



Synthesis and Thermal Characterization of Polyurethanes obtained from Linseed oil and Olive oil-based Polyols

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ABSTRACT

Using vegetable oils as a substitute for fossil feedstock have become a hot topic in polymer science. Vegetable oils are abundant, less-costly and renewable resources. The present study was aimed at creating bio-based polyols from linseed oil (*Linum usitatissimum*) and olive oil (*Gossypium barbadense*). Polyurethanes obtained from bio-based polyols were synthesized with two different isocyanates, 4, 4'-methylene diphenyl diisocyanate and hexamethylene diisocyanate, for different polyol/isocyanate ratios; they were further characterized by Fourier-Transform Infrared Spectroscopy, Thermogravimetric analysis, Differential Scanning Calorimetry, and Scanning Electron Microscopy, concluding that *Linum usitatissimum* and *Gossypium barbadense* could be considered as valid alternatives for the synthesis of bio-based polyols.

Keywords: Bio-based polyols; *Gossypium barbadense*; *Linum usitatissimum*; Polyurethanes.

1. INTRODUCTION

With the jeopardizing environmental issues such as global warming and waste disposal, switching from fossil fuels to renewable energy resources can make a significant contribution to long-term sustainability (Meier *et al.* 2007). Surfactants (soaps), lubricants, plasticizers, cosmetics, monomers (e.g., dimer acids and polyols), and agrochemicals are only a few of the produced items that employ vegetable oils (VOs) as ingredients or components. VOs are chemical compounds that are generally made up of triesters of glycerol and fatty acids, commonly known as triglycerides, and belong to the fats or lipids family. They are particularly adaptable due to their composition and qualities, allowing them to be employed in the creation of a wide range of polymeric products. Fig. 1 shows the fundamental chemical structure of vegetable oil triglycerides, which are highly functionalized molecules, employed in the manufacture of crosslinked polymers. Soybean oil, palm oil, castor oil, cotton seed, and safflower oils are some of the VOs that have been studied and have industrial applications (Meier *et al.* 2007; Jin and Park, 2007). Linseed's composition is typical of the unsaturated fatty acid group. It contains approximately 9-11% saturated (5-6% palmitic acid and 4-5% stearic acid) and 75-90% unsaturated fatty acids (50-55% linolenic

acid, 15-20% oleic acid) (Novoa and Flores Loyola, 2012), while corn oil rich in *Olive oil* is composed mainly of triacylglycerols (triglycerides or fats) and contains small quantities of free fatty acids (FFA), glycerol, phosphatides, pigments, flavor compounds, sterols and microscopic bits of *olive* (Valdes *et al.* 2009). Despite the presence of saturated fatty acids in both VOs, their fatty acid profiles indicate that they might be employed as raw materials to substitute petroleum-based building blocks and monomers. Around 35% of cotton cellulose fibre is consumed in textiles and spun manufacturing, while cotton seed is consumed for fresh sowings and edible oil extraction for use as feed and other industrial purposes. The byproducts of the cotton crop is used in the livestock business. In this research work linseed and olive oils were used as feedstock for preparation of bio-polyols and bio-based polymeric products like polyurethanes. These materials were characterized by FTIR, TGA, DSC and SEM.

2. EXPERIMENTAL

2.1 Materials

A local market provided linseed oil LIRIO® (iodine value 136-178) and olive oil LIRIO® (iodine value 74-94). Hydrogen peroxide (35%, Faga Lab®),

glacial acetic acid (99%, Faga Lab), and sulfuric acid (37%, Faga Lab) were used in this experiment. 4, 4'-methylene diphenyl diisocyanate, MDI (98%, Sigma-Aldrich) and hexamethylene diisocyanate, HDI, (99%, Sigma-Aldrich) were used as cross-linking isocyanates.

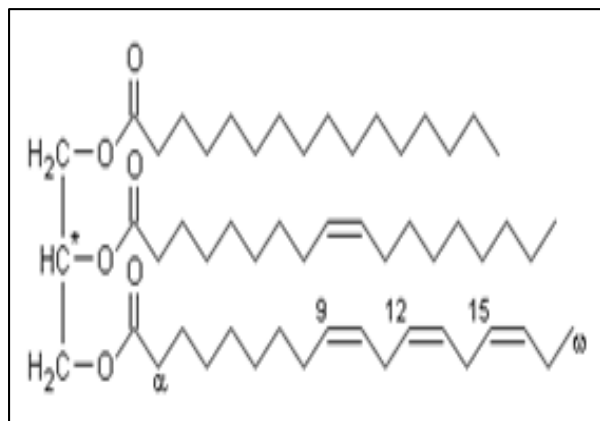


Fig. 1: Chemical structure of triglycerides of vegetable oils

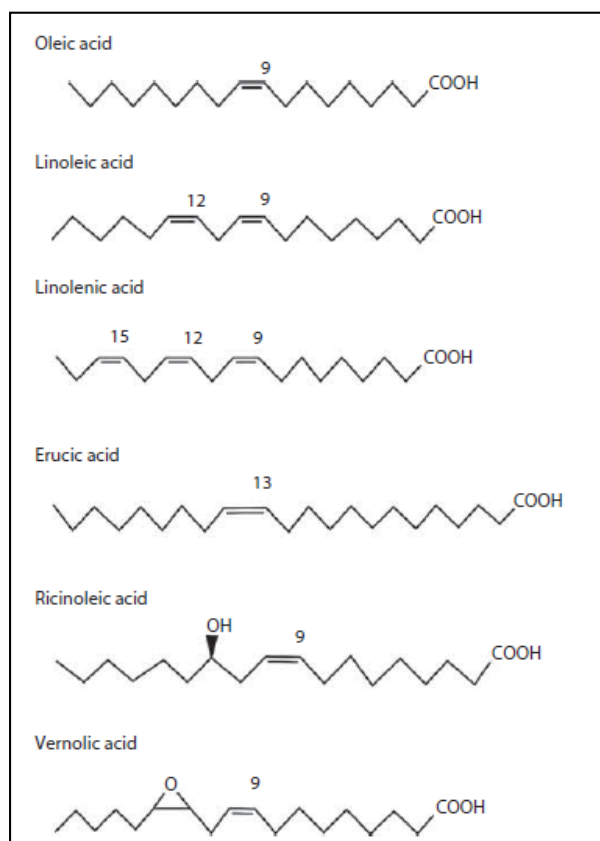


Fig. 2: Chemical structure of unsaturated fatty acids of vegetable oils

2.2 Preparation of Polyols

Polyols were synthesized in a glass reactor using 100 g of linseed or olive oil and 35 g of glacial acetic acid, by mixing them mechanically and heating up to

85 °C. The reaction chamber was then filled with drop-wise addition of 30% (v/v) hydrogen peroxide (110 g) and 0.5 mL concentrated sulfuric acid, and the entire mixture was reacted for 4 hours with peracetic acid formed *in situ*. All polyols were washed in a saturated sodium bicarbonate solution until pH was neutral before analysis (Novoa and Flores Loyola, 2012). These items were dried in a vacuum oven at 60 °C for 24 hours before being analysed using FTIR spectroscopy. Following the general method of analysis, the hydroxyl numbers in all formulations were determined. The hydroxyl number is the number of milligrams of potassium hydroxide necessary to neutralize the acetic acid generated by the hydrolysis of one gram of acetylated fat.

2.3 Synthesis of Polyurethanes

The reaction of the above-synthesized polyols with 4, 4'-methylene diphenyl diisocyanate and hexamethylene diisocyanate yielded polyurethanes. Bio-based polyols and hexamethylene diisocyanate or 4, 4'-methylene diphenyl diisocyanate (diisocyanate index 1.2, 1.4 or 1.6) were separately heated at 50 °C. Warm polyols and isocyanate were vigorously mixed for 10 minutes before being cast on aluminium trays and left as such for 15 minutes. To finish curing, the trays were placed in a vacuum oven at 80 °C for 24 hours. Finally, the materials were removed from the trays and analyzed for their structural, thermal and morphological properties.

2.4 FTIR Spectroscopy

A Bruker IFS 66/S infrared spectrometer (Bruker Analytik, Germany) equipped with an attenuated total reflectance (ATR) device was used to collect the FTIR data in transmission mode. The FTIR spectra were taken in the 4000–500 cm^{-1} range, with 128 scans and a spectral resolution of 4 cm^{-1} . Before each measurement, a background spectrum was run to eliminate the effect of humidity and carbon dioxide in the air through spectra subtraction.

2.5 Thermogravimetric Analysis (TGA)

A TGA/SDTA 851e Mettler Toledo thermal analyzer was used to examine the raw linseed and olive oils, as well as the bio-based polyols and all of the polyurethanes synthesized in this research work. In order to ensure complete degradation of reactant, the final products were weighed in the range of 5–7 mg and heated from 30 to 700 °C at 10 °C min^{-1} , under N_2 atmosphere at the flow rate of 50 mL min^{-1} . The initial degradation temperature (T_5) was calculated from the TG curve as the temperature where 5 wt.% of the initial mass was lost, while the temperature at the maximum degradation rate (T_{max}) was determined as the maximum peak from the first derivative of TG curve (DTG curve).

2.6 Differential Scanning Calorimetry (DSC)

A TA Instruments Q2000 calorimeter (New Castle, DE, USA) was used to record DSC thermograms for all the samples, under nitrogen atmosphere (50 mL min⁻¹). Samples (5-10 mg) were sealed in aluminium pans and heated at 10 °C min⁻¹ from 90 to 150 °C, then quenched to 90 °C and heated again at 10 °C min⁻¹. The inflection point of the region where a shift in the signal baseline was detected was used to determine the glass transition temperatures (T_g), from the second heating scan.

2.7 Scanning Electron Microscopy (SEM)

Morphological analyses of the surface of polyurethanes were carried out using a JEOL model JSM-840 Scanning electron microscope (Jeol USA Inc., Peabody, MA, USA) operating at 10 kV. Samples were previously coated with gold to turn them into conductive materials, using a metallizer - (Au)/Evaporator Balzers, Model SCD 004 (Oerlikon Balzers, Liechtenstein).

3. RESULTS AND DISCUSSION

Fig. 3 and Fig. 4 show the FTIR spectra of polyols, as well as linseed and corn oils. Raw vegetable oil spectra revealed the characteristic peak caused by the stretching of the C=O bond, as well as the C=C-H stretching vibration band. Both bands were thought to be the carboxylic acid's and fatty acids' straight unsaturated chains' fingerprints, respectively. These changes in the FTIR spectra indicated that the VO's C=C-H bonds had been modified, indicating that polyols had been successfully formed. Both polyols with high hydroxyl numbers were also given a hydroxyl number (mg KOH g⁻¹), which is the most common way of expressing the concentration of hydroxyl groups in polyols. These figures were comparable to those reported for polyols made from soybean oil, palm oil, castor oil, linseed oil, and safflower oil, which are the most commonly used vegetable oils for bio-based polyol production (Meier *et al.* 2007; Jin and Park, 2007; Petrovic *et al.* 2005).

Polyols and polyurethanes with diisocyanate indexes of 1.2, 1.4 and 1.6 were synthesized after the successful formation of polyols and polyurethanes was confirmed (with both HDI and MDI). The infrared spectra of polyurethanes made from polyols of linseed and olive oils with MDI and HDI 1.2 are shown in Figures 3 and 4. The isocyanate group (-NCO) has a characteristic stretching signal that can be used to determine if the amount of isocyanate added is sufficient to complete the reaction with polyols and could indicate isocyanate residues in polyurethanes (Petrovic *et al.* 2005; Javni *et al.* 2003). Residual isocyanate was only detected in polyurethanes synthesized with MDI, which

could be attributed to MDI's more rigid structure compared to HDI's. Because of this lack of flexibility, some isocyanate groups may be left unreacted when interacting with OH moieties found in polyols (Yilgor *et al.* 2015).

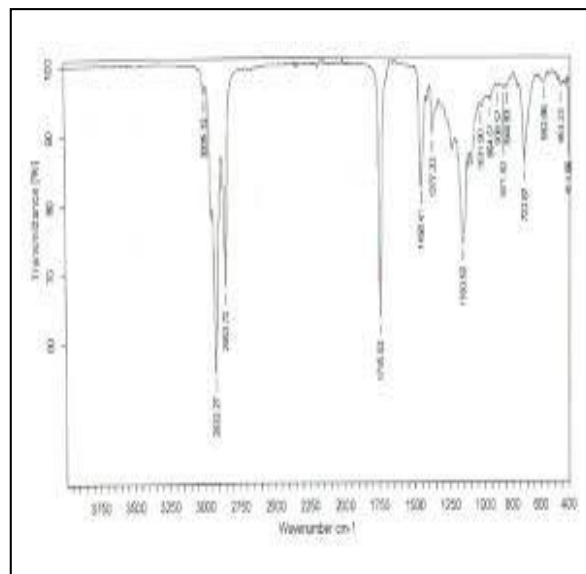


Fig. 3: FTIR spectroscopy of Linseed oil

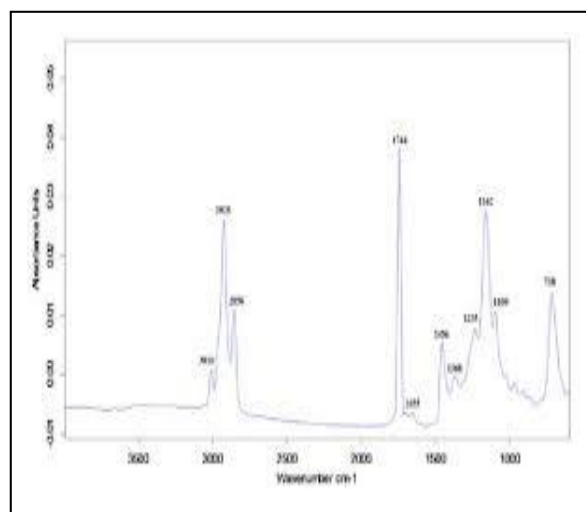


Fig. 4: FTIR spectroscopy of Olive oil

TGA was used to investigate the thermal stability of polyurethanes in a nitrogen atmosphere. For polyurethanes and their corresponding olive and linseed-based polyols, the initial decomposition temperature (T_5) and the temperature at the maximum degradation rate (T_{max}) were determined. It should be noted that the thermal behavior of urethanes is relatively unstable. According to some authors, urethane bond decomposition in bio-based polyurethanes begins with the training of a primary amine or olefin at about 150-220 °C, resulting in the formation of secondary amines and carbon dioxide, followed by the degradation of the polyol

backbone at about 400 °C (Javni *et al.* 2003; Guo *et al.* 2000). Polyurethanes made with polyols from linseed and olive oils and MDI as a cross linker were having similar thermal behavior. As previously discussed and observed by FTIR, the high thermal stability of polyurethanes derived from olive and linseed polyols could be related to the ester linkages in these polyols. When it comes to the processing window of polyurethanes, their high thermal stability was found to be an advantage.

Each polyurethane had only one T_g value, indicating that they were successfully synthesized without the presence of excess polyol. T_g values for Polyurethanes made from corn polyol and both isocyanates (HDI and MDI) ranged from 10 to 48 °C, while those for polyurethanes made from cottonseed polyol and both isocyanates ranged from 13 to 43 °C. All T_g values for HDI-synthesized polyurethanes were lower than the room temperature, whereas those for MDI-synthesized polyurethanes were greater. These findings have suggested that polyurethanes made with MDI have a more rigid structure than those made with HDI due to the stiffness of phenyl groups in MDI compared to the flexibility of CH_2 groups in HDI (Yilgor *et al.* 2015). Additionally, the polyol/isocyanate ratio had a minor effect on these T_g values. Dangling chains arising from the polyol are present in polymer networks based on triglycerides. The nature of the monomer, and thus the number of available hydroxyl groups in the polyols, the position of the hydroxyl group in the fatty acid chain (middle or end of the chain) and the isocyanate structure - all influence the glass transition temperature of polyurethanes compared to polyols (Zlatanovic *et al.* 2004).

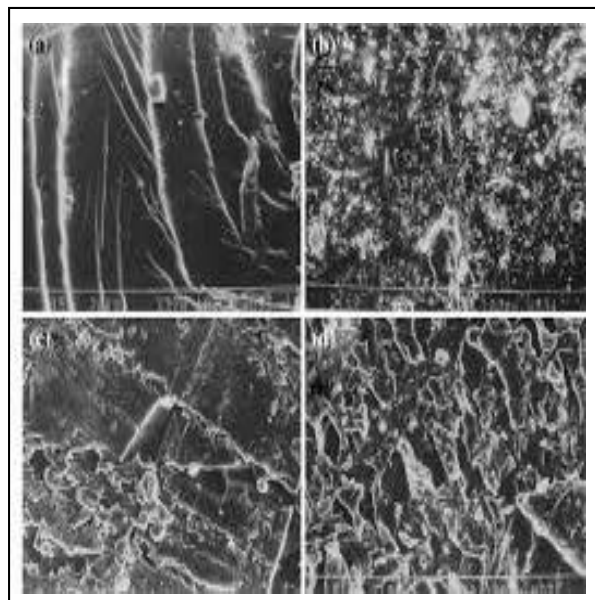


Fig. 5: SEM Micrographs of surfaces (×100) of PU, obtained from Linseed oil.

SEM micrographs of the polyurethane surfaces were shown in Fig. 5 and Fig. 6. Since the micrographs were taken from the surface of the PU films, the polyurethanes synthesized with linseed polyol and HDI 1.4 (a) and MDI 1.4 (b) had irregular surfaces, but with a small number of pores (bubbles) in the latter case, which can be attributed to the effect of the vacuum during the curing process. In the case of polyurethanes made with olive polyol, irregular surfaces were observed, but no signs of pore formation were discernible during processing. These findings have shown that polyurethanes derived from bio-based polyols were generally compact and non-porous. This apparent uniformity, with no detectable variance between all formulations, might be explained by networks generated between isocyanates and hydroxyl groups of polyols.

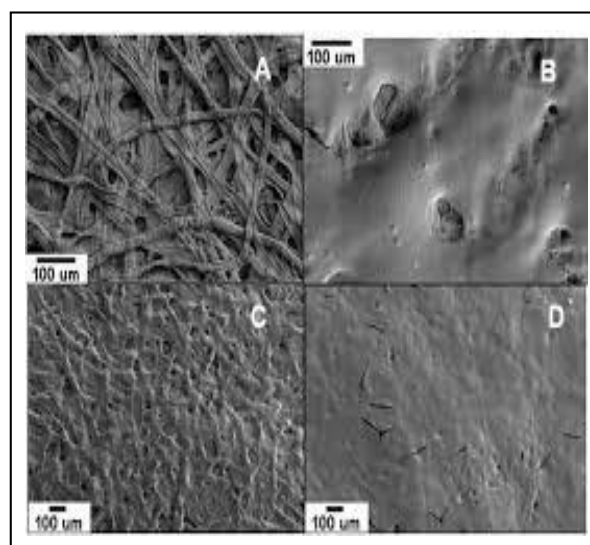


Fig. 6: SEM Micrographs of surfaces (×100) of PU, obtained from Olive oil

4. CONCLUSION

The primary structural, thermal and morphological features of bio-based polyols generated from linseed and olive vegetable oils were investigated after their synthesis was effective. The FTIR spectra revealed the typical structure of polyols derived from vegetable oils, with a high number of hydroxyl groups. Polyurethanes made with both types of bio-based polyols, as well as HDI and MDI, had homogeneous, non-porous morphologies and excellent thermal stability. Di-isocyanate only altered the T_g values, showing that polyurethane synthesized with 4, 4'-methylene diphenyl diisocyanate are tougher than those synthesized with hexamethylene diisocyanate. Linseed and olive oils proved to be viable options for the preparation of high-functional bio-based polyols, which will be environment-friendly polyurethanes.

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