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Characterization of a Biodegradable Polyurethane Elastomer Derived from Castor Oil

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Abstract Vegetable oils are considered the renewable raw materials with a good functionality, the most abundant and the cheapest, to produce the polyurethane (PU). The castor oil with high degree of unsaturation and low hydroxyl functionality, can act as a bio-based polyol to synthesize the PU. In this project, the structure of this oil is characterized and the percentage of ricinoleic acid was estimated by the reaction with a monoisocyanate and FTIR analysis. PU elastomer was prepared from castor oil (CO) with a petrochemical derived aliphatic diisocyanate (IPDI), in the presence of catalyst, and the condition of stoichiometry. The rheological properties were analyzed for knowledge of the evolution of the polymeric mixture viscosity. The elastomer obtained showed good thermal and mechanical properties. The PU based castor oil had low degree of water uptake, and relatively good degree of toluene swelling.

Keywords Bio-based polyurethane, Fatty acid, Castor oil, Elastomer

1. Introduction

Polyurethane is known as one of the materials having great importance in the industry with excellent properties. Polyurethanes have broad applications in many different fields such as foams (flexible, semi-rigid and rigid), elastomers, adhesives, coatings and fibers [1-5]. The polyurethanes are obtained by the polyaddition reaction of polyols and polyisocyanates [6, 7]. The obtained polyurethane properties depend on the molecular weight, degree of crosslinking, the ratio of NCO/OH, effective intermolecular forces and the stiffness of different chain segments [8, 9]. The polyurethane chain is composed of a soft segment derived from polyol and a hard segment derived from diisocyanate and a chain extender [10-12] (Figure 1).

The nature of the hydrogen bonding in the rigid segment causes a strong mutual attraction leading to the formation of microdomains of rigid and flexible segments which act as physical crosslinks thermoreversible providing formation of the elastomeric property of polyurethane [11, 12]. The amount of hard segments play an important role on the physical properties of polyurethane and considerably on its glass transition temperature [13, 14]. Majority of the polyols used in manufacturing of polyurethanes are polyether polyols, representing 75% of consumption, and polyester polyols, which represent about 25% of the mark [2, 6, 11, 15, 16]. Both are made from chemicals products derived from fossil resources. During the last years, replace products derived from petroleum resources [6, 10] by bio-based compounds, which reduce the consumption of fossil fuels and emissions of greenhouse gas to the end of the products life, is a very interesting subject [17, 18]. The raw materials from vegetable oils are important sources to produce Bio-based polyols in polyurethane structure [17-23]. Vegetable oils are triglycerides, combination of three fatty acids and one glycerol molecule [1, 22-24] (Figure 2).

These fatty acids can be saturated, presenting non-reactive chains, or unsaturated, presenting carrier chains of double carbon-carbon bonds functionalizable [1, 22, 24]. The parameters influencing the properties of these oils are determined by the fatty acid groups and their distribution. What distinguishes these vegetable oils there between is their fatty acid composition [1, 2]. These fatty acids are liquid at room temperature because of their high unsaturated contents. For most applications, the triglycerides cannot be used in the raw state and must be functionalised after chemical modification via the unsaturations and ester functions, in order to obtain bio-based polyols which are capable of reacting with polyisocyanates. Polyurethanes synthesized based on these plant oils have a very heterogeneous composition. This heterogeneity polyurethane network makes it difficult to explain a correlation between the PU structure and the final properties [1, 17].

Among the vegetable oils, castor oil is only one of the oils which naturally contains hydroxyl groups and it can be directly used as a polyol for polyurethane preparation [1-3, 22] (Figure 3). These hydroxyl groups lead to a uniform

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integrated network in the produced polyurethane, which usually results in good mechanical properties [1, 12]. Therefore, due to the good functionality of these polyols based on castor oil, mainly, the semi-flexible or semi-rigid [1] polyurethanes are obtained which are applied in the interpenetrating polymer networks and elastomers [17, 25]. The castor oil triglyceride is characterized by the presence of ricinoleic [3, 13, 16, 23, 25, 26] fatty acid with a long aliphatic chain [27] (Figure 4). Unsaturated industrial castor oil comprises of 80%-90% of ricinoleic acid [3, 8, 13, 16, 17, 28]. Ricinoleic acid is a hydroxyl fatty acid, 18-carbone, it having a double bond at the 9th and 10th carbon and an alcohol functional group on the 11th carbon [13, 17, 26]. Typically, the castor oil contains about 2.7 hydroxyl groups per triglyceride [8, 25] and it also has a low hydroxyl number [8, 25].

This project follows the two objective: confirms the large percentage of the ricinpleique acid in castor oil, and synthesizes an elastomer of bio-based polyurethane made of this biodegradable oil and isophorone diisocyanate in the ratio NCO/OH = 1 by using the One-shot formulation method. Furthermore, the effect of the castor oil application was evaluated on the physical, mechanical and thermal properties of the final polyurethane elastomer.

2. Experimental

2.1. Materials

The Castor oil (purity 80% and M_w= 932 gr.mol^{-1}) was purchased from the Merck Sigma-Aldrich in Germany. In addition, the Cyclohexyl isocyanate (M_w=125.17 gr.mol^{1}), the Isophoron diisocyanate (3-isocyanatomethyl-3, 5, 5-trimethylcyclohexyle) _ with the commercially name of IPDI (M_w=222.29 gr.mol^{-1}), the Dibutyl tin dilaurate known as the catalyst _with the commercially name of DBDL (M_w=631.55 gr.mol^{-1}) _, the Potassium hydroxide (≥85% KOH) and the Toluene (≥99.8%, anhydrous) were provided by Sigma Aldrich company.

The high reactivity of the hydroxyl group leads to the absorption of the water molecules from the surrounding environment. During the polymerization, a portion of the NCO functional groups reacts with the molecules of water. To avoid these secondary reactions, it is necessary to eliminate moisture in castor oil, before use [8, 17, 29, 30]. Castor oil was dried in a vacuum oven at 110°C for 12h.

2.2. The Polyurethane Synthesis

2.2.1. The Synthesis with Monoisocyanate

Considering that the castor oil is completely pure (100%), 7.3 gr of castor oil was mixed with 3.1 gr of IPDI and also, 0.2 wt. % of total weight of the mixture, the catalyst was added into a three-necked flask, at the room temperature for 8 hours, under a dry nitrogen.

It should be reminded that the monoisocyanate used in this mixture got exceeded about 10% more than of the weight counted in the stoichiometric, in order to determine the NCO rate used by the excessive amount of isocyanate found in the spectrum obtained by infrared [31, 32].

2.2.2. The Synthesis with Diisocyanate

In this research, the NCO/OH ratio was 1, indicates that [NCO] = [OH] during polymerization [31].

2.82 gr of Isophoron diiocyanate was mixed with 7.17 gr of castor oil (with purity of 80%) in stoichiometric: n (OH) = n (NCO) and with the catalyst at 0.2 wt. % of mixture, with regard to the total weight of castor oil and the IPDI in thermostat oil tub at 40°C, in a dry nitrogen and agitator of 200 rpm.min^{-1}, for 30 minutes. The polymer mixture resulted a viscose solution and it was poured out onto a teflon plate of 2mm thickness. The plate was put in a vacuum oven at 100°C, for 24 hours to get dried.

2.3. Measurements

2.3.1. Characteristics of castor oil

The hydroxyl value of castor oil was determined according to ASTM D1957-86.

Hydroxyl functionality, which is the number of hydroxyl group per molecule, was experimentally calculated by the following formula [3]:

$$\text{Functionality} = \frac{\text{Molecular Weight}}{\text{Equivalent Weight}} \quad (1)$$

Where, the Equivalent weight is defined as:

$$\text{Equivalent Weight} = \frac{56100}{\text{Hydroxyl Number}} \quad (2)$$

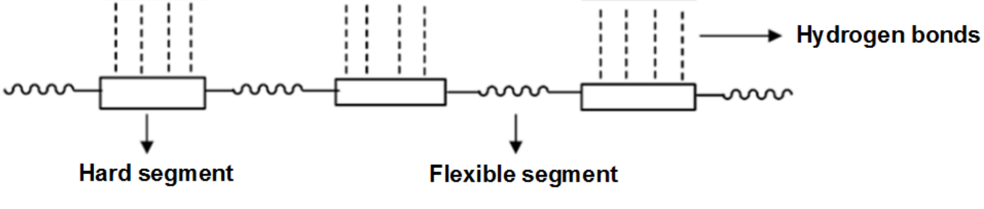

Figure 1. Linear segmented polyurethane chain structure

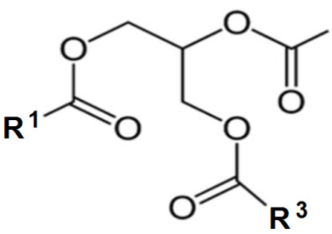

Figure 2. Structure of a triglyceride with fatty acid (R1, R2 and R3)

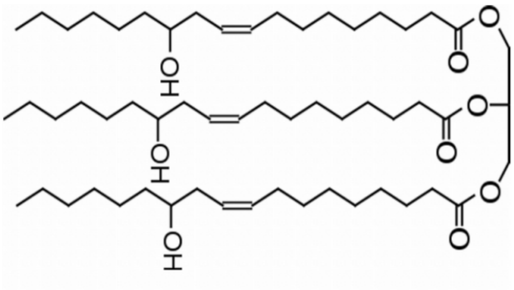

Figure 3. Chemical formula of castor oil

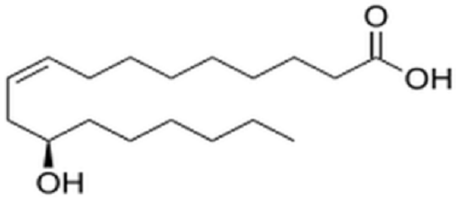

Figure 4. Structure of ricinoleic fatty acid

That according to ASTM 1957-86, the hydroxyl value is determined by the mass of KOH which is equivalent to the hydroxyl groups in 1 g of castor oil [33]. By substituting the formula of equivalent weight into the Eq. 1, the functionality would be:

$$\text{Functionality} = \frac{\text{Hydroxyl Number} \times \text{Molecular Weight}}{56100} \quad (3)$$

The average data obtained from these measurements are summarized in Table 1.

2.3.2. Consumption rate of NCO Group Oil

Evolution of transformation rate of **isocyanate** group over time will be obtained by using the following formula [10]:

$$\text{Tx[NCO]} = \frac{[\text{NCO}]_0 - [\text{NCO}]}{[\text{NCO}]_0} = 1 - \frac{\text{A(NCO)[t]}}{\text{A(CH}_2\text{)[t]}} : \frac{\text{A(NCO)[t}_0\text{]}}{\text{A(CH}_2\text{)[t}_0\text{]}} \quad (4)$$

Where $[NCO]_0$ is the concentration NCO group at the initial time that corresponds to the spectrum of the mixture after a few moments of agitation at room temperature, A (NCO) $[t_0]$ and A (NCO) [t] are integrated absorbance of NCO at the initial time and t of the reaction, and A (CH2) $[t_0]$, A (CH2) [t] are the integrated absorbance of CH2 at the initial time and t of the reaction.

Integrated absorbance of NCO is normalized by dividing by the integrated absorbance CH2, because the number of these groups does not vary during the reaction.

2.3.3. Purity of Castor Oil

Once the isocyanate consumes rate is determined from the amount of excess isocyanate observed in the spectrum, it deduces the amount of alcohol functions in the oil and therefore its purity.

The weight and the percentage of ricinoleic acid in the castor oil is calculated by the following experimental formulas obtained during the experiments:

Table 1. Physical properties of Castor oil

Polyol	OH number (mg KOH/gr)	Functionality
Castor oil	160.72	2.67

$$n(\text{OH}) = \frac{m_{\text{iso}}}{M_{\text{iso}}} \times \text{Tx [NCO]} \quad (5)$$

$$n_{\text{AR}} = \frac{n(\text{OH})}{3} \quad (6)$$

$$m_{\text{AR}} = \frac{n_{\text{AR}}}{M_{\text{HR}}} \quad (7)$$

$$\text{Purity of castor oil} = \frac{m_{\text{AR}}}{M_{\text{HR}}} \times 100 \quad (8)$$

Where, m_{iso} and M_{iso} are the mass of monoisocyanate uses and the molecular weight of monosisocyanate, n_{AR} is the mole number of ricinoleic acid, m_{ar} is the mass of ricinoleic acid, and M_{HR} is the molecular weight of the castor oil.

2.4. Analysis

2.4.1. The Fourier Transform Infrared Spectroscopy

This analysis is performed using a Thermo Electron Corporation spectrometer (IR 200 Series). The range of this analysis extends from 4000 to 500cm^{-1}. The spectra were obtained using the OMNIC 7.3 software which also allows measuring the peak area. A background is done before each absorbance spectrum for reduce unwanted peaks in the spectrum by placing the pellets **KBr**. These pellets are prepared by hydraulic press of fine powder of potassium bromide, between two cylinders.

The FTIR analysis of the mixture is carried out at different time points in order to follow the progress of the chemical reaction. The spectrum is introduced a total absorbance value.

2.4.2. Rheology

Rheology is the study of polymer flow. The viscosity of polyurethane mixture, obtained by castor oil and IPDI, was determined by the remoter AR 2000 ex TA Instruments; a percentage of strain of 1%, a 10Hz scan rate and a 4 mm gap were chosen. The evaluation of the polyurethane viscosity was accomplished, with regard to the temperature at 25°C and 50°C, and also by adding a concentration of 0.2 wt. % of catalyst.

2.4.3. Water uptake

The water absorption of the polyurethane was measured by immersing the polyurethane film (10mm×10mm×2mm) in 50mL of water, at 30°C in a humidified incubator, during

14 days. After the time interval, the polyurethane film was removed from the water, and also the excess water on the surface was removed; further, the polyurethane film was weighed with an analytical balance. The percentage of water absorption was calculated according to the following formula [6, 8, 22]:

$$\text{Water uptake }\% = \frac{M_w - M_d}{M_d} \times 100 \tag{9}$$

Where M_d and M_w are respectively the weights of dry and wet sample.

2.4.4. Swelling

The equilibrium swelling was carried out by immersing the polyurethane film in Toluene at 30°C, during 72h. The measure of the weights of swollen polyurethane film was carried out in every 4 hours during the first 24 hours and continued in every 12h, until finding the constant weight. The equilibrium degree of swelling (Q) was calculated by following formula [15]:

$$Q = \frac{W_P / d_P + W_S / d_S}{W_P / d_P} \tag{10}$$

Where W_P is known weight of dry polymer, W_S is weight of solvent at equilibrium, d_P is defined for the density of polymer and finally, d_S is identified for solvent density.

The crosslinking density (V_C) and the average molecular weight between two crosslinks (M_C) of polyurethane were determined by the swelling test, according to the Flory-Rehner formula [2, 6, 22, 26, 34]:

$$Mc = \frac{V_S d_P \left(V_P^{1/3} - \frac{V_P}{2}\right)}{\ln(1 - V_P) + V_P + X_{12} V_P^2} \tag{11}$$

Where V_S is the molar volume of the solvent, V_P is the volume fraction of polymer in the swollen state, and X_{12} is defined for the parameter of the polymer-solvent interaction of the solvent [6, 26], that this parameter is calculated by the following formula:

$$X_{12} = \frac{V_S(\delta_P - \delta_S)^2}{RT} \tag{12}$$

Where δ_P and δ_S are the solubility parameters of the polymer and solvent. Toluene solubility parameter is 18.2 $(J.cm^{-3})^{1/2}$ [6] and the polyurethane solubility parameter was determined by the cohesive energy of the system in swelling test according to the Eq. 10.

Eventually, the crosslinking density was calculated according to the following formula [26]:

$$V_c = \frac{d_P}{M_c} \tag{13}$$

2.4.5. Mechanical Properties

The mechanical properties were determined according to ASTM D638. The mechanical testing was performed by using an MTS tensile tester (USA). The measurements were performed at room temperature with a load cell (load one) of 500N and crosshead speed (crosshead speed) of 50 mm/min. All Tensile strength (σ), elongation at break (ε), and the Young's modulus (E) were measured with the polyurethane film with dimension 70mm × 25mm × 2mm (length × width × thickness). The data presented are an average of 4 different measures and they were recorded by the QT TestWorks software.

2.4.6. Thermal Analysis (DSC)

Differential scanning calorimetry test was performed on a TA Instruments 2920 machine. The analysis was made with a sample weight of 10 mg, placed in aluminum capsules. The Scanning is carried out in temperature from -20°C to 220°C under nitrogen. The heating and cooling speed was set at 10°C/min.

3. Results and Discussion

3.1. FTIR

The infrared spectrum of the Bio-based polyurethane, based on Castor oil and the Cyclohexyl isocyanate, in the initial, middle and final time, were shown in Figure 5. Broadband between 3200 cm^{-1} and 3600 cm^{-1}, corresponded to the OH functions existing in castor oil. The stretching vibration band of the NCO function of the isocyanate was evident between 2250 cm^{-1} and 2400 cm^{-1}. The bands on the stretching vibration of the CH2 group and the carbonyl group (C = O) of the urethane bond are observed at 2855 cm^{-1} and 1742 cm^{-1}, respectively. Reducing progressively the band of the NCO group noted the progress of the reaction between the hydroxyl function and isocyanate, during polymerization. In parallel this event, a new band appeared at 3340 cm^{-1} which corresponds to the NH stretching vibration. The establishment of hydrogen bonds between the NH function, the C = O group, and an oxygen castor oil, leading to the formation of a urethane bond (-NH-COO-) in the bio-based polyurethane structure. The small NCO band observed in the spectrum at the end of polymerization, corresponds to the excess isocyanate which remains without reacting with the OH of the castor oil functions.

Evolution of the NCO group consumption rate is calculated by the expression given in Formula. CH2 band in the spectrum band taken as reference, considering that the number of CH2 group is stable during the reaction. Normalizing the integrated absorbance of the NCO band by dividing the integrated absorbance CH2, eliminates variations in the total absorbance. The rate of isocyanate consumption over time is demonstrated in Table 2.

Table 2. Isocyanate consumption rate of the mixture castor oil/cyclohexyl isocyanate according to time

Time	T_X[NCO]
0 min	00.0 %
2h	50.6 %
4h	51.9 %
6h	70.5 %
8h	72.6 %

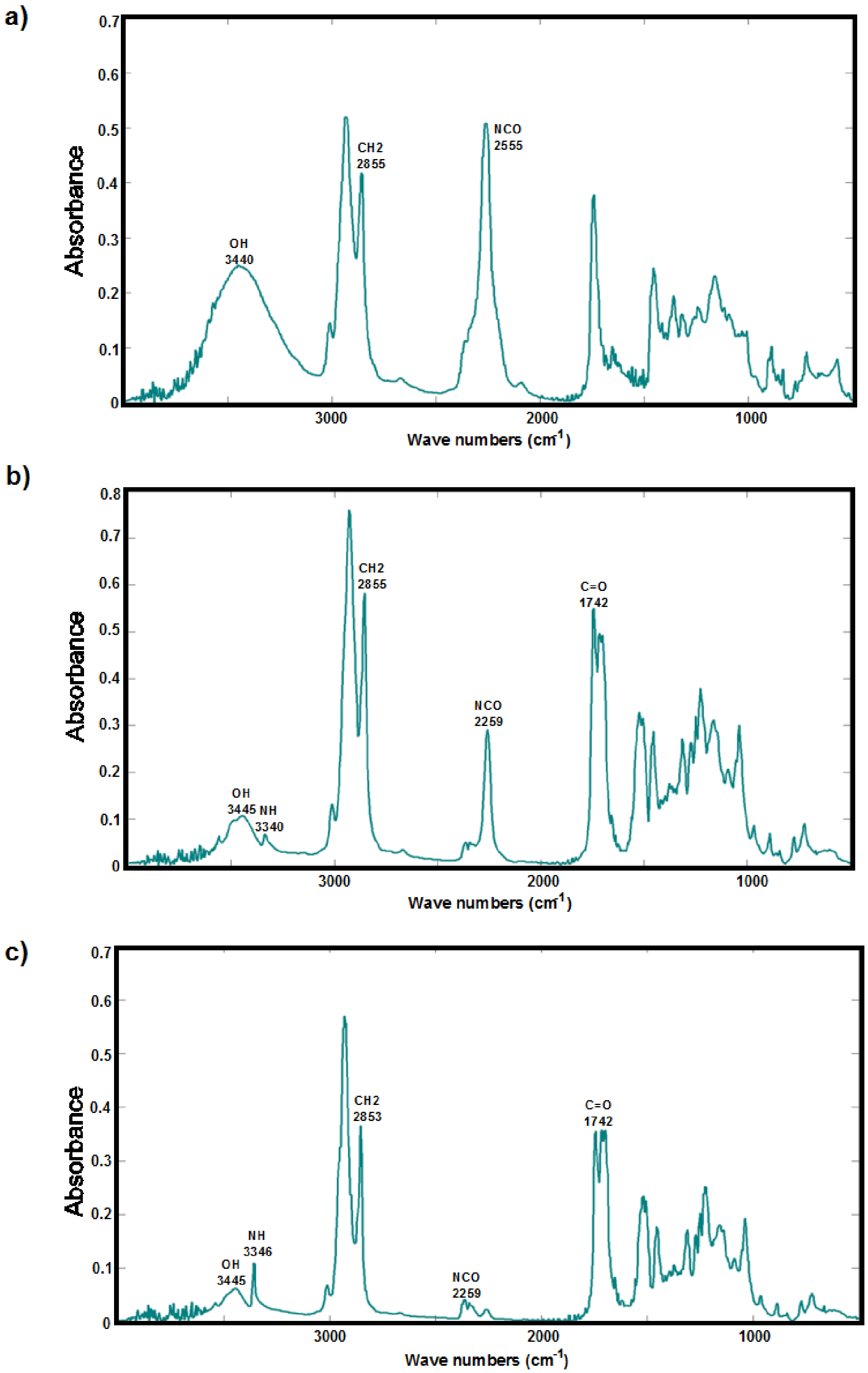

Figure 5. FTIR spectra of the mixture castor oil/cyclohexyl isocyanate synthesized at room temperature with 0.2 wt. % DBTDL in different moments of the reaction (a, b and c, at 0min, 4h and 8h, respectively)

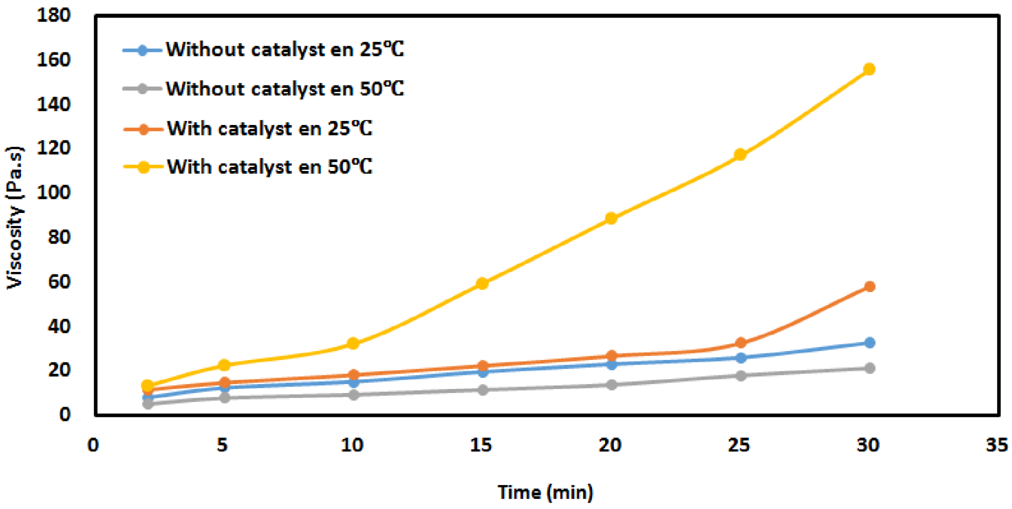

Figure 6. Evolution of the viscosity of the mixture castor oil/IPDI according to time and catalyst

Table 3. Viscosity of bio-based polymer from castor oil in the first 30 minutes of reaction according to time and catalyst

Viscosity (Pa.s) / Time (min)	Without Catalyst en 25°C	With Catalyst en 25°C	Without Catalyst en 50°C	With catalyst en 50°C
10	15.1	26.7	13.65	88.60
20	22.9	32.5	17.81	117.13
30	34.8	58.0	21.04	156.00

Experimental percentage of ricinoleic acid in castor oil could be determined from the percentage of isocyanate reacted after 8h (72.6%) according to the expressions given in the formulas. Purity of castor oil is obtained 78.9%, which was almost equal to that of the industrial castor oil and it is also found in literature.

3.2. Viscosity

The study of rheological properties, initially focuses on the viscosity evaluation of the polyurethane system according to the temperature and depending on the catalyst, as it allows to know the progress of the reaction. Figure 6 shows that the increase of the temperature of a polyurethane system slowly decreases the viscosity of the polymer in a short time. It should be noted that the increase of PU mixture temperature in a long period of time leads to increase speed of polymerization. So, the concentration of 0.2% catalyst had a great importance on the reactivity between castor oil and IPDI, therefore, a higher viscosity is evident. The reaction started quickly and the growth of the chains leads to an increase of the viscosity.

The chain length [36] and the molecular weight [12] of soft segment have a great influence on the viscosity of polyurethane. The More the chain length increases, the more the viscosity of the polymer increases. Castor oil with a large aliphatic chain and a low relative molecular mass (932 $gr.mol^{-1}$) shows a polyurethane with a good rate of viscosity progress, particularly in the presence of catalyst (DBTDL). The results of viscosity are summarized in Table 3.

3.3. Water Uptake

The water absorption is one of the polyurethane physical properties, which is of great importance to the durability of the polymer. Because the polyurethane degradation rate increases with the absorption of the more water. Bio-based Polyurethane, based on castor oil and IPDI, indicates a per-centage of water absorption equal to 2.36% which corresponds to a hydrophobic nature of this PU. The hydrocarbon chains of racinoleic acid, in the castor oil structure, are the big aliphatic chains which make the lower penetration of water molecules in the PU network. This result shows that the PU based on the castor oil has a good resistance to water degradation.

3.4. Swelling and Cross-Linking Density

The swelling test is a method used to measure the crosslinking density, which is calculated according to the Flory-Rehner theory based on affine network. The crosslinking density is defined by the number of crosslinking per unit volume [15]. The results obtained for the degree of swelling (Q), the crosslinking density (V_C), and the average molecular weight between two cross-links (M_C) are shown in Table 4.

The swelling obtained for PU rate is 3.08%, which results in the presence of cross-linking in the polyurethane film which reflects the high level ricinoleic acid in the castor oil structure and leads to a good chemical resistance. But, because of the low hydroxyl functionality in its structure and the ratio NCO / OH = 1, its cross-linking density does not have a significant value. While if the NCO/OH ratio increases, the upper cross-linking density will be achieved [17, 29] through increasing a bonding hydrogens [14]. The upper average molecular weight between two cross-links (M_C) is originated from high chain length which increases the distance between two urethane groups [31]. These parameters are also effective on the polymer Tg [2.35], and the higher M_C and lower cross-linking density of the polyurethane decreases the polyurethane Tg.

Table 4. Swelling properties and molecular weight between cross-links of the network of the bio-based polyurethane elastomer made from castor oil

Polymer	**Degree of Swelling (Q) %**	**Flory-Rehner**	
		$V_c \times 10^3$ (mol/cm^3)	M_c (gr/mol)
CO + IPDI	3.08	1.3	1131

Table 5. Stress data for bio-based polyurethane made from castor oil

Polyurethane	**Tensile Strength (MPa)**	**Elongation at Break (%)**	**Young's Modulus (MPa)**
CO + IPDI	31.8	426.5	4.16

3.5. Mechanical Properties

The stress-strain curve obtained by the tensile test for bio-based polyurethane which is set forth in Figure 7. Table 5 shows the results of this curve for the polymer mechanical properties.

The polymer structure, the ratio of NCO/OH and the degree of crosslinking [5, 15] are the most effective elements on the mechanical properties. Castor oil naturally contain 80% ricinoleic acid and the hydroxyl groups distributed heterogeneous on its chain triglyceride [3], which leads to the network affinity in the final polyurethane structure, which corresponds to good mechanical properties. In the NCO/OH =1 ratio, the use of castor oil with a high degree of unsaturation, with an aliphatic disocyanate (IPDI), gives relatively good tensile strength. High elongation at break of polymer defined by the long chain aliphatic fatty acid in castor oil [4] and the average molecular weight between two cross-links (M_C) which derive from the flexibility of the obtained polyurethane chains. The Low Young's modulus of polyurethane corresponds to the low hydroxyl functionality of castor oil. The young's modulus also affects the glass transition temperature (Tg) of PU, and low modulus decreases the Tg. higher elongation at break and lower Young's modulus was observed, and according to the level of obtained tensile strength, it corresponds to a semi-rigid elastomer.

3.6. DSC

The differential scanning calorimetry is one of the techniques for measuring the glass transition temperature (Tg) of polyurethane elastomer. The Figure 8 presents the thermal behavior of polyurethane elastomer synthesized.

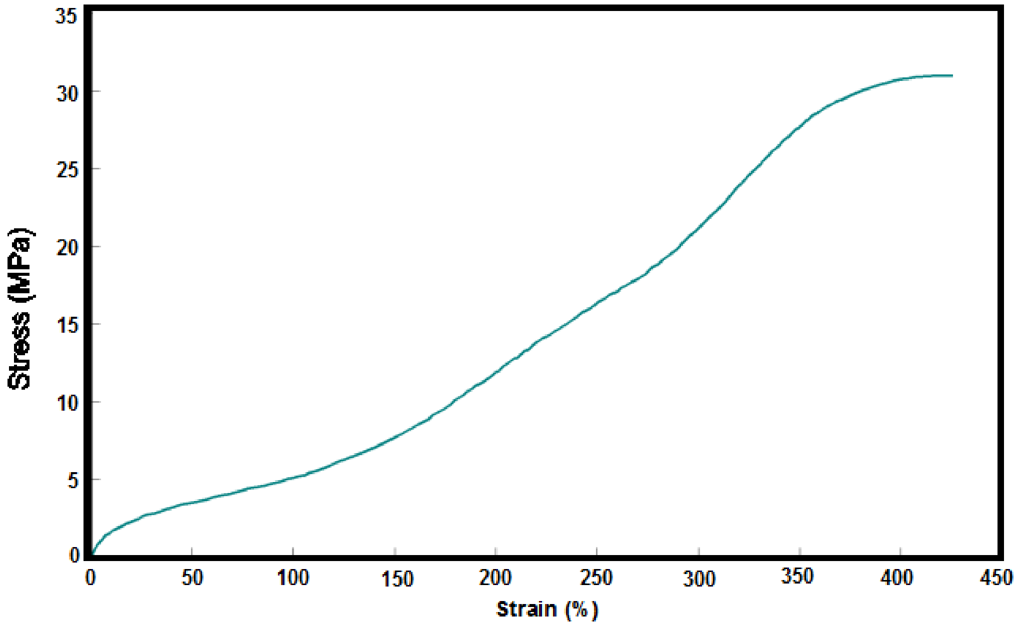

Figure 7. Stress-strain curve for bio-based polyurethane elastomer made from castor oil

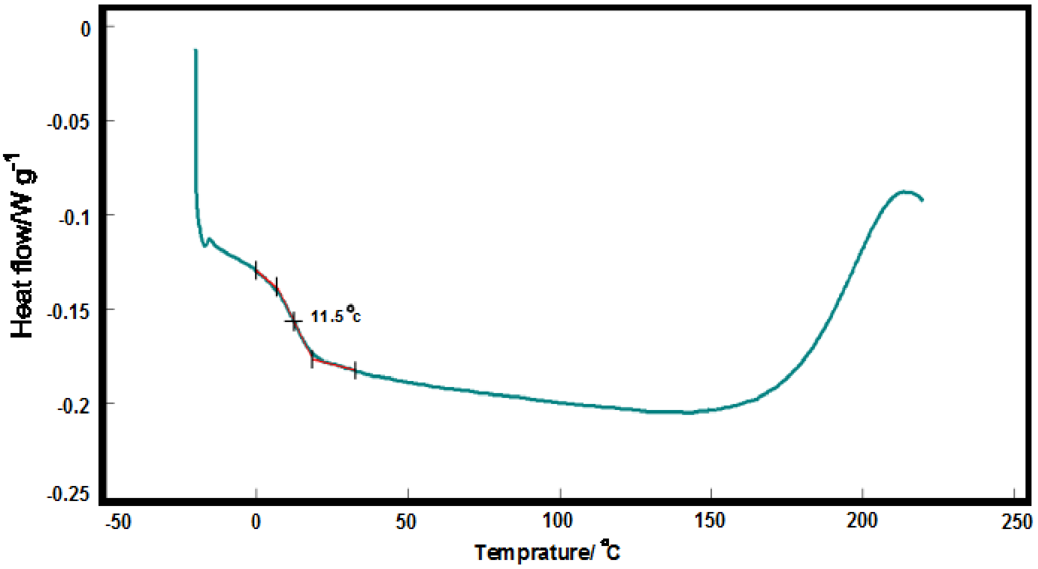

Figure 8. DSC curve of bio-based polyurethanes made from castor oil

The cross linking density [2, 29, 46], crystallinity [26], hydroxyl number and polyol functionality are the most important parameters on the glass transition temperature (Tg). By reducing hydroxyl number and functionality, the crosslinking density and therefore, the crystalline phase decreases which causes a low Tg [35]. Castor oil has an amorphous structure with a hydroxyl number of 163 and a low hydroxyl functions leads to low crosslinking density.

The result of DSC curve shows a Tg = 11.5°C in the polyurethane network that drive from flexibility of chain and chain mobility [17, 29]. This obtained glass transition temperature (more than 0°C) shows a good affinity in the final PU which leads to the fatty acid structure of castor oil.

4. Conclusions

Castor oil with hydroxyl functionality of 2.67 and hydroxyl number of 163 has been used as a bio-based polyol to synthesize a new polyurethane elastomer. The presence and the structure of ricinoleic acid in this oil is of great importance on the final polymer properties. The FT-IR spectrum determines the ricinoleic acid poucentage (≅80%). This oil has a high degree of unsaturation which leads to good mechanical properties. The castor oil based PU elastomer shows a relatively good tensile strength (31.8 MPa), while it also has a high elongation at break (426.5%) drive from the large fatty acid chain. The presence of a low cross-linking density confirmed in the polyurethane elastomer, according to the Flory-Rehner; and it showed a hydrophobic nature according to the water uptake test. The reason for this discrepancy in the physical properties can be explained by homogeneous distribution of the hydroxyl groups on the chains in castor oil, thanks to a uniform structure of triglycerides, which leads to the affinity network. By creating this affinity network and having a higher degree of unsaturation of castor oil, a relatively high Tg (preferably less than room temperature) is a evident for bio-based PU system; regarding the chain mobility in the structure final elastomer. These properties obtained can be attributed to training a semi-rigid elastomer.

Abbreviations

PU	Polyurethane
CO	Castor oil
IPDI	Isophorone diisocyanate
OH	Hydroxyl group
NCO	Isocyanate group
DBTDL	Dibutyl tin dilaurate
FTIR	Fourier transform-infrared spectroscopy
ASTM	American Society for Testing and Materials
DSC	Differential scanning calorimetry

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