

Synthesis and Thermal Characterization of Polyurethanes Obtained from Cottonseed and Corn Oil-Based Polyols

Karina Cruz-Aldaco¹, Erika Flores-Loyola², Cristóbal Noé Aguilar-González¹, Nuria Burgos³, and Alfonso Jiménez^{3*}

¹Food Research Department, School of Chemistry, Autonomous University of Coahuila, Blvd. Venustiano Carranza S/N Col. República Oriente, 25280, Saltillo, Coahuila, Mexico

²School of Biological Sciences, Autonomous University of Coahuila, Carretera Torreón-Matamoros Km 7.5 Ciudad Universitaria Torreon, Coahuila, Mexico, C.P.27000, Torreón, Coahuila, Mexico

³Analytical Chemistry, Nutrition and Food Sciences Department, University of Alicante, Campus San Vicente, E-03690, San Vicente del Raspeig, Alicante, Spain

Received January 15, 2016; Accepted March 31, 2016

ABSTRACT: The use of vegetable oils to replace fossil feedstock has become an area of opportunity and a priority for study in the field of polymer science. Vegetable oils are considered as renewable resources with high potential, low cost and full availability. The aim of this study is the synthesis of biobased polyols from cottonseed oil (*Gossypium barbadense*) and corn oil (*Zea mays*) as feedstock. Their synthesis was successfully performed, as can be concluded from the determination of their hydroxyl index as well as the structural and thermal characterization carried out in this work. Polyurethanes from biobased polyols were synthesized with two different isocyanates (HDI and MDI) and variable polyol/isocyanate ratio and they were further characterized by infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry and scanning electron microscopy, concluding that cottonseed and corn oils could be considered as valid alternatives for the synthesis of biobased polymeric materials.

KEYWORDS: Corn oil, cottonseed oil, biobased polyols, polyurethanes, vegetable oils

1 INTRODUCTION

In an age of increasing environmental problems, such as global warming and waste disposal, the change from fossil feedstock to renewable resources can considerably contribute to the sustainable development [1]. The differences in the resource consumption are so high that those products based on vegetable oils (VOs) could clearly be considered an environmentally benign alternative to petrochemical products [2]. In the chemical industry, VOs are used as ingredients or components in many manufactured products, such as surfactants (soaps), lubricants, plasticizers, cosmetic products, monomers (e.g., dimer acids and polyols) and agrochemicals. In addition, they have been used for decades in paint formulations, as flooring materials, coatings and resin applications [3]. VOs are part of a major family of chemical compounds known as fats or lipids, mainly conformed by triesters of glycerol and fatty

acids, commonly known as triglycerides. Their composition and properties give them high versatility to permit their participation in the preparation of a sort of different polymeric materials [4]. However, VOs should be functionalized to increase their ability to form chemical bonds with other monomers and to serve as building blocks for polymers [5]. Triglycerides of vegetable oils, whose basic chemical structure is shown in Figure 1, are highly functionalized molecules and consequently they have been used in the synthesis of crosslinked polymers by two main approaches. The first one takes advantage of the naturally occurring functional groups present in triglycerides, such as the internal double bonds, hydroxyl groups and oxirane rings, which can be polymerized by different methods. The second strategy is based on chemical modifications taking place prior to polymerization [6]. Some of the VOs already studied and with industrial applications include soybean oil, palm oil, castor oil, linseed and safflower oils [1, 7].

The composition of cottonseed oil is typical of the group of unsaturated fatty acids and it is conformed mainly of oleic acid (33.1%) and linoleic acid (39.6%), as reported by Valdes *et al.* [8], while corn oil is rich in oleic acid (25.8%), linoleic acid (58.9%) and linolenic

*Corresponding author: alfjimenez@ua.es

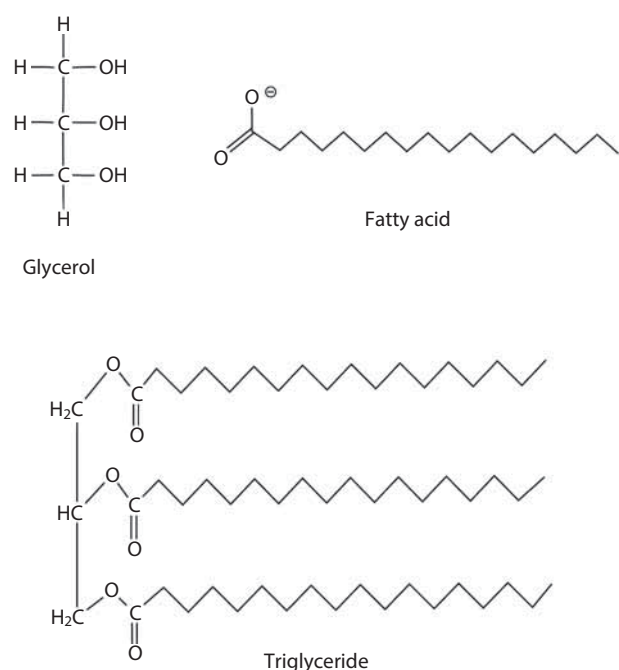


Figure 1 Chemical structure of triglycerides of vegetable oils.

acid (1.1%) (Figure 2) [8, 9]. Even when these oils contain a certain amount of saturated fatty acids, the fatty acid profiles of both VO provide them the potential as raw materials for the replacement of petroleum-based building blocks and monomers. In addition, corn and cotton crops are a highly social culture in Mexico, generating direct and indirect labor, as they are able to produce a high number of original products and by-products from their manufacturing, such as original cotton and seed in the case of the cotton industry. Around 35% of cotton (fiber form) is used for the fabrics and spun manufacturing, while 54% (seed form) is used for new sowings and edible oils extraction for further use as feed and other industrial applications. The rest of the initial mass of cotton (by-products) is used for the livestock industry [10].

The aim of this study is the use of cottonseed and corn oils as feedstock in the synthesis of bio-polyols and bio-based polymeric materials such as polyurethanes. These materials were synthesized and further characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

2 EXPERIMENTAL

2.1 Materials

Cottonseed oil LIRIO® (iodine value 102–112) and corn oil LIRIO® (iodine value 108–118) were obtained from

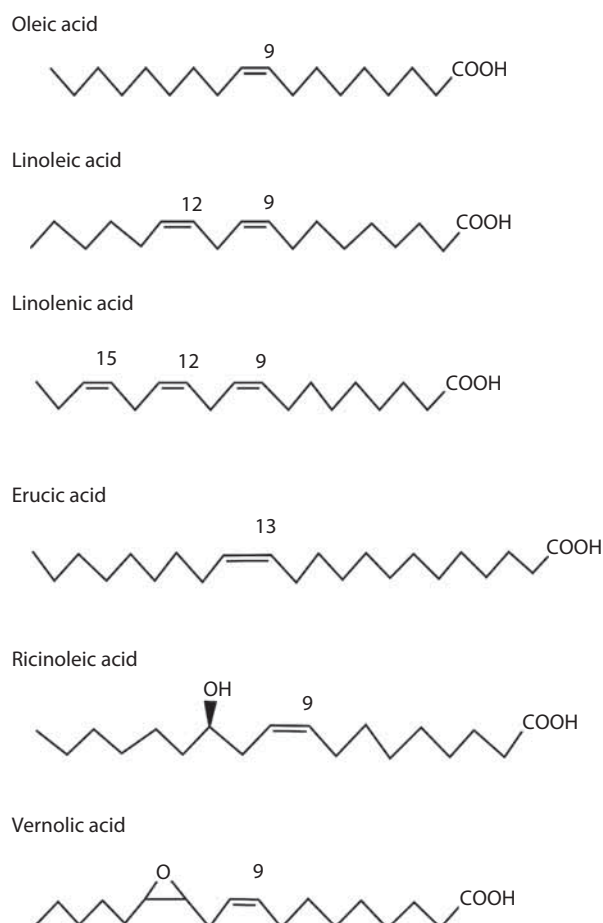


Figure 2 Chemical structure of unsaturated fatty acids of vegetable oils.

a local market. The reagents used in this study were hydrogen peroxide (35%, Faga Lab®), glacial acetic acid (99%, Faga Lab) and sulfuric acid (37%, Faga Lab). The crosslinking isocyanates were 4,4'-methylene diphenyl diisocyanate, MDI (98%, Sigma-Aldrich) and hexamethylene diisocyanate, HDI (99%, Sigma-Aldrich).

2.2 Preparation of Polyols

The synthesis of polyols was carried out in a glass reactor where 100 g of cottonseed or corn oil and glacial acetic acid (35 g) were mixed by mechanical stirring and heated at 85 °C. Then, 30% (v/v) hydrogen peroxide (110 g) and 0.5 mL of concentrated sulfuric acid were added dropwise to the reaction chamber and the whole mixture was reacted for 4 h with peracetic acid formed *in situ*. Prior to analysis, all polyols were washed with a saturated sodium bicarbonate solution until neutral pH [11]. These products were dried in a vacuum oven at 60 °C for 24 h and then characterized by FTIR spectroscopy. The hydroxyl numbers in all formulations were determined by following the general method of analysis

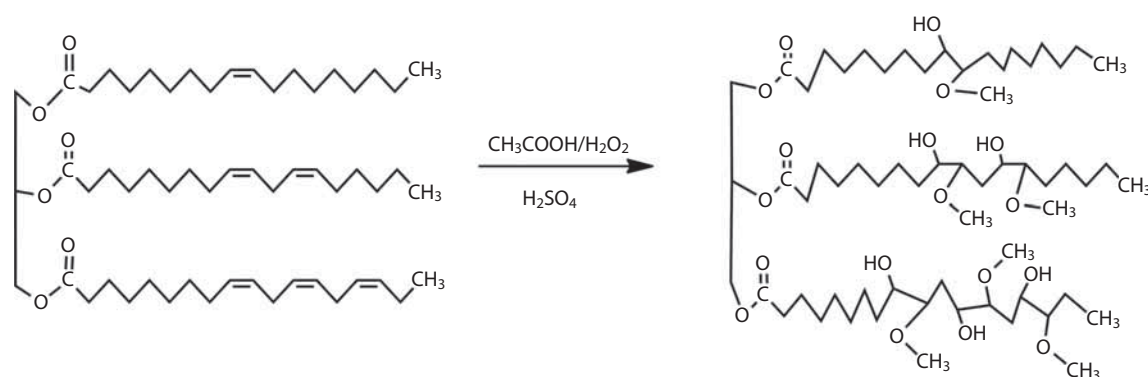


Figure 3 General modification scheme of the unsaturated bonds of vegetable oils in the synthesis of polyols.

MGA 0491 [12]. The hydroxyl number is defined as the number of milligrams of potassium hydroxide needed to neutralize the acetic acid produced by the hydrolysis of one gram of acetylated fat. Figure 3 shows a general schematic representation of the hydrolysis reaction that the unsaturated moieties of fatty acids suffer during the synthesis of polyols from VO.

2.3 Synthesis of Polyurethanes

Polyurethanes (PUs) were obtained by reaction of the above-synthesized polyols with MDI and HDI. Biobased polyols and HDI or MDI (diisocyanate index 1.2, 1.4 and 1.6) were separately heated at 50 °C. Warm polyols and the corresponding isocyanate were vigorously mixed for 10 minutes and they were cast on aluminum trays and allowed to stand for 15 min. Then, trays were placed in a vacuum oven at 80 °C for 24 h to complete curing. Materials were finally removed from the trays and the analysis of their structure, thermal and morphological properties was carried out.

2.4 FTIR Spectroscopy

The FTIR tests were collected in transmission mode using a Bruker IFS 66/S infrared spectrometer (Bruker Analytik, Germany) equipped with an attenuated total reflectance (ATR) device. The FTIR spectra were recorded in the 4000–500 cm^{-1} region, using 128 scans and 4 cm^{-1} of spectral resolution. A background spectrum was performed before each measurement to avoid the effect of humidity and carbon dioxide presence in the air by spectra subtraction.

2.5 Thermogravimetric Analysis (TGA)

The raw cottonseed and corn oils, as well as the biobased polyols and all the polyurethanes synthesized in this study, were analyzed by using a TGA/SDTA 851e Mettler Toledo thermal analyzer

(Schwarzenbach, Switzerland). Samples were weighed in the range of 5–7 mg and were heated from 30 °C to 700 °C at 10 °C min^{-1} under nitrogen atmosphere (flow rate 50 mL min^{-1}) in order to ensure the complete degradation of samples. The initial degradation temperature (T_g) 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 curves (DTG curve).

2.6 Differential Scanning Calorimetry (DSC)

The DSC thermograms for all samples were recorded with a TA Instruments Q2000 calorimeter (New Castle, DE, USA) under nitrogen atmosphere (50 mL min^{-1}). Samples (5–10 mg) were sealed in aluminum pans and heated from –90 °C to 150 °C at 10 °C min^{-1} , followed by quenching to –90 °C and further heating to 150 °C at 10 °C min^{-1} . Glass transition temperatures (T_g) were determined from the second heating scan as the inflection point of the region where a shift in the signal baseline was detected.

2.7 Scanning Electron Microscopy (SEM)

Morphological analyses of the surface of PUs were performed with a scanning electron microscope JEOL model JSM-840 (Jeol USA Inc., Peabody, MA, USA), operated at 10 kV. Samples were previously coated with gold to turn them into conductive materials with a metallizer (Au)/Evaporator© Balzers, model SCD 004 (Oerlikon Balzers, Liechtenstein).

3 RESULTS AND DISCUSSION

The FTIR spectra of polyols and cottonseed and corn oils are shown in Figure 4. The spectra of raw vegetable

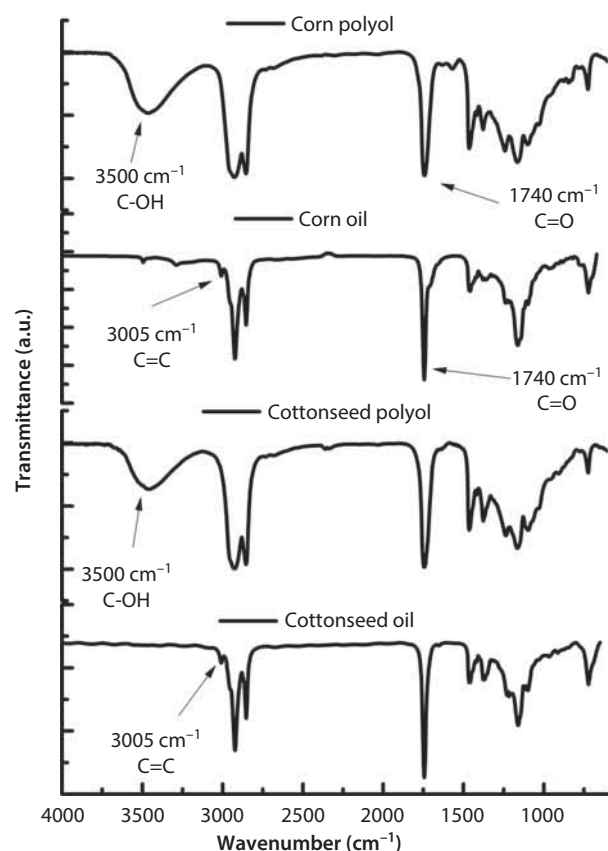


Figure 4 FTIR spectroscopy analysis of cottonseed and corn oils and their corresponding synthesized polyols.

oils showed the characteristic peak at 1740 cm^{-1} due to the stretching of the $\text{C}=\text{O}$ bond, while the $\text{C}=\text{C}$ -H stretching vibration band was observed at 3005 cm^{-1} . Both bands are considered as the fingerprint of the carboxylic acid and the straight unsaturated chain of the fatty acids, respectively [9, 12]. After the hydrolysis reaction, which transforms oils in polyols, a reduction in the intensity of the stretching $\text{C}=\text{C}$ -H signals as well as the appearance of broad signals at about 3500 cm^{-1} , corresponding to the stretching of O-H groups, were observed. These variations in the FTIR spectra were indicative of the modification of $\text{C}=\text{C}$ -H bonds of the VO and therefore they represent the confirmation of the successful formation of polyols. The hydroxyl number (mg KOH g^{-1}), which is the most frequent way of expressing the concentration of hydroxyl groups in polyols [11, 13], was also determined for both polyols, which showed high hydroxyl numbers: 216 and 165 mg KOH g^{-1} for corn and cottonseed oil-based polyols, respectively. These values are similar to those reported for polyols based on soybean oil, palm oil, castor oil, linseed oil and safflower oil, which are the vegetable oils more commonly used for the production of biobased polyols [1, 7, 11, 13].

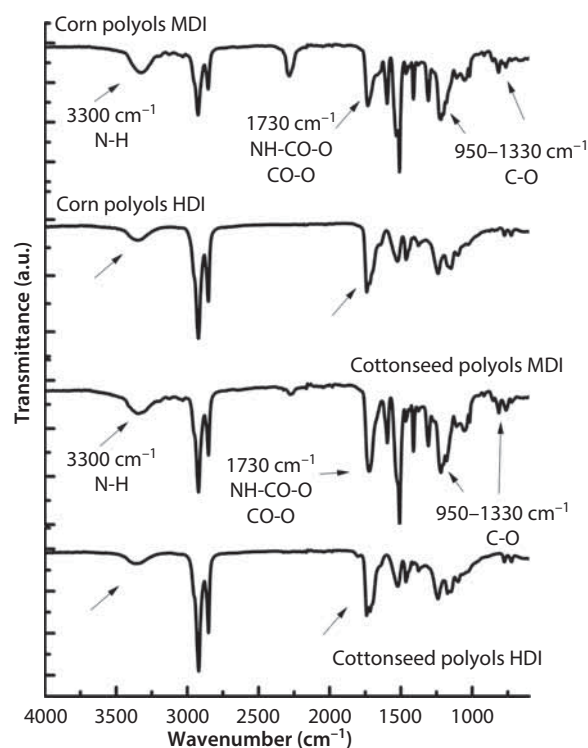


Figure 5 FTIR spectroscopy analysis of polyurethanes obtained from cottonseed- and corn-based polyol with MDI and HDI (1.2 of molar index).

Once confirmed, the successful formation of polyols and polyurethanes were synthesized with diisocyanate indexes 1.2, 1.4 and 1.6 (with both HDI and MDI). Figure 5 shows the infrared spectra of polyurethanes obtained from polyols of cottonseed and corn oils with MDI and HDI 1.2. It can be observed that the $3380\text{--}3400\text{ cm}^{-1}$ band corresponding to the stretching signal of the $\text{C}-\text{OH}$ group in the polyols disappeared, while the appearance of the $\text{N}-\text{H}$ urethane stretching signals at 3300 cm^{-1} is a clear indication of the successful reaction between biobased polyols and isocyanates. Combined stretching signals were obtained for urethane and carbonyl groups $-\text{NH}-\text{CO}-\text{O}$ and $\text{CO}-\text{O}$ at 1730 cm^{-1} and for $\text{N}-\text{H}$ and $\text{C}-\text{N}$ at 1540 cm^{-1} [14, 15]. The isocyanate group ($-\text{NCO}$) has a characteristic stretching signal at 2270 cm^{-1} , which could be indicative of isocyanate residues in polyurethanes and can be used to determine if the amount of isocyanate added is enough to complete the reaction with polyols [13, 14]. Only in the case of PUs synthesized with MDI residual isocyanate was observed, which could be attributed to the more rigid structure of MDI compared to that of HDI. This lack of flexibility could restrict the interaction with OH moieties available in polyols, leaving some isocyanate groups unreacted [16].

Thermal stability of PUs was studied by TGA under nitrogen atmosphere. Table 1 shows the initial

decomposition temperature (T_5) and the temperature at the maximum degradation rate (T_{max}) determined for polyurethanes and their corresponding corn and cottonseed-based polyols. It should be noted that urethanes are relatively unstable in their thermal behavior. Some authors indicated that the urethane bond decomposition in biobased polyurethanes starts at about 150–220 °C by training a primary amine or olefin, resulting in the formation of secondary amines and carbon dioxide, followed by the degradation of the polyol backbone at about 400 °C [14, 17]. All the polyurethanes synthesized in this work showed high thermal stability, since T_5 values were about 315 °C and T_{max} values, associated with the polyols structure, were between 420 and 460 °C (Table 1). Figure 6 shows the thermal behavior of PU synthesized with polyols from cottonseed and corn oils using MDI as crosslinker. As can be seen, both

Table 1 Thermal degradation parameters (T_5 and T_{max}) of polyurethanes obtained from corn and cottonseed polyols, determined under nitrogen atmosphere by TGA.

Corn PU materials	T_5 (°C)	T_{max} (°C)	Cottonseed PU materials	T_5 (°C)	T_{max} (°C)
1.2 HDI	318	460	1.2 HDI	316	455
1.4 HDI	316	460	1.4 HDI	316	455
1.6 HDI	316	450	1.6 HDI	315	420
1.2 MDI	316	455	1.2 MDI	317	460
1.4 MDI	303	460	1.4 MDI	316	470
1.6 MDI	315	453	1.6 MDI	316	450
Corn polyol	338	400	Cottonseed polyol	343	420

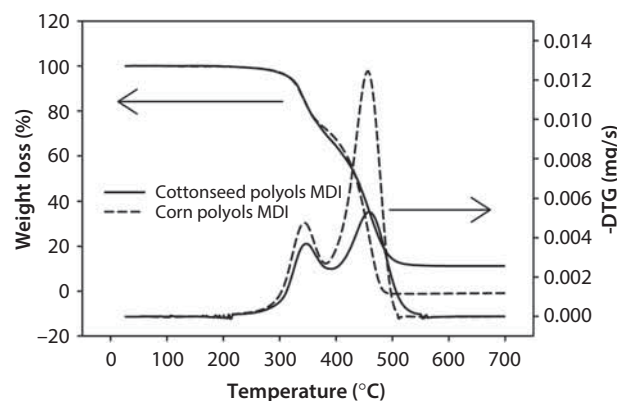


Figure 6 Thermogravimetric analysis of PU obtained from cottonseed and corn polyols with MDI under nitrogen atmosphere.

PU show a similar thermal behavior. The high thermal stability of polyurethanes obtained from corn and cottonseed polyols could be related with the ester linkages in these polyols, as already discussed and observed by FTIR. The high thermal stability of PUs is an advantage when considering their processing window.

The T_g values of both monomers were determined from the second heating scan in DSC analysis as -45.9 °C and -60.5 °C for corn and cottonseed polyols, respectively (Table 2). Only one T_g value was observed for each polyurethane, indicating the success in their synthesis, without the presence of excess polyol. The T_g values for PUs obtained from corn polyol and both isocyanates (HDI and MDI) were between 10 °C and 48 °C, respectively; while those obtained for PUs based on cottonseed polyol and both isocyanates were between 13 °C and 43 °C. As can be observed, all T_g values for those PUs synthesized with HDI were below room temperature, while those prepared with MDI were above room temperature. These results indicate that PUs prepared with MDI have a more rigid structure than those prepared with HDI due to the rigidity of phenyl groups in MDI compared with the flexibility of CH_2 groups in HDI [16]. Furthermore, a slight effect of the polyol/isocyanate ratio was observed on these T_g values. Polymer networks based on triglycerides contain dangling chains arising from the polyol. The increase in the glass transition temperature of polyurethanes with respect to those of the polyols is related to the nature of the monomer, and therefore, with 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 [5].

Table 2 Glass transition temperatures (T_g) determined from the second heating scan in DSC analysis (10 °C min^{-1}) of polyurethanes obtained from corn and cottonseed polyols.

Corn PU materials	T_g (°C)	Cottonseed PU materials	T_g (°C)
1.2 HDI	18.5	1.2 HDI	13.9
1.4 HDI	10.5	1.4 HDI	13.4
1.6 HDI	11.2	1.6 HDI	13.9
1.2 MDI	45.6	1.2 MDI	43.1
1.4 MDI	43.4	1.4 MDI	40.6
1.6 MDI	48.4	1.6 MDI	41.9
Corn polyol	-45.9	Cottonseed polyol	-60.5

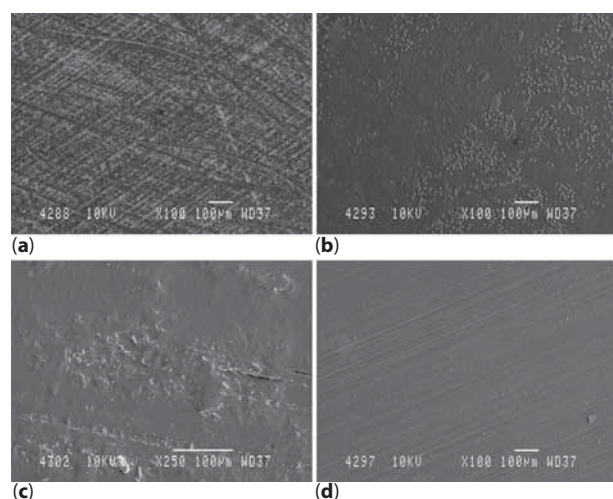


Figure 7 SEM micrographs of surfaces ($\times 100$) of PU obtained from (a) cottonseed polyol with 1.4 HDI; (b) cottonseed polyol with 1.4 MDI; (c) corn polyol with 1.4 HDI; and (d) corn polyol with 1.4 MDI.

The SEM micrographs of the polyurethane surfaces are shown in Figure 7. The PUs synthesized with cottonseed polyol and HDI 1.4 (a) and MDI 1.4 (b) showed irregular surfaces, but with a small quantity of pores (bubbles) in the latter case, which can be attributed to the effect of the vacuum during the curing process, since the micrographs were taken from the surface of the PU films. In the case of PUs synthesized with corn polyol and HDI at 1.4 (c), irregular surfaces were observed, but no signals of the formation of pores during processing were appreciable. However, for the PU obtained with corn polyol and MDI 1.4 (d) a homogeneous and smooth surface, with no irregularities or pores, was observed. These results suggest that, in general, the polyurethanes obtained from biobased polyols are compact and nonporous materials. This apparent homogeneity could be attributed to the networks formed between isocyanates and hydroxyl groups of polyols, with no noticeable differences between all the formulations.

4 CONCLUSIONS

The synthesis of biobased polyols obtained from cottonseed and corn vegetable oils was successfully performed and these polyols were characterized by their main structural, thermal and morphological properties. The FTIR spectra showed the typical structure reported for polyols obtained from vegetable oils, with high hydroxyl numbers. Polyurethanes synthesized by using both types of biobased polyols and HDI and MDI showed homogeneous and

nonporous morphologies with high thermal stability. The effect of diisocyanate was observed only on the T_g values, indicating that PUs synthesized with MDI are harder than those synthesized with HDI. Therefore, cottonseed and corn oils could be considered as valid alternatives for the synthesis of biobased polyols with high functionalities for further use in the production of environmentally friendly polyurethanes.

ACKNOWLEDGMENTS

The authors thank the Spanish Ministry of Economy and Competitiveness (MAT2014-59242-C2-2-R) and CONACYT-Mexico (No.CB06825 and doctoral scholarship No.234299/212279) for their financial support.

REFERENCES

1. M.A.R. Meier, J.O. Metzger, and U.S. Schubert, Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* **36**, 1788–1802 (2007).
2. M. Eissen, J.O. Metzger, E. Schmidt, and U. Schneidewind, 10 years after rio – concepts on contribution of chemistry to a sustainable development. *Angew. Chem.* **41**, 414–436 (2002).
3. R. De Vasconcelos Vieira Lopes, D.N.P. Loureiro, A.P.T. Pezzin, A.C.M. Gomes, I.S. Resck, and M.J.A. Sales, Synthesis of polyols and polyurethanes from vegetable oils – kinetic and characterization. *J. Poly. Res.* **20**, 238–246 (2013).
4. S. Dinda, A.V. Patwardhan, V.V. Goud, and N.C. Pradhan, Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids. *Biore. Tech.* **99**(9), 3737–3744 (2008).
5. A. Zlatanovic, C. Lava, W. Zhang, and Z.S. Petrovic, Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *J. Poly. Sci.: Part B: Polym. Phys.* **42**, 809–819 (2004).
6. L. Montero de Espinosa and M.A.R. Meier, Plant oils: The perfect renewable resource for polymer science. *Europ. Poly. J.* **47**, 837–852 (2011).
7. F.L. Jin and S.J. Park, Thermal and rheological properties of vegetable oil-based epoxy resins cured with thermally latent initiator. *J. Ind. Eng. Chem.* **13**, 808–814 (2007).
8. I.L. Valdes, O. Farfan, O. Sterner, and A. Giménez Turba, Preliminary studies about the chemical characterization of fatty acids from *Bertholletia excelsa* fruit's oil by gas chromatography. *BIOFARBO* **17**, 47–53 (2009).
9. S. Sun, G. Yang, Y. Bi, and H. Liang, Enzymatic epoxidation of corn oil by perstearic acid. *J. Am. Oil Chem. Soc.* **88**, 1567–1571 (2011).
10. R. Retes López, S. Moreno Medina, F.G. Denogean Ballesteros, M. Martín Rivera, and F. Ibarra Flores, Profitability analysis cotton crop in sonora. *Rev. Mex. de Agroneg.* **19**(36), 1156–1166 (2015).

11. I.C. Novoa and E. Flores Loyola, Síntesis de poliols por modificación de química de aceite de algodón. *Química Hoy* **2A**, 38–43 (2012).
12. General Methods of Analysis, Pharmacopoeia of the United Mexican States, Hydroxyl number MGA 0491.
13. Z.S. Petrovic, W. Zhang, and I. Javni, Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. *Biomacromolecules* **6**, 713–719 (2005).
14. I. Javni, W. Zhang, and Z.S. Petrovic, Effect of different isocyanates on the properties of soy-based polyurethanes. *J. Appl. Polym. Sci.* **88**, 2912–2916 (2003).
15. S. Bandyopadhyay-Ghosh, S. Ghosh, and M. Sain, Synthesis of soy-polyol by two step continuous route and development of soy-based polyurethane foam. *J. Polym. Environ.* **18**, 437–442 (2010).
16. I. Yilgör, E. Yilgör, and G.L. Wilkes, Critical parameters in designing segmented polyurethanes and their effect on morphology and properties: A comprehensive review. *Polymer* **58**, A1–A36 (2015).
17. A. Guo, I. Javnil, and Z. Petrovic, Rigid polyurethane foams based on soybean oil. *J. Appl. Pol. Sci.* **77**, 467–473 (2000).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55