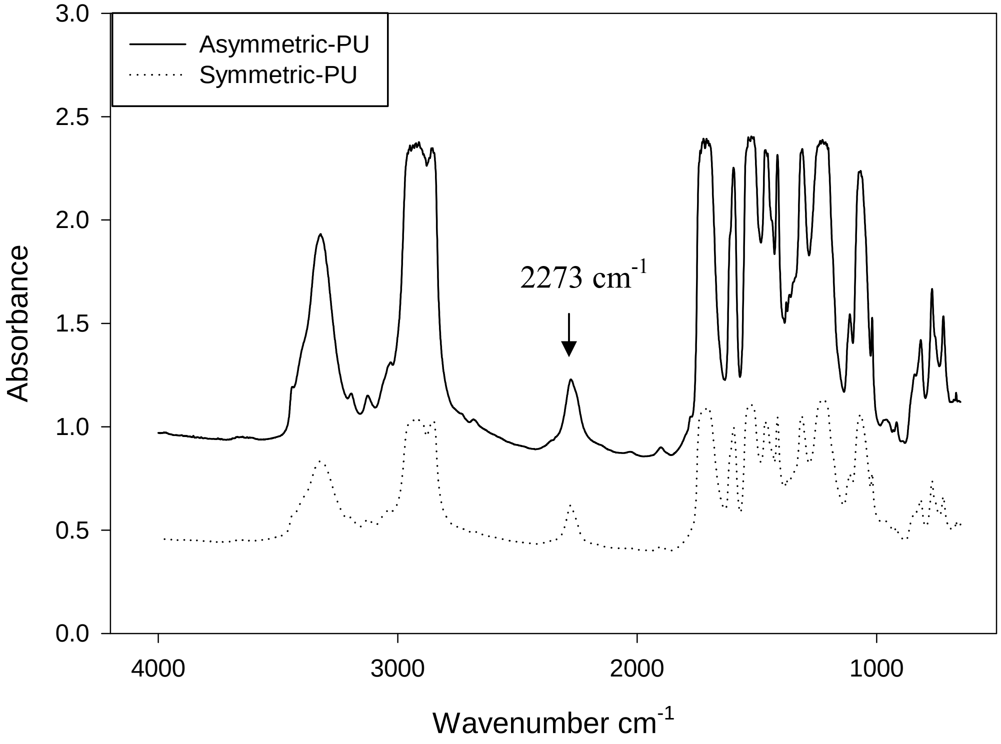

Figure 3.2: General FTIR spectra of A-PU and S-PU where the isocyanate region is shown at 2273 cm$^{-1}$.

Figure 3.3 focuses on the C=O and N-H vibrational bands. The N-H stretching region showed two distinct bands. The band centered at 3444 $cm^{-1}$ corresponds to the free N-H region (3441-3446 $cm^{-1}$) and the band centered at 3329 $cm^{-1}$ corresponds to the bonded N-H region (3324-3329 $cm^{-1}$)[28,29]. There are also two stretching regions attributed to the C=O group. The band centered at 1734 $cm^{-1}$ corresponds to the free carbonyl group (1731-1733 $cm^{-1}$) while the band centered at 1707 $cm^{-1}$ corresponds to the H-bonded-carbonyl group (1699-1706 $cm^{-1}$)[28,29] (Figure 3.3). These results indicated that both of the PU matrices undergo physical bonding. The FTIR spectrum of the A-PU, S-PU and M-PU[21] matrices were found to be similar.

The amorphous character of both the asymmetric and symmetric networks was verified by XRD (Figure 3.4). The spectrum showed two broad peaks at 2 theta ≈ 7° and 2 theta ≈ 20°. Similar results were found in other amorphous PUs[30]. The latter broad peak was identified as a characteristic of amorphous polymers[21,31]. The peak at 2 theta ≈ 7° is equivalent to an intermolecular distance of 1.7 nm. This long range ordering peak is usually found in segmented partially crystalline PUs. However, melting the sample to 300°C in the DSC (data not shown) did not reveal the presence of a high temperature melting peak, which further confirmed the amorphous structure of A-PU and S-PU.

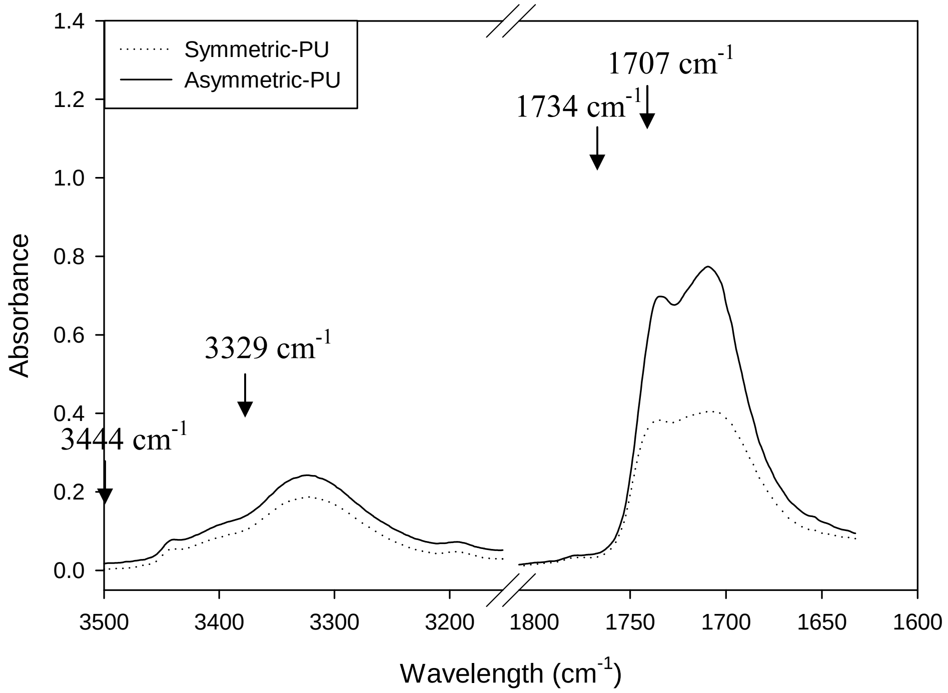

Figure 3.3: FTIR spectra of C=O and N-H stretching of A-PU and S-PU

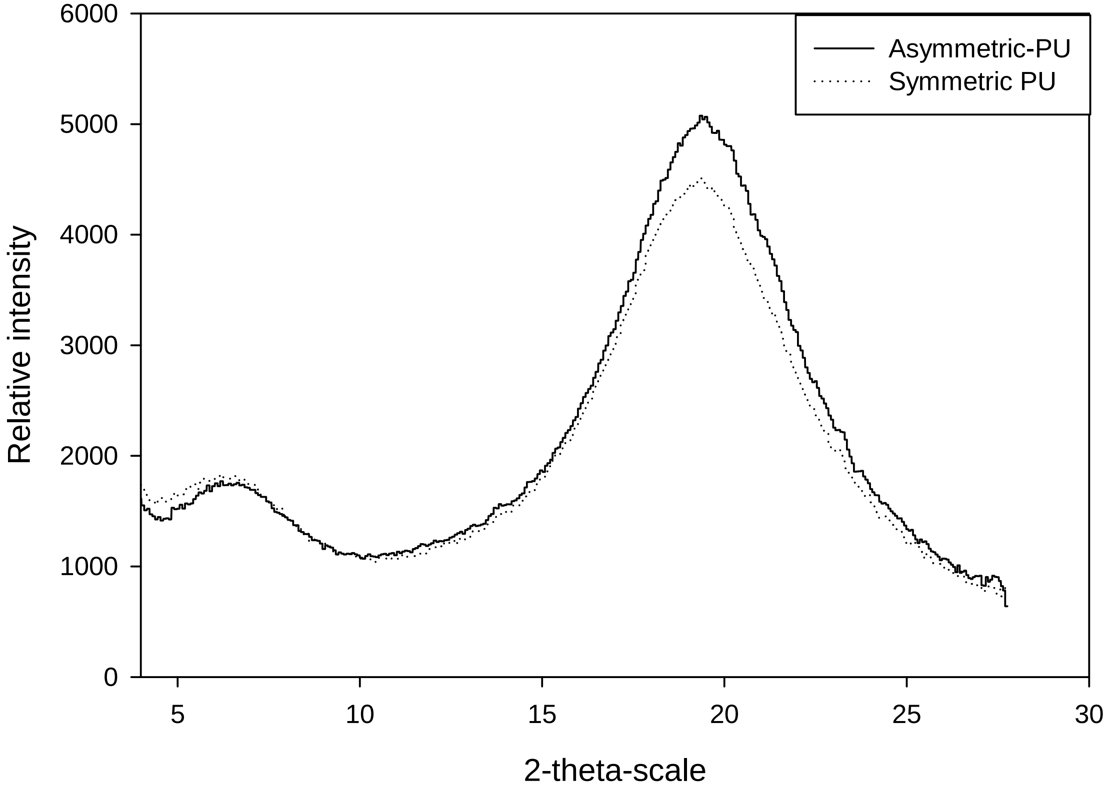

Figure 3.4: WAXD data of A-PU and S-PU

### 3.3.3 Mechanical and Physical Properties.

In this study, only the topological effect (crosslinking effect) could influence the Tg. Tg values recorded by DMA were 34.8 °C and 40.4 °C for A-PU and S-PU, respectively (Table 3.1). The differences in Tg could be explained by the concentration of unreacted isocyanate which could have been higher within the A-PU matrix than the S-PU matrix, suggesting that less MDI would have reacted with the asymmetric monomers. This phenomenon could explained by two factors. First, from the representation of the idealistic network structure (Figure 3.5), the proximity of the alcohol groups in position 1 and 2 of the asymmetric structure can result in steric hindrance. Furthermore, the size of the MDI molecule might also played an important factor in reducing the interaction with the asymmetric monomer. When one MDI molecule reacts in position 1, a second molecule of MDI will have to overcome its steric hindrance before reacting in position 2.

Since the OH: NCO ratio used in the polymerization process of A-PU, S-PU and M-PU was identical; the difference in Tg was then explained by the difference in the post-curing conditions. In both cases, the gelation and the vitrification occurred at 75 °C. Once the vitrification process is completed, the reactivity of the thermoset material decreases significantly. The post-curing at elevated temperature is then required to complete the reaction. The A-PU and S-PU post-curing conditions were 35 °C lower than the M-PU (110 °C).

|  | Tg (°C) from DMA | ρ at 23 °C ($g/cm^3$) |
|---|---|---|
| A-PU | 34.8±1.5 | 1.016±0.006 |
| S-PU | 40.4±1.6 | 1.006±0.002 |

Table 3.1: Glass transition temperatures obtained by DMA for the A-PU and S-PU matrices

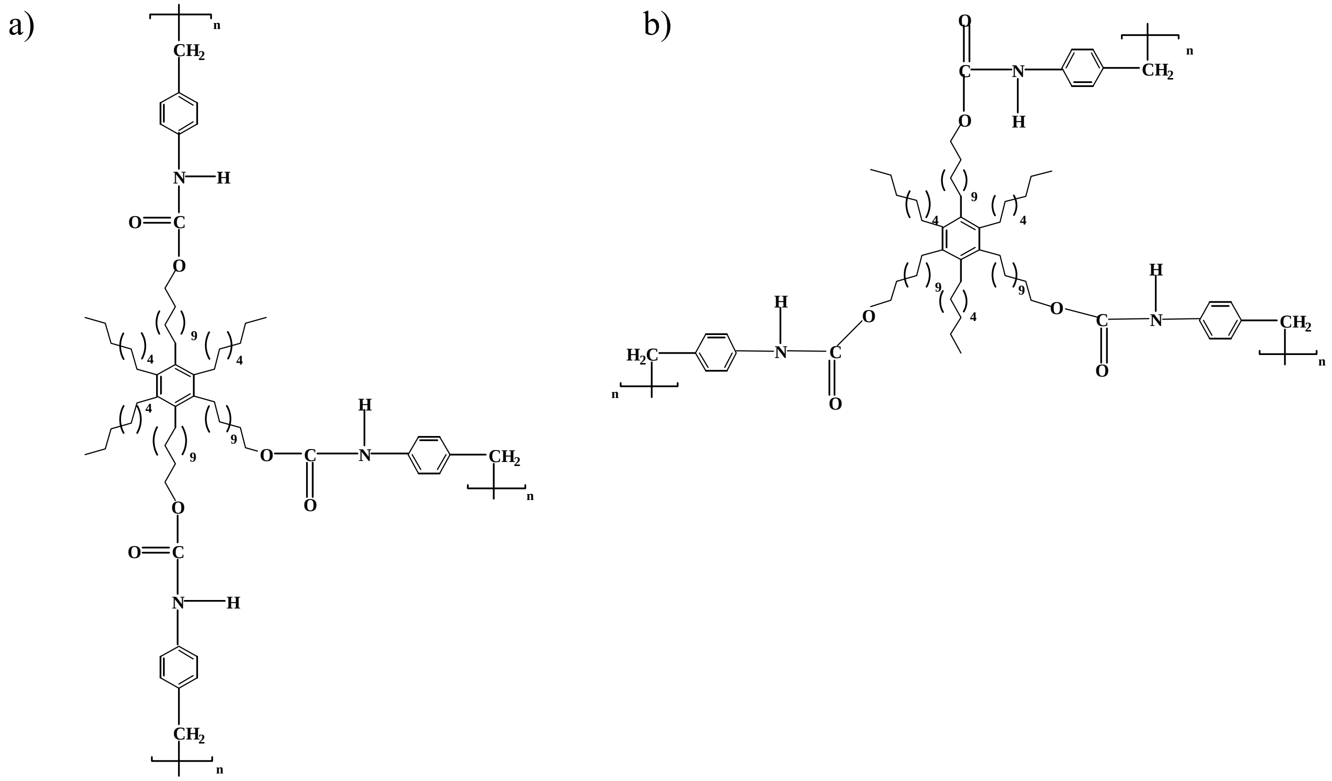

Figure 3.5: Idealized network structures for a) A-PU and b) S-PU

Monteavaro *et al.*[32] , who worked with PU networks from soy oil, reported a Tg variation of 5 °C when applying a variation of 40 °C in the post-curing process. However, Li and Larock[33] reported that the crosslinking density of their soybean oil PUs decreased when post-cured at 110 °C for an exposure time of 5 hours. Consequently, since the curing behavior of the A-PU, S-PU and M-PU are not well understood due to their novelty, the post-curing condition of the A-PU and S-PU was set at 75 °C to avoid the de-crosslinking.

A higher Tg value is an indication of the increase in chain connectivity. It raises the stiffness of the matrix and thus reduces the loss modulus. This was observable by the tan curves (Figure 3.6), where the ratio of the loss modulus to the storage modulus is shown. The PU samples experienced a general trend where the tan δ peak intensity decreased as the crosslinking density increased. Figure 3.6 also revealed that the A-PU and S-PU have similar damping properties which corresponded to a tan δ value ≥ 0.3 over a range of temperature greater than 20 °C. These specifications fulfilled the requirements for efficient damping properties of homopolymers[34]. The curves maxima also corresponded to the transition from the glassy state to the rubbery state. The corresponding temperature is also reported as the Tg (Table 3.1).

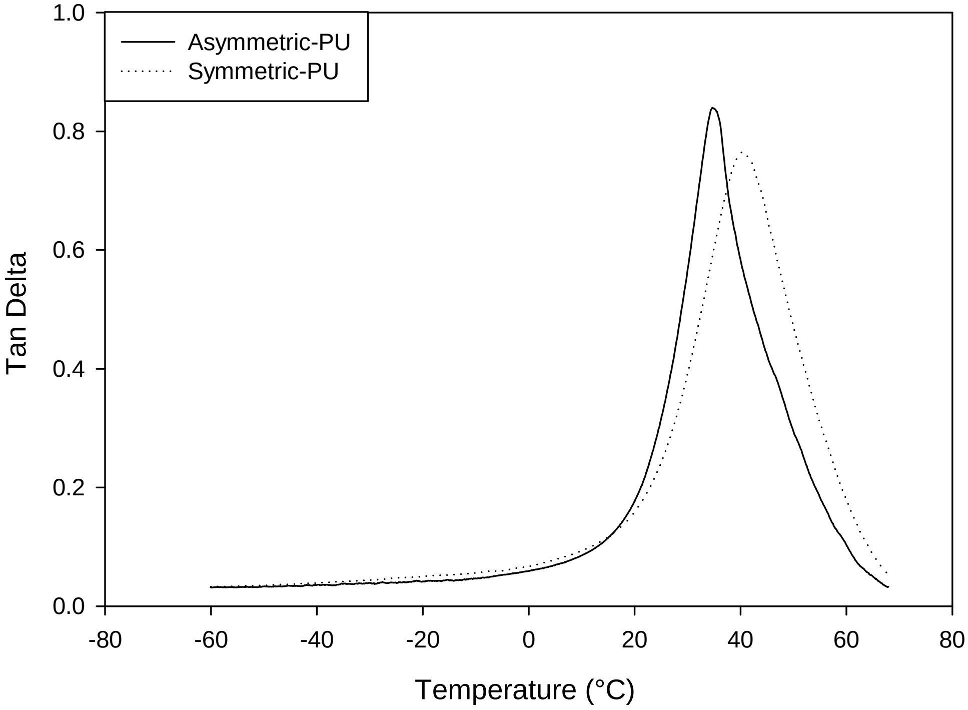

Figure 3.6: Loss tangents of A-PU and S-PU measured by DMA

The Tg values of both polymers being close to room temperature, the stress-strain curves of the samples showed a behavior similar to that of rubber (Figure 3.7). The trend in the modulus of both PUs at low strain was found to be different. It is suggested that a higher crosslinking density of the S-PU would have raised the modulus, which would be in agreement with the Tg values and the DMA results. A-PU displayed a tensile stress and an elongation at break of 13 MPa ± 1 % and 46 ± 3 %, respectively. S-PU displayed a tensile stress and an elongation at break of 14 MPa ± 1 % and 50 ± 9 % respectively. The similarity of these results can be explained by the fact that both matrices had the same ratio of aromatic content, the same carbon-carbon chain length between the aromatic structure and the hydroxyl groups as well as the same ratio of dangling chains. It is then expected that the M-PU would have the same mechanical properties as the A-PU and S-PU. Vegetable oil based PUs crosslinked with MDI having similar OH: NCO ratio and functionality as the A-PU and S-PU provide a wide range of mechanical properties. As a comparison, the tensile strengths of A-PU and S-PU were of lower values but higher elongation at break than of epoxidized soybean oil PUs (46 MPa, 7%)[35] and rhodium catalyzed hydroformylated soybean oil-PU (38 MPa, 17 %)[4]. Inversely, the A-PU and S-PU had similar tensile strength and lower elongation at break than ozonolyzed-hydrogenated canola oil based PU (14 MPa, 75%)[25].

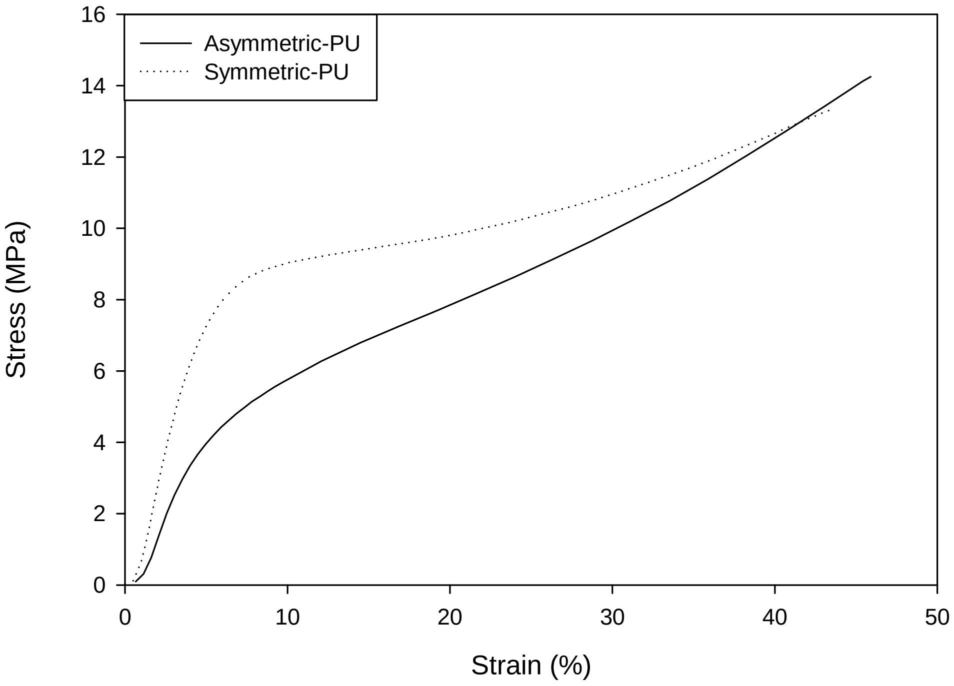

Figure 3.7: Stress-strain curves of A-PU and S-PU

An attempt to evaluate the $M_c$ and $v_e$ values through the elastomeric plateau modulus built from the storage modulus master curves was made using Equation 2. The rubber elasticity theory proposes the affine and phantom models, among others, for the evaluation of $M_c$ and $v_e$. The affine network model assumes that 1) the network deformation is proportional to the deformation of the network strands and 2) that the junction points are pinned to an elastic background and do not fluctuate during deformation[36]. The later assumption is also valid for the phantom model but only at the chains' end. It also acknowledges that the crosslinks can fluctuate around their average position. However, the model assumes the strands to be ideal, i.e. the chain ends to be joined at crosslinks. As a consequence, this model neglects the defects that normally occur in a real network such as dangling ends and dangling loops. Since the phantom model allows the strands to unrestrictedly fluctuate, it lowers the modulus value if compared to the affine model, where the junctions are considered steady. A real network will then have a modulus value lower than the one predicted by the affine model but higher than the one predicted by the phantom model.

In this study, Tg values from the tan δ plot were used as the reference temperatures for the construction of the storage modulus (E') master curve as a function of the log of the reduced frequency ($fa_t$). The viscoelastic responses of the A-PU and S-PU were then acquired based on the time-temperature superposition principle by shifting the isothermal response curves along the horizontal axis, with the exception of the responses at reference temperature (Figure 3.8). No vertical shift was applied.

As the Tg value of the S-PU matrix was higher and due to the trend of the tan δ curves explained previously (Figure 3.6), it was expected that the plateau modulus of the A-PU matrix would have a lower E' value than the S-PU matrix. Surprisingly, the E' values at the plateau were 44 MPa and 12 MPa for A- and S-PU respectively. Consequently, the corresponding $M_c$ values were 177 g/mol (A-PU) and 654 g/mol (S-PU). Clearly, this method has been unsuccessful regarding the present samples since these Mc values correspond to a point of crosslink at every 14 (A-PU) and 54 (S-PU) carbons. It is worth mentioning that Lligadas et al.21 also made an attempt to make a qualitative evaluation of the crosslinking density through the DMTA technique. It was found that the E' plateau value of more tightly crosslinked matrices was lower than less crosslinked matrices, which is also a deviation from the normal trend.

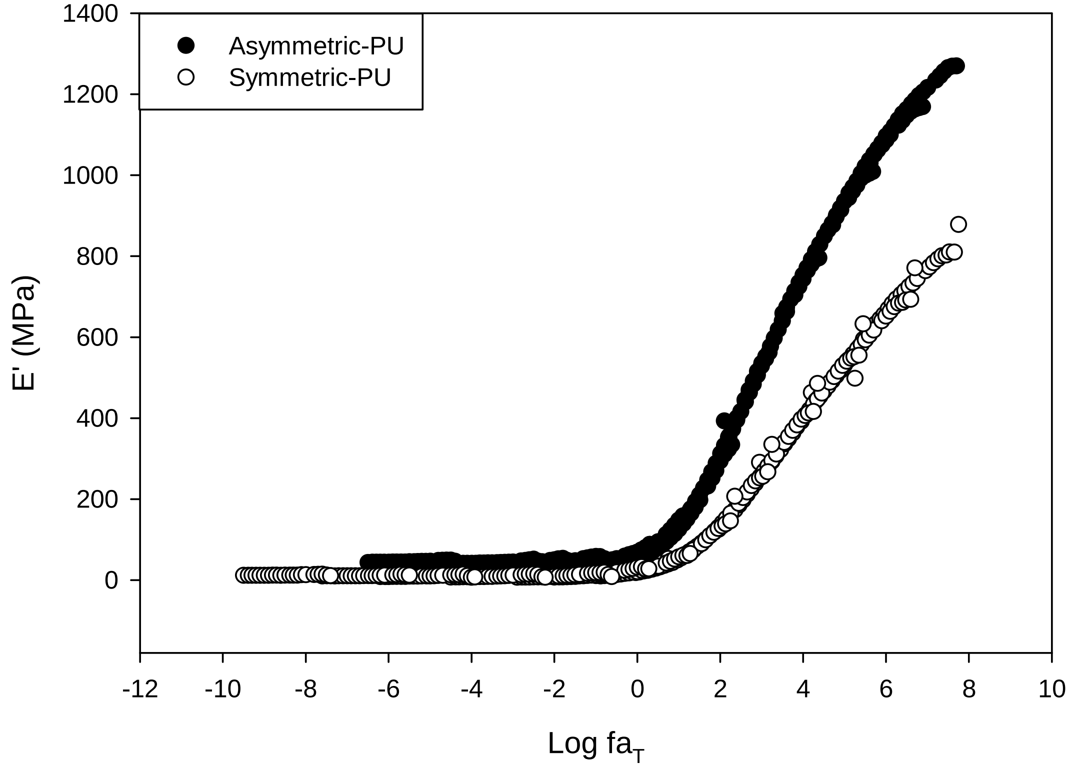

Figure 3.8: Master curves of the storage modulus (E') for A-PU and S-PU as a function of the log of the reduced frequency ($fa_t$)

### 3.3.4 Thermal Stability.

The TGA-FTIR was used to study the thermodegradation patterns of the monomers and polymers. The asymmetric monomers presented one degradation phase of 2.18 %/°C at 442 °C and the symmetric monomers presented one phase of 1.88%/°C at 433 °C (data not shown). These degradation stages were studied through FTIR under an inert gas and showed a characteristic band at 2920 cm$^{-1}$, which revealed the release of octene attributed to the degradation of the monomer's dangling chains. Because the release of octene was first noted at approximately 365 °C for both monomers, it was assumed that their thermostability was similar.

The thermodegradation stages of vegetable oil based polyurethane networks have been commonly studied through TGA. From the TGA curves (Figure 3.9), a 5 % weight loss was present at 321 ºC (A-PU) and 314 ºC (S-PU). These temperatures are comparable to the M-PUs which presented a 5% weight loss at 327 °C. Interestingly, the A-PU and S-PU were found to be thermally more stable than the aromatic triol based PUs from cardanol[23]. This latter did exhibit a 10% weight loss at 250 °C compared to roughly 340 °C for the A-PU and S-PU.

Javni *et al.*[7] who worked with eight types of vegetable oil based PUs of functionality varying from 2 to 4, demonstrated that these PUs shows two to three degradation phases. The first derivative curves of the A-PU and S-PU showed that their thermodegradation patterns were similar. The A-PU presented two degradation phases: 1.00 %/°C at 424°C and 0.87 %/°C at 454°C. The symmetric-PU also presented two phases: 0.87%/°C at 421°C and 0.87%/°C at 446°C. The first volatile compound detected for both samples showed characteristic bands at 2354 $cm^{-1}$ and 667 $cm^{-1}$, indicating a release of $CO_2$. It is known that vegetable oil based PUs start their degradation by dissociation into polyols and precursors of urethanes[7]. The release of $CO_2$ gas was associated to the dissociation of urethane linkage into primary amine and olefin[37]. Similarly to their corresponding monomers, the degradation of the dangling chains started at 365 °C for both matrices. The FTIR detected the presence of octene at the last degradation step for both samples. Finally, the ring degradation started at 700°C, indicated by the presence of carbon monoxide at 2150 $cm^{-1}$ and either ethylene or ethene at 959 $cm^{-1}$ for both matrices.

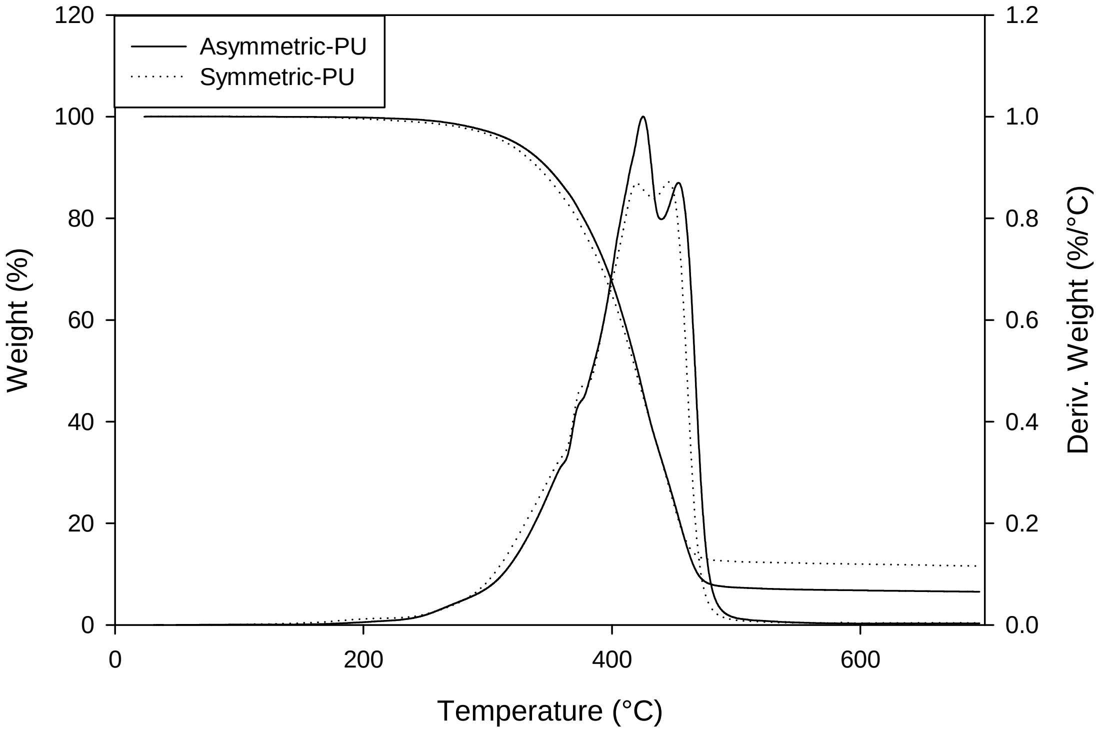

Figure 3.9: Thermal stability and first derivative curves of A-PU and S-PU as a function of the temperature

## 3.4 Conclusion

This study was conducted to determine the effect of the hydroxyl group positioning of the asymmetric and symmetric monomers on the different mechanical and physical properties of their corresponding PUs matrices. It was qualitatively determined by FTIR that both of the PU matrices had unreacted isocyanate. It was also determined that the urethane linkage was existent for both matrices. The Tg of A-PU was lower than the S-PU. It was assumed that less crosslinker reacted with the asymmetric monomers probably due to the steric hindrance induced by the two adjacent hydroxyl groups. However, both of these matrices had similar stress and strain at break. It also was found that the geometry of the monomers and their corresponding PU matrices did not have a significant impact on the thermodegradation of the matrices.

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# 4 Physical properties of new polyurethane foams from benzene polyols synthesized from erucic acid*

## 4.1 Introduction

Research on vegetable oil-based polyurethanes (VOBP) foams is heavily focused on the development of rigid[1-13] and flexible foams,[14-19] since these foams constitute the major uses of PU in the market.[20] In order to obtain flexible foams, polyols should have molecular weights ranging between 3000 and 6000 and a functionality of approximately 3.[20] Since most vegetable oil-based polyols have molecular weights below 1000, petroleum based polyols are usually added to the formulation in order to attain the molecular weight requirements for this type of foam. Recently, it was found that the addition of 20% to 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.[15,19,21]

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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.[7,22-34]

It was even found that VOBP foams can afford similar or superior physical properties compared to petroleum based foams.[6] 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 here investigated since Yue et al.[35] and Lligadas et al.[36] 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 as well as aromatic diisocyanate in the production of PU foams.

This study therefore presents the physical properties of the new high density triol-based PU foams. Unlike most of the PU foam systems found in the literature, the triol-based PU foams were allowed to rise in a closed mold container in order to increase their density and hence increase the mechanical properties. Recently, Narine et al.[8] produced high density foams from vegetable oil based polyols. Their foams systems include polyols with only primary hydroxyl groups (canola polyols and glycerin), secondary hydroxyl groups (soybean polyols and glycerin) and finally unmodified castor oil and glycerin. The addition of glycerol was not necessary in the formulation of the triol-based PU foams since the benzene ring within the polyol structure was believed to offer increased rigidity over foams made with aliphatic polyols. Consequently, the physical properties of the triol-based PU foams were compared with the canola polyol-based PU foams investigated by Narine et al.[8] since both systems had polyols containing only terminal primary hydroxyl groups.

## 4.2 Experimental Section

### 4.2.1 Material and monomer synthesis.

The reagents, synthesis pathway and characterization methods used for the synthesis of the tri-substituted benzene polyols are detailed elsewhere[35]. 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, USA.

### 4.2.2 Preparation of polyurethane foams.

Benzene triol-based polyurethane foams were prepared following the formulation in Table 4.1. The polyol, water (blowing agent), DABCO, DBDTL and surfactant were vigorously stirred by hand in a polystyrene container for 3 minutes 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 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 ºC for 24 hours. The foams were stored at room temperature for at least 5 days after post-curing before any measurements were taken.

### 4.2.3 Rheometric measurements.

The viscosity of the triol monomers was measured with an AR 2000 Rheometer (TA instrument USA) in a shearing mode with a shearing rate of 50.0 $s^{-1}$.

### 4.2.4 FTIR.

The FTIR equipment used was a Nicolet Magna 750 coupled with a MCT-A detector and a Nicolet Nic-Plan 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 to 650 $cm^{-1}$. The nominal resolution was 4 $cm^{-1}$. Before each sample spectrum, a background spectrum was recorded.

### 4.2.5 Closed Cell Content.

The closed cell content was determined using the ASTM D6226-05 standard. The Pycnometer used was an AccuPyc 1330 (Micrometrics, GA, USA) with a standard sample holder of 10 $cm^3$.

### 4.2.6 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.

### 4.2.7 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, USA). 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 minutes, then cooling the samples down to -120 °C at a rate of 5 °C/min and holding for 5 minutes. 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, USA) equipped with a liquid nitrogen cooling system. The foams' dimensions were 17.2 × 11.2 × 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.

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

### 4.2.9 Scanning electron microscopy.

A SEM (Phillips XL30 ESEM $LaB_6$ from FEI Company, Oregon USA) 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 approximately $9.4\times10^{-5}$ 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.

## 4.3 Results and Discussion

The synthesis of triols monomers from erucic acid through a tricyclomerization reaction yielded a mixture of asymmetrical and symmetrical molecules (Fig. 3.1). 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 in order 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[23] 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. Because of these side-reactions, glycerol had to be added to the canola polyol based-PU foam formulation in order 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.[5,8] Unlike the foams produced from canola-based polyols using ozonolysis and hydrogenation technology,[8] there was no need to add glycerol to increase the hydroxyl content. Table 4.1 presents the triol-based PU foam formulation used in this study and the canola-polyol[8] foam formulation.

The viscosity of the triol monomers was 11.6 Pa.s at 25 ºC, a value which required 4 parts of water to generate a sufficient concentration of $CO_{2(g)}$ for the necessary foaming activity. Note that the viscosity of the triol monomers is significantly higher than the canola-polyols (0.90 Pa.s)[23]. The reactivity of the foaming reaction was monitored through the cream time, gel time, and rising time (Table 4.1). 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

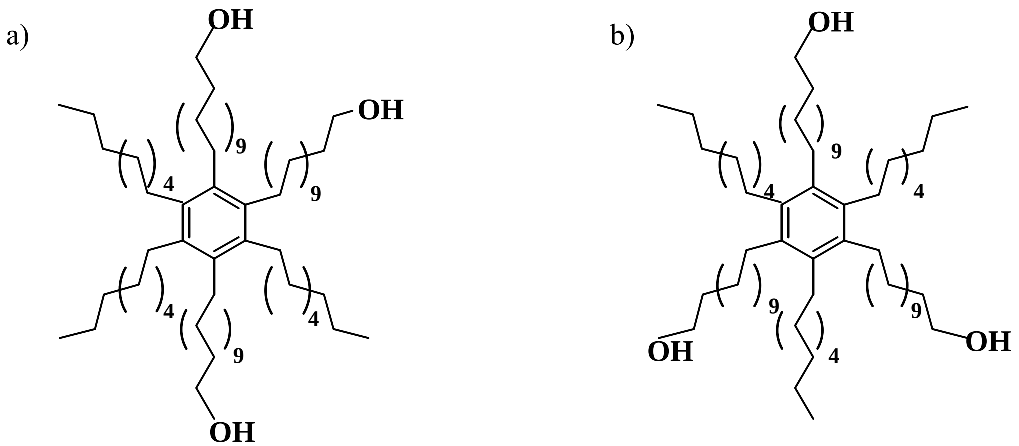

Figure 4.1: Chemical structures of the triol monomers where a) represent the A-PU and b) represent the S-PU.

|  | Triol polyols-based PU foam | Canola polyols-based PU foam[8] |
|---|---|---|
| Cream time (s) | 11 | 10 |
| Gel time (s) | 42 | 40 |
| Rise Time (s) | 35 | 15 |
| Density (kg/m$^3$) | 147 ± 3 | 159 ± 3 |
| Closed-cell Content (%) | 52 ± 3 | 68 ± 4 |
| $T_g$ (ºC) | 51 | 58 |
| Compressive strength (kPa) | 700 ± 88 | 770 ± 145 |
| Young Modulus (MPa) | 19 ± 2 | 22 ± 8 |

Table 4.1: Physical properties of triol- and canola-polyol[8] based PU foam formulations.

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.[37] 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[8] are similar (Table 4.2). 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 $CO_{2\,(g)}$ into the matrix.

The triol-based PU foams were analyzed by FTIR in order to confirm urethane linkage formation. The FTIR spectrum is shown in Figure 4.2. The peak centered at 2277 $cm^{-1}$ is characteristic of free NCO content which is due to the use of excess isocyanate.[38] The C=O and N-H vibrational regions present are characteristic of urethane linkages.[39] The bands centered at 1710 $cm^{-1}$ and 1725 $cm^{-1}$ indicate the presence of bonded and free C=O groups respectively and the bands centered at 3333 $cm^{-1}$ and 3441 $cm^{-1}$ correspond to the H-bonded and free N-H groups respectively.[40,41] The presence of urea was not clearly detected since the carbonyl urea C=O stretching region from the free urea to the bidentate area spread from 1640 $cm^{-1}$to1700 $cm^{-1}$, which could be overlapping with the urethane C=O region (1699 $cm^{-1}$-1733 $cm^{-1}$)[40-42]. It is now known that VOBP foams have similar foaming reactions to petroleum based PUs[43] where the third phase of foam development involves urea microphase separation and cell opening.

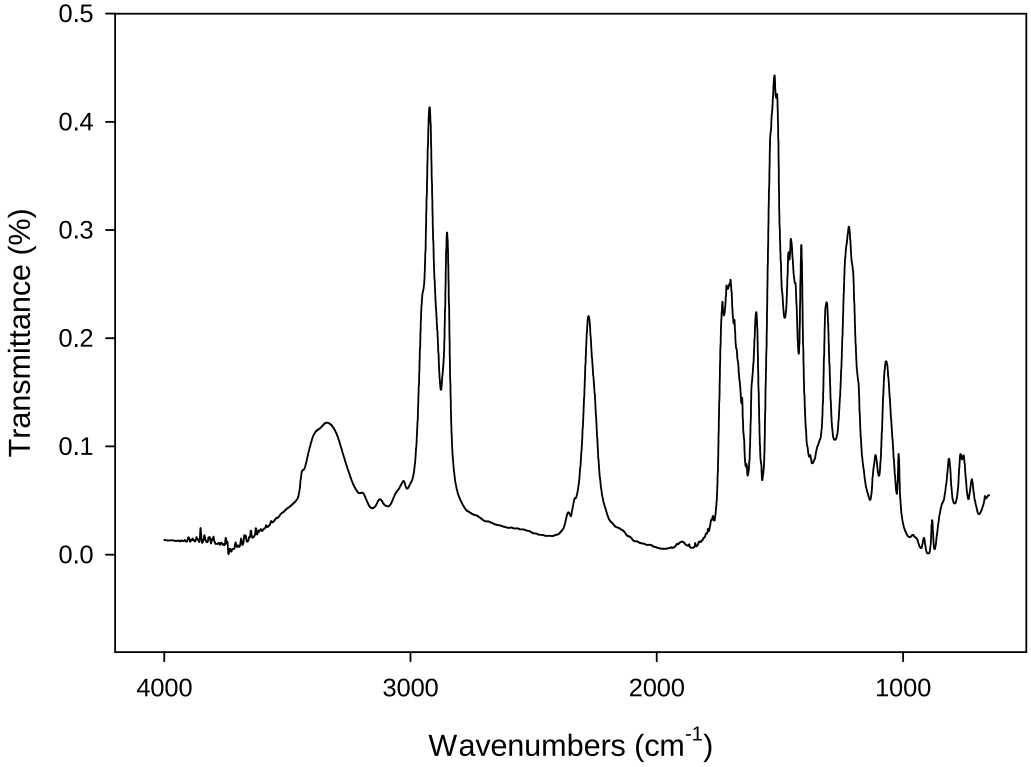

Figure 4.2: General FTIR spectra of triol-based PU foam.

The $T_g$ measured by DSC (Figure 4.3) and DMA (Figure 4.4) are 47 ± 2 ºC and 51 ± 2 ºC respectively. As expected, these $T_g$ results are superior (about 20 ºC higher) than the corresponding plastic sheets made from the same polyols[44] due to the reaction between water and isocyanate which result in the formation of hard urea domains.[16,37] Foam matrices prepared by Narine et al[8] were composed of primary hydroxyl group canola oil-polyols and secondary hydroxyls group soybean and castor oil polyols. All of these matrices had higher $T_g$ values (Table 4.2) 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.[5] It has been shown that the addition of 2 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 3 parts of glycerin.[8] 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[4]. In addition, the canola polyol mixture[8] had non-negligible amount of carboxylic acid within due to ozonolysis. Carboxylic acid reacts with isocyanate to form amide[37] and in order 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.[6]

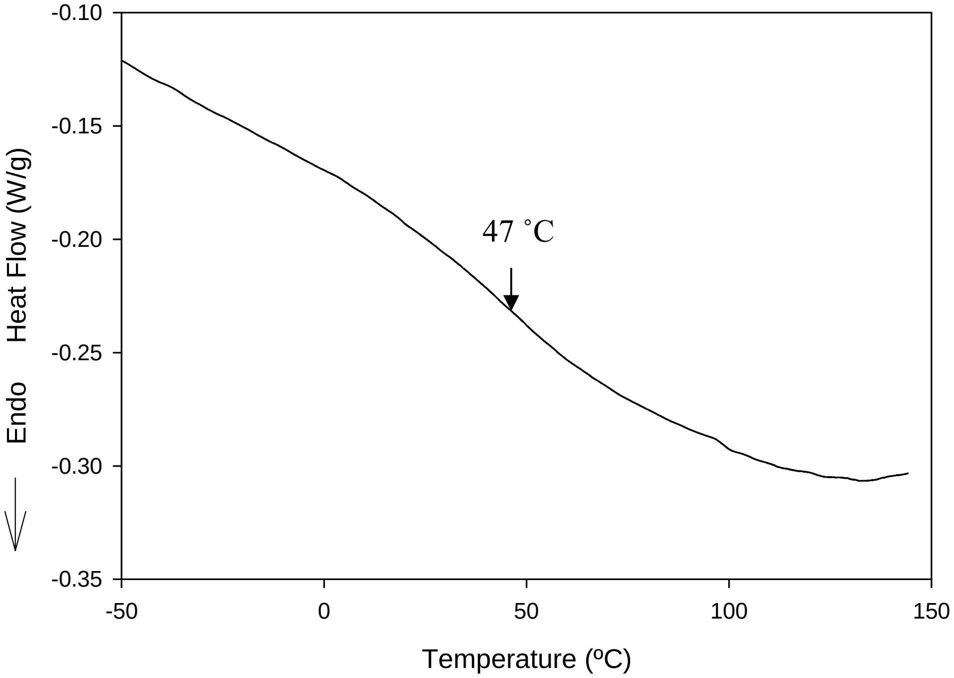

Figure 4.3: MDSC curve of triol-based PU foam.

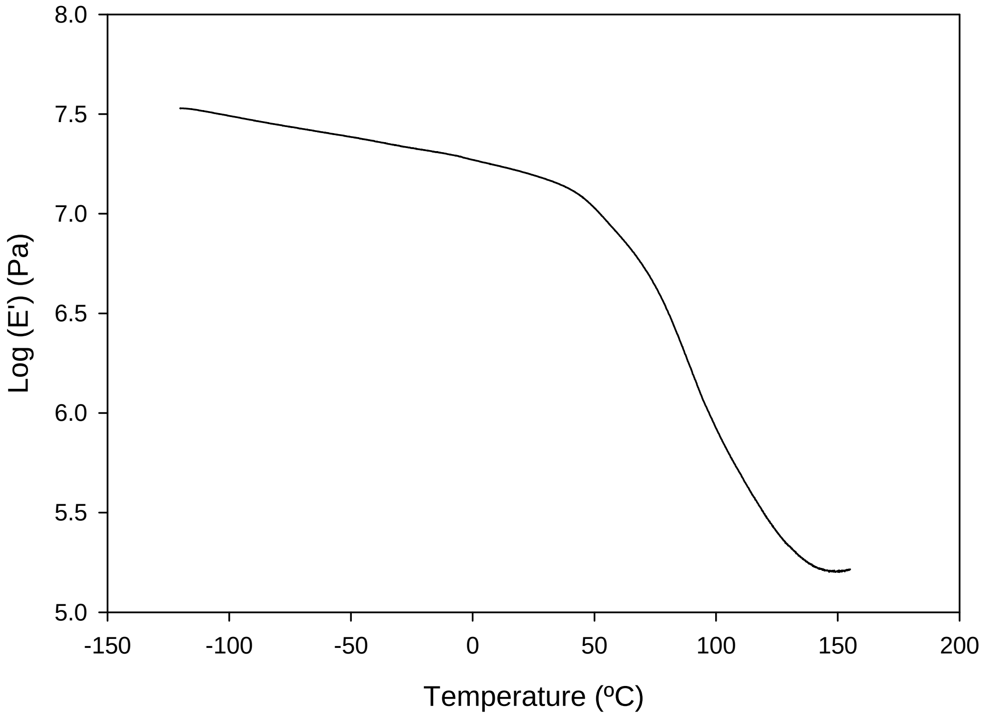

Figure 4.4: Triol-based PU foam storage modulus as a function of the temperature.

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.[43,45] 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.[43,45] The triol-based PU foams have a lower closed cell content (52 %) and larger cell size (0.26-0.50 mm) (Figure 4.5) compared to the canola polyol-based PU foam (68%, 0.25 mm) (Table 4.2). 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.[4] 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 4.2), 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-based PU foams (700 ± 88 KPa) and the Young modulus (19 ± 2 MPa ) (Figure 4.6 and Table 4.2) are lower than the reported values from Narine et al[8] (Table 4.2). As mentioned, this was attributed to the different cellular structure of

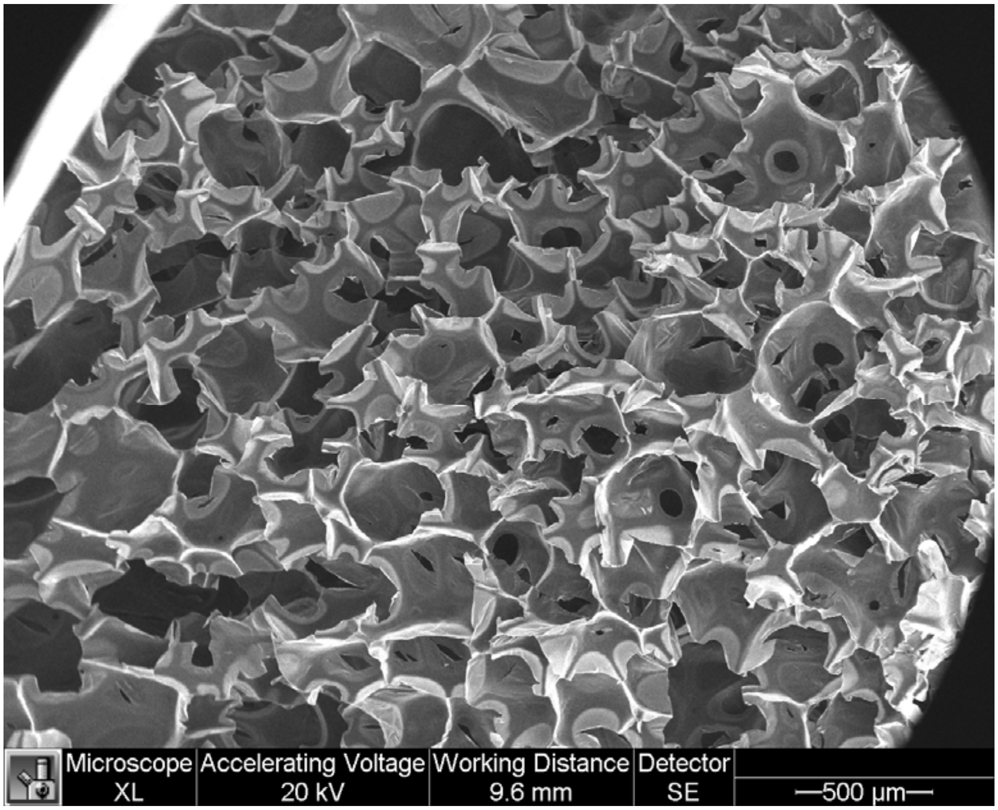

Figure 4.5: Scanning electron microscopy of triol-based PU foam.

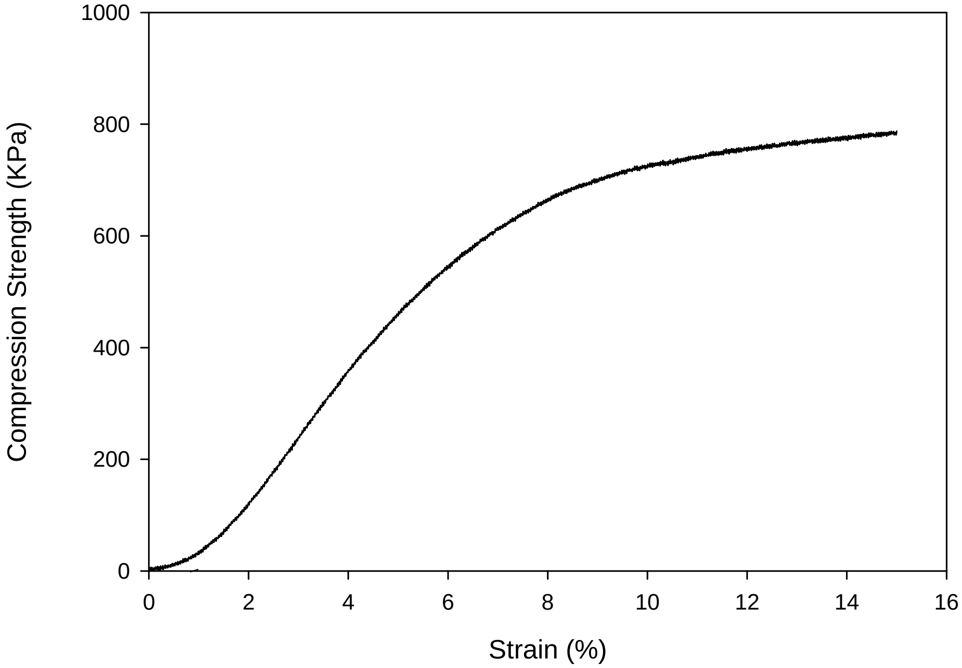

Figure 4.6: Compression strength versus strain of triol-based PU foam.

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.[46]

Figure 4.7 shows the TGA and derivative TGA curves of the triol-based PU foams. From this figure, the thermodegradation started at around 210 °C which is characteristic of urethane linkage degradation. The derivative TGA reveals two degradation stages where the first stage appears at 340 °C with a rate of degradation of 0.4 %/°C and the second stage appears at 451 °C with a degradation rate of 0.74 %/°C. These results are similar to those found for other vegetable oil-based PU foam systems.[5,8] 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.[44] The last degradation stage is attributed to the breakdown of the polyol backbone.

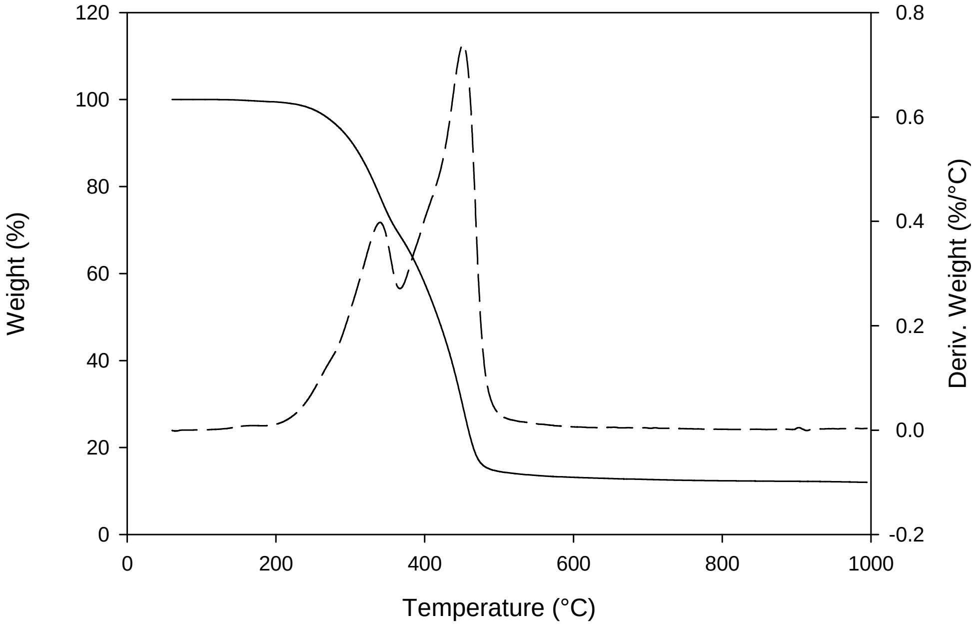

Figure 4.7: TGA and derivative TGA curves of triol-based PU foam.

## 4.4 Conclusion

It has been shown that the physical properties of high density triol-based PU foams are similar to high density canola, castor, and soybean foams[8] containing glycerin within their formulation. The addition of glycerol 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.

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# 5 Conclusion

Advancement in the preparation of polyurethane (PU) plastic sheets and foams derived from aromatic monomers was successfully accomplished. As discussed in Chapter 2, HPLC results confirmed the large scale separation and purification of the aromatic asymmetric and symmetric triol monomers. In order to study the influence of the hydroxyl group positioning on the physical properties of the PU plastic sheets, both the symmetric and asymmetric isomers were crosslinked individually with MDI into PU sheets. The successful polymerization of these components into PUs was confirmed through FTIR where the N-H and C=O regions were well defined. In addition, the FTIR spectra qualitatively suggested that the free NCO content of A-PU was superior to the S-PU. This was later confirmed through the Tg, where the Tg of S-PU was superior to the A-PU; indicating a greater crosslinking density. This was theorized to be due to the steric hindrance induced by the adjacent hydroxyl groups of the asymmetric monomer molecules. The Young modulus of the S-PU was found to be superior to the A-PU, which confirmed that the molecular weight between crosslinks was inferior for the S-PU. However, the tensile strength and elongation at break of both matrices were found to be similar. The thermodegradation pattern of both matrices was also found to be similar to most of the vegetable oil-based PU. Hypothesis 1 was therefore addressed. Although the crosslinking density of both PUs was found to be different, it seemed that their discrepancy was not significant enough to imply major differences in their physical properties.

Since no major differences were found between the physical properties of the A-PU and S-PU plastic sheets, the asymmetric and symmetric monomers were then combined in order to synthesize PU foams (Chapter 3). Once again the assessment of the urethane linkage formation was done through FTIR. It was found that the physical properties of the triol based-PU foams were similar to foams synthesized with a mixture of glycerol and linear polyols from canola oil having terminal primary hydroxyl groups. The addition of glycerol to the canola polyols-based PU foams had the advantage of increasing the crosslinking density of these matrices. As a consequence, the Tg of canola polyols based-PU foam was found to be superior to the triol-based PU foams. The addition of glycerol along with a greater content of catalyst, and lower water content in the foam formulation provided superior closed cell content, even though the viscosity of the triol monomers was greatly superior. This slightly favored the mechanical properties of canola polyols based-PU foams over the triol based-PU foams. However, these results do not fail hypothesis 2 as the physical properties of our foams were comparable to the canola polyol based-PU foams without the addition of glycerol. It is suggested therefore that the benzene ring improved the rigidity of the triol-based PU foams compared to vegetable oil-based aliphatic monomers polymerized into foam. Furthermore, the reactivity and the viscosity of the triol monomers increased the technical difficulties encountered when polymerizing them into foams. As a consequence, the amount of catalyst had to be reduced, resulting in lower closed cell content and therefore lowering the compressive strength. The expected increase in rigidity of the PU foams produced using the aromatic polyols may also have been somewhat mitigated by the 12-carbon chain to which the hydroxyl groups were attached to the benzene ring, and which lacked the rigidity of the benzene ring. Additionally, the presence of the three dangling C8 carbon chains without hydroxyl functionality also served to further decrease the rigidity of the resulting polyurethane foams, as these chains in the polyurethane matrix could not support stress transduction.

Clearly, then further optimization needs to be done on formulation of the triol based-PU foam matrices in order to access the expected superiority of the physical properties of foams made with the aromatic monomers over the aliphatic monomers. One obvious improvement would be the reduction of the pendant aliphatic chains attaching the hydroxyl moiety to the benzene ring, and another would be the elimination of the other dangling chains without hydroxyl functionality, or at least a drastic shortening of their lengths. One step towards this has already been made, with the development, by Song and Narine[1], of a hexaol aromatic monomer. However, it should also be noted that such molecules tend to have strong hydrogen bonding, leading to high viscosities in the polyol melt, which presents significant challenges to cross-linking and processing.

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[1] Song, D.; Narine, S. S.; *Chemistry and Physics of Lipids* 2008, **155**, 43-47.

# 6 List of Published Papers

1. **Marie-Josée Dumont** and Suresh S. Narine, *Characterization of soapstock and deodorizer distillates of vegetable oils using gas chromatography,* Lipid Technology, 2008, 20, 136-138.
2. **Dumont MJ.**, Narine SS., *Characterization of flax and soybean soapstocks, and soybean deodorizer distillate by GC-FID*, Journal of the American Oil Chemist's Society, 2007, 84, 1101-1105.
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