CHEMICAL ENGINEERING TRANSACTIONS

VOL. 79, 2020

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Enrico Bardone, Antonio Marzocchella, Marco Bravi

ISBN 978-88-95608-77-8; **ISSN** 2283-9216

DOI: 10.3303/CET2079057

Production of Polyurethanes from used Vegetable Oil-Based Polyols

Diana Moreno[a], Marco Velasco[b], Dionisio Malagón-Romero[b]*

[a] Universidad ECCI. Industrial Engineering Department. Carrera 19 No. 49 – 20. Bogotá, Colombia.
[b] Universidad Santo Tomás. Mechanical Engineering Faculty. Carrera 9 51-11. Bogotá, Colombia.
dionisiomalagon@usantotomas.edu.co

One problem in different cities around the world is the production of waste cooking oil. The principal application of this waste is a raw material for biodiesel production. Other possibility is the production of polyurethane. In this paper, it is presented the experimental research carried out in order to obtain polyols as intermediate for production of polyurethane. We used castor oil as control for the polyurethane production. Relations were defined for the synthesis by weight to weight (w / w), where 4 products are obtained from polyols from castor oil and used respectively, in this case the identification of the products is made according to their relationship in weight used to be castor oil: polyols (60: 100) and (40: 100) applying the same experimental design for the used oil polyols. They were characterized to determine their basic properties in terms of resistance to chemical attack, stress-strain, the results were analyzed according to the bibliography that allowed the experimental design and in the same way comparing it with the commercial rigid polyurethane. It is concluded that a rigid polymer was obtained that has similar behavior to commercial polyurethanes where it allows to continue carrying out research that allows finding a model to obtain the product that generates less environmental impact, less consumption of "crude" and better quality of life.

1. Introduction

Polyurethane is a linear polymer formed by carbamate ester bonds or urethanes (Babb, 2012). There are multiple types of polyurethane with various chemical structures that allow behaviors as thermosetting or thermoplastic with elastomers features. The most common thermosetting polyurethanes come in the form of foam that is used as a thermal insulator or cushioning material (Tahir et al, 2016; Sipaut et al., 2012). Furthermore, thermoplastic polyurethanes are used in the manufacturing of adhesives, sealants, shoe soles, paints, textile fibers, prophylactic and automotive parts, among many other uses (Sipaut et al., 2012). Due to its versatility, it is estimated that polyurethane is the sixth most widely used polymer in the world with an annual market, in 2016, close to 53 billion euros (Cornille et al, 2017). The European Association of plastics manufacturers estimates that in 2015 about 27 million metric tons of polyurethanes were produced, which constitute about 8% of the total 323 metric tons of manufactured polymers that year (Geyer et al, 2017). The production of polyurethanes generally requires reactions between diphenyl methane diisocyanates and conventional polyols usually obtained from petrochemical processes. However, price variability, adverse environmental effects and uncertainty about available oil reserves make the sustainable production of polymers from this resource unlikely (Alam et al, 2014; Desroches et al, 2012; Kong et al, 2013). Therefore, in recent years methods have been developed to obtain vegetable oil (Desroches et al., 2012). In addition to allowing the production of polyurethanes from renewable sources, it has been found that these polymers can exhibit biodegradability. Vegetable oils are defined as triesters of glycerol and fatty acids (saturated or unsaturated), and they are composed mainly of triglycerides (93-98% wt), diglycerides, monoglycerides and phosphoglycerides as minor components(Sharmin et al, 2015). Triglycerides are the product of the esterification reaction between glycerol and three fatty acid molecules. The length of fatty acids usually consists of 12 to 22 carbon atoms. They can be saturated or unsaturated with double bonds located at carbon 9, 12 and 15 (Zhang et al, 2014). About 95% of the total weight of triglycerides has this characteristic, so this property favored the reactivity of triglycerides (Zhang et al, 2014). Additionally, fatty acids can have various

Paper Received: 23 July 2019; Revised: 18 January 2020; Accepted: 4 March 2020
Please cite this article as: Moreno D.C., Velasco M.A., Malagon-Romero D., 2020, Production of Polyurethanes from Used Vegetable Oil-based Polyols, Chemical Engineering Transactions, 79, 337-342 DOI:10.3303/CET2079057

functional groups such as double bonds, epoxy, hydroxyl, ester and other groups that make them highly reactive (Alam et al., 2014).

Different papers have been published in the direction of changing petroleum as raw material for vegetable oils. Castor oil is preferred due to the presence of a hydroxyl group in its fatty acid molecular structure. The problem for using other type of vegetable oils is the absence of this hydroxyl group, so it is necessary to modify the fatty acid structure for adding hydroxyl groups. These compounds are called polyols. Echeverri et al. (2015) present a protocol for obtaining polyols in the laboratory from soybean oil: in this way a molar ratio glycerol and oil of 3:1, using as catalyst sodium hydroxide or sodium methoxide. The yield of monoglycerides was 48.6% (Araújo and Lima, 2011; Desroches et al, 2012)

A disadvantage of the use of vegetable oils as raw material to obtain substitutes for petroleum products is their relative high cost and that they change the use of lands originally used for food production or as forest reserves. A possible solution to this problem is the recycling of vegetable oils used for frying once they have been used. It is estimated that more than 27 million tons of used cooking oil are produced each year in the world and that its cost is 2 to 3 times less than the cost of virgin vegetable oils. Its availability and price make it an alternative to produce oil substitutes (Sharmin et al, 2015). Therefore, the aim of this paper is showing a process for synthesis of polyols and polyurethane derived from waste cooking oil.

2. Materials and methods

2.1 Oils characterization

Castor oil was purchased from commercial chemistry shop in Bogota Colombia and cooking oil was recollected in fried chicken roaster in Bogota (Colombia). Both oils were filtrated trough a filter paper (pore size 5-8 μm, qualitative filters Grade 292, BOECO) in vacuum pump system by triplicate and store at ambient conditions. The oil Characterization was made thought the proposed protocols in the International standards more used: Density IUPAC 2.101 (IUPAC, 2016), Iodine Index ISO 3961, the test was made with potassium iodine, Wijs reactant, chloroform, and sodium thiosulfate (Pancreac trademark) (ISO, 2009b), Saponification value ISO 3657 with potassium hydroxide and hydrochloric acid (Merck trademark) (ISO, 2013) and Acid value ISO 660, in this test used diethyl ether, ethanol with 95% of purity and potassium hydroxide (Merck trademark) (ISO, 2009c). All reactants were analytical grade.

2.2 Polyol synthesis

According to consulted literature, polyol synthesis was developed at temperature of 250 °C. The tests were carried out in a 250 ml glass reactor equipped with 3 nozzles, one of which will be used to place the condenser, another to add reagents and the last one to record temperature. A Factorial Experimental Design was implemented with two molar oil to glycerol ratio (4:1 and 3:1), three reaction time (40, 60 and 80 minutes) and two catalysts (sodium hydroxide and potassium hydroxide) at 1% w/w (Zhang et al, 2014). For each test 70 g of oil were added and the amount of glycerol was calculated and added to the reactor. Catalyst was weighted and dissolved in ethanol (solvent). The solution of catalyst was added to the reactor, which was heated with a heating mantle at 250 °C. Once the reaction time was finished, the catalyst was neutralized using 98 % sulfuric acid. The content of the reactor was transferred to a separation funnel and was left in decantation by 24 hours and separated by gravity. Once the polyols were obtained, the characterization of products were performed. The structures present in the products were determined by infrared spectroscopy (Bruker) in the wavelength range of 3500 to 500 cm^{-1}.

2.3 Polyurethane synthesis

For the synthesis of Polyurethane was used the polyol obtained in the best conditions for polyol synthesis. The polyol is mixed with MDI (Methylene diphenyl diisocyanate, Sigma Aldrich trade mark, analytic grade). The experimental design of the reaction have one variable (mass of MDI) and two levels (40 and 60 g of MDI for each 100 g of polyol).The reaction used ethylene diamine and Stannous Octoate as catalyzer(Shirke et al, 2015). Likewise, methylene chloride is used as a physical expansion agent and silicone as a co-blowing agent

2.4 Polyurethane characterization

The resistance of the polyurethanes obtained to the chemical attack was evaluated. For this, a sample was made according to the ASTM D543-67 in which the resistance of the material to reagents at room temperature was evaluated: toluene, 10% hydrochloric acid and 99% chloroform, all the reactants are analytic grade (Pancreac). A sample of the polyurethane of area of 100 mm^2 was immersed into 10 ml of solvent by seven days, next to that the final weight of the samples was taken. The effect of each of the solvents on the surface of the obtained polymer is evaluated verifying the mass difference (Valero et al, 2009).

The stress-strain tests were performed in universal testing machine (UTM) INSTRON H10KS. The deformation speed was 5 mm / min at room temperature (close to 19 ° C), according to ISO 1926-2009 standard(ISO, 2009a)· In this test six repetitions were made per test evaluated. The sample was molded taking recommendations of the ISO 1926-2009.

3. Results and discussion

3.1 Characterization of castor and waste cooking oil

The characterization of the two oils was done according to the literature consulted (Puspa and Puspita, 2015). Reviewing the results of Table 1 the density is very similar for both oils and does not have difference for these ones. The acid value is higher for used cooking oil than castor oil. This value is due to the use of oil during cooking process (Puspa and Puspita, 2015), and it is an indicator of low quality and poor handling or storage. This aspect is important for utilizing waste cooking as raw material for producing materials. The iodine index indicates the unsaturation in the oils(Chebet et al, 2016), and it was found that in cooking oil used has a higher value than castor oil, indicating that despite cooking it preserves the instaurations of crude oil (Pascacio et al, 2016). This behavior is an advantage for other types of reaction, because the presence of a double bond is most reactive that a single bond(Miao et al, 2014). Finally, the saponification index indicates the reactivity of the compound for obtaining soaps, so the triglycerides contained in the crude oil did not decompose during cooking

Table 1: Characterization of castor oil and waste cooking oil.

Test	Cooking oil	Castor Oil
Acid Value (ml Oleic Acid/ L Oil)	2,26 ±0,199	1,3±0,148
Saponification value (mg KOH/ g Oil)	193,55±8,92	179,37±39,99
Iodine Index (g de I /100g OIL)	89,89±5,03	87,56±7,62
Density (g/ml)	0,901±0,035	0,943±0.032

3.2 Polyols Characterization

Production of polyols was measured as the ratio g of polyol obtained per ml of oil used, this ratio was expressed as percentage. In Table 2 are presented results about production of polyol. According to this table, the ratio of polyol is higher in castor oil than in waste cooking oil. Best conditions corresponding to molar relation 4:1 and time of 80 minutes for cooking oil and 60 minutes for castor oil. However, the results obtained with castor oil were upper than cooking oil, the cost of cooking oil is lower than castor oil, so it is a good alternative for polyols production. Additionally, the ratio of polyol produced is high and is promising for developing an industrial process.

On the other hand, the infrared characterization presented in Figure 1. A signal, which can be attributed to stretching vibrations of OH groups was noticed at A (3200-3600 cm^{-1}). The absorption bands at B (2800-3000 cm^{-1}) can be associated with the symmetric and asymmetric stretching vibrations of CH bonds in methylene groups presented in aliphatic chains and methyl end groups. The signals at C (1600-1800 cm^{-1}), could be attributed to the stretching vibrations of C=O bonds and unconjugated C=C stretching bonds in oil structure. In D (900-1200 cm^{-1}) there can be observed multiple absorption bands characteristic for vibrations of C-O-C ether and ester groups, which is related to the structure of prepared polyol (Hejna et al., 2017). Since these results we conclude that waste cooking oil is a possible raw material for polyol production.

Table 2: Yield of polyol obtained from cooked oil and castor oil

	Molar Ratio (oil to glycerol)			
Time reaction (min)	Cooking oil		Castor Oil	
	3:1	4:1	3:1	4:1
40	34,38±0,18	42,20±0,88	47,34±1,54	82,12±5,02
60	59,87±6,01	47,26±1,86	79,14±6,17	98,23±1,04
80	59,39±3,34	71,82±0,63	90,55±1,20	87,17±4,06

Once polyol was obtained and separated, was used as raw material for polyurethane production. Polyurethane obtained was submitted to different chemical solvents and it is reported the characterization in the Table 3. The solvent that most induced weight loss was chloroform ($CHCl_3$) on the polyurethane from castor oil. Additionally, polyurethanes were more resistant to hydrochloric acid. This is due to the special characteristics that castor oil contains compared to solvents such as chloroform and its limited solubility when exposed to aromatic reagents as toluene (Cardona et al, 2010). The behavior of the rigid foams of polyurethane against aromatic hydrocarbons such as toluene swell the polymer at room temperature, when it absorbs it loses its mechanical properties and can lose approximately 50% by weight. Results obtained in this paper, showed that chemical behavior it is better for polyurethane produced from vegetable oils than petrochemical raw materials. This aspect is important for defining final applications, in another investigations with castor oil and another vegetable oils the polymers obtained shows insulating characteristics and moderate resistance to impact, being able to be used in the refrigeration, textile and other industries

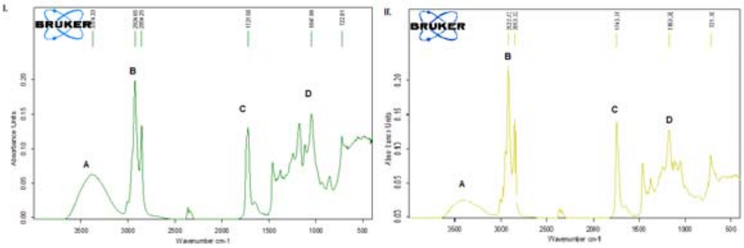

Figure 1: Absorbance of FTIR (Fourier Transformed Infra-Red of Polyol obtained with molar relation of glycerol to oil of 4:1 and 80 minutes of reaction for: a) waste cooking oil and b) castor oil.

Table 3. Chemical resistant of polyurethane obtained.

	Polyurethane from Cooking Oil		Polyurethane from Castor Oil	
MDI: Polyol Ratio	40:100	60:100	40:100	60:100
Chemical attack resistance (mass difference)				
HCl	-0,87%	-4,98%	-5,06%	-2,98%
$CHCl_3$	-19,35%	-15,21%	-23,73%	-35,94%
C_6H_5-CH_3	-20,27%	-11,60%	-6,22%	-22,04%

Respecting to mechanical properties, there is a great variability in mechanical behavior. It was observed that polyurethane made with cooking oil has higher tensile strength than polyurethane from castor oil. Tensile strength of cooking oil 60:100 polyurethane specimens were between 2,227 MPa and 9,907 MPa, and average tensile strength of 4,844 MPa; compared with castor oil 60:100 specimens with tensile strength between 0,191 MPa and 0,369 MPa, and average of 0,49 MPa (Figure 2). Similarly to other studies, polyurethane obtained from castor oil have properties has a low modulus of elasticity and low resistance. This is mainly due to lower curing rate of the oil as a result of the low functionality and reactivity of the functional groups (secondary hydroxyls) which causes the formation of polyurethane with an irregular structure with low crosslink density (Valero et al, 2009).

In the case of the addition of the isocyanate, the difference in strength presented by the two samples is remarkable because the polyurethane in relation to 60: 100 reaches a greater tensile strength than the polyurethane in relation to 40: 100 and castor oil polyurethanes. The higher the amount of isocyanate used, the greater the degree of crosslinking the polymer presents, thus giving better resistance to stress.

A visual inspection shows the color and principal structure of the obtained polyurethanes (Figure 3). The cooking oil polyurethane presents a structure stronger and a darker color, in case of the castor oil polyurethane the texture is very brittle and have no consistence. For improving color in the industry the reaction is mixed with calcium hydroxide (Cardona et al, 2010). Color is important depending on the future application of the polymer. In this case it is recommended to give an application in which the color does not interfere as thermal insulation, avoiding an additional step in the obtaining process.

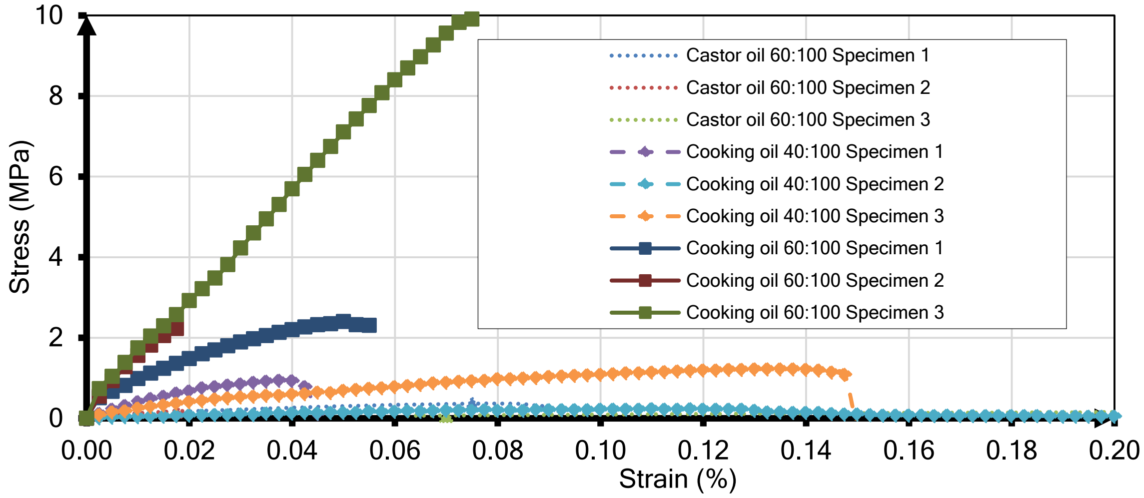

Figure 2: Stress – Strain Curves

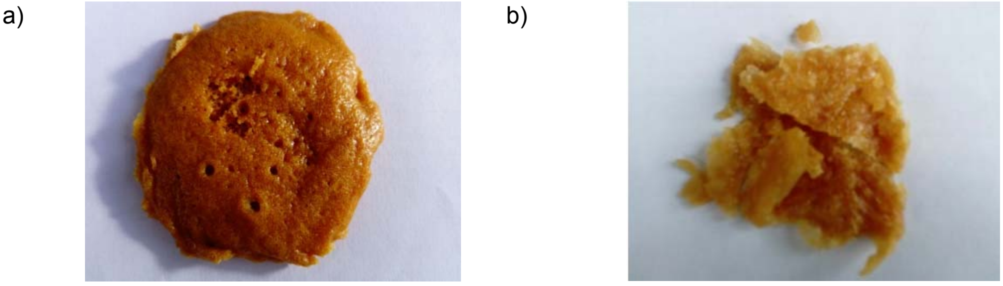

Figure 3: Visual aspect of obtained polyurethanes. a) from cooking oil, b) from castor oil

4. Conclusions

The characterization of oils showed us that both oils were able to react with glycerol due to their saponification value which indicated reactivity. The castor oil was used mainly as a comparison because several previous investigations used this oil as a source to obtain polyurethane. When the polyol was obtained, maximum yields of 90% were obtained for the castor oil and 72% for the used cooking oil. The infrared spectrophotometry determined that both oils had the main structures associated with polyols such as hydroxyl, carboxyl and ester groups. In the case of the castor oil the vibratory intensity for hydroxyl groups was higher indicating a greater reaction potential to form polyurethane. After the synthesis of the polyurethane, the characterization was made, and it was found that the cooking oil has a higher resistance to the chemical attack. The solvent with the greatest impact on mass loss was chloroform, since for castor oil it reported a mass loss of 36% and for used cooking oil of 19%. Finally, in the mechanical resistance test, medium broken strength values of the piece indicate that the polyurethane obtained from cooking oil (60:100) is the most resistant since average tensile strength is 4,844 MPa. These results indicate that the polyurethane obtained with used cooking oil can be used in applications that require high impact resistance.

References

Alam M., Akram D., Sharmin E., Zafar F., Ahmad, S., 2014, Vegetable oil based eco-friendly coating materials: A review article, Arabian Journal of Chemistry, 7(4), 469–479.

Araújo B., Lima D. P., 2011, Glicerol: um breve histórico e aplicação em sínteses estereosseletivas, Química Nova, 34(2), 306–319.

Babb D. A., 2012, Polyurethanes from renewable recourses. In: Rieger B, Künkel A, Coates G.W., Reichardt R., Dinjus E., Zevaco T.A. (Eds.), Synthetic Biodegradable Polymers (pp. 315–361). Munchen: Springer Berlin Heidelberg.

Cardona V, Gonzalez C, Franco C, Cardeño L, Rios, L. A., 2010, Obtención de monoglicéridos de aceite de ricino empleando glicerina refinada y cruda: Estudio de las principales variables del proceso, Vitae, 17(2), 128–134.

Chebet J., Kinyanjui T., Cheplogoi, P., 2016, Impact of frying on iodine value of vegetable oils before and after deep frying in different types of food in Kenya, Journal of Scientific and Innovative Research, 5(5), 193–196.

Cornille A., Auvergne R., Figovsky O., Boutevin B., Caillol S., 2017, A perspective approach to sustainable routes for non-isocyanate polyurethanes, European Polymer Journal, 87, 535–552.

Desroches M., Escouvois M., Auvergne R., Caillol S., Boutevin, B., 2012, From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products, Polymer Reviews, 52(1), 38–79.

Echeverri D. A., Rios L. A., Rivas B. L., 2015, Synthesis and copolymerization of thermosetting resins obtained from vegetable oils and biodiesel-derived crude glycerol, European Polymer Journal, 67, 428–438.

Geyer R., Jambeck J., Law, K., 2017, Production, use, and fate of all plastics ever made, Science Advances, 3, e1700782.

Hejna A., Kirpluks M., Kosmela P., Cabulis U., Haponiuk J., Piszczyk, Ł., 2017, The influence of crude glycerol and castor oil-based polyol on the structure and performance of rigid polyurethane-polyisocyanurate foams, Industrial Crops and Products, 95, 113–125.

ISO. 2009, ISO 1926: Rigid cellular plastics — Determination of tensile properties.

ISO. 2009b, ISO 3961: Animal and vegetable fats and oil - Determination of iodine value (Vol. 2).

ISO. 2009c, ISO 660:2009 Animal and vegetable fats and oils - Determination of acid value and acidity.

ISO. 2013, ISO 3657 Animal and vegetable fats and oils. Determiantion of saponification value.

IUPAC. 2016, IUPAC 2101: Determination of Density.

Kong X., Liu G., Qi H., Curtis J. M., 2013, Preparation and characterization of high-solid polyurethane coating systems based on vegetable oil derived polyols, Progress in Organic Coatings, 76(9), 1151–1160.

Miao S., Wang P., Su Z., Zhang, S., 2014, Vegetable-oil-based polymers as future polymeric biomaterials. Acta Biomaterialia, Vol. 10, pp. 1692–1704.

Mohd T., Wan S., Nor H., Enderus N., Ismail, N. A., 2016, Synthesis of Waste Cooking Oil-Based Polyol Using Sugarcane Bagasse Activated Carbon and Transesterification Reaction for Rigid Polyurethane Foam, Materials Science Forum, 846, 690–696.

Pascacio T., Rosales A., Torrestiana, B., 2016, Evaluación y caracterización de grasas y aceites residuales de cocina para la producción de biodiésel: Un caso de estudio, Revista Internacional de Contaminacion Ambiental, 32(3), 303–313.

Puspa N., Puspita, D., 2015, Pre-Treatment of Waste Frying Oils for Biodiesel Production, Modern Applied Science, 9(7), 99.

Sharmin E., Zafar F., Akram D., Alam M., Ahmad, S., 2015, Recent advances in vegetable oils based environment friendly coatings: A review, Industrial Crops and Products, 76, 215–229.

Shirke A., Dholakiya B., Kuperkar K., 2015, Novel applications of castor oil based polyurethanes: a short review, Polymer Science Series B, 57(4), 292–297.

Sipaut C. S., Murni S., Saalah S., Hoon T. C., Ibrahim M., Rahman I. A., Abdullah, A. A., 2012, Synthesis and Characterization of Polyols from Refined Cooking Oil for Polyurethane Foam Formation, Cellular Polymers, 31(1), 19–38.

Valero M., Pulido J., Ramírez A., Cheng Z., 2009, Determinación de la densidad de entrecruzamiento de poliuretanos obtenidos a partir de aceite de ricino modificado por transesterificación, Polímeros, 19(1), 14–21.

Zhang M, Pan H., Zhang L., Hu L., Zhou Y., 2014, Study of the mechanical, thermal properties and flame retardancy of rigid polyurethane foams prepared from modified castor-oil-based polyols, Industrial Crops and Products, 59, 135–143.