http://dx.doi.org/10.21577/0100-4042.20170921 *Quim. Nova,* Vol. 45, No. 9, 1060-1066, 2022

SYNTHESIS OF TOLUENE DIISOCYANATE URETHANE PREPOLYMER USING CASTOR OIL AND EVALUATION OF MECHANICAL PROPERTIES

Mayara Q. Savioli* and José R. R. Bortoleto
Departamento de Ciências, Instituto de Ciência e Tecnologia de Sorocaba, Universidade Estadual Paulista "Júlio de Mesquita Filho", 18087-180 Sorocaba – SP, Brasil

Recebido em 23/01/2022; aceito em 19/05/2022; publicado na web em 01/07/2022

This research is the synthesis of urethane prepolymer cast elastomer which had been produced using toluene diisocyanate and castor oil to replace the synthetic polyol, from petroleum origin, and the evaluation of mechanical properties of the polyurethane. The focus was to replace polyol from petroleum to vegetable material looking for renewable resources. The reactions occurred in a pilot reactor considering the process temperature of 70 °C and 0.5 bar of pressure. After the reactions, all prepolymers reacted with the chain extender to cast in sheet molds for mechanical properties. The chains extenders chosen to react with the prepolymers were 4,4'-methylenebis(2-chloroaniline) and castor oil. The better results achieved 65 Shore A as hardness, 35% as rebound resilience, 36.22 mm^3 as abrasion resistance, 570.12 psi as tensile strength, 325.39% as elongation and 29.53 kN m^{-1} as tear resistance; achieved using a blend between castor oil and polytetramethylene ether glycol with 2000 g mol^{-1} as molecular weight. Thought the mechanical results tests, the castor oil can replace the synthetic polyol depending on applications which did not require a high tensile strength and tear resistance, such as rolls for graphics and cellulose processes, billets seals, cushions and general parts used for industrial segment.

Keywords: polyurethane; castor oil; vegetable polyol; cast elastomers; urethane systems; hot cast.

INTRODUCTION

Polyurethanes are part of a versatile group of materials that are used in a wide range of applications, as foams, coatings, adhesives, medical implants, industrial components, shoe soles, electrical encapsulation, rollers and engineering components.[1]

Urethane groups are present in polyurethane systems synthesized through a chemical reaction between a polyol and a diisocyanate. Depending on the application of polyurethane some additives may be required, such as catalysts, chain extenders, crosslinkers, plasticizers, silicon and others.[2] To the polyurethane elastomer curing, is necessary to add chain extender, usually a low molecular weight, in general diol or amine. The diol (OH groups) or amine (NH groups) react with the NCO groups present in the urethane prepolymer and the reaction cure started.[3,4,5]

According to Jiang *et al.* (2018), the flexible segment of polyurethane provides elasticity, while the rigid segment is responsible for the strength and stiffness through points of physical crosslinking. The crosslinking results from covalent bonds between the polymer molecules, obtaining a product with high molecular weight. The rigid segment tends to cluster in domains, due the locking of polymeric chains.[2]

The urethane prepolymer used in this research is from a vegetable castor oil. Usually, it is used a synthetic polyol to produce the prepolymer, ether or ester, which have a petroleum as origin, non-renewable resource.[6] According to Hussain (2019), the extraction polyol via petrochemical process caused pollution due residues in the environment, so it is necessary developments from researches to replace this material, preferable from vegetable and renewable resource.[3]

Due the concerns about the scarcity of petroleum in the future and the sustainability, this work is focused to replace the synthetic polyol of the formulation to a vegetable polyol, that is widely available in Brazil.[5,7] The synthetic polyol in the polyurethane formulation increased the environmental concern. Castor oil was choosing due vegetable oil structure based on hydroxyls acids and glycerin, therefore there are positions of hydroxyls groups (-OH) and ester bonds that can be react lonely or modifying with chemical components resulting in polyols, biodiesel and surfactants to react with isocyanates to form the polyurethane.[8,9] This research is innovative for urethane hot cast segment due major studies were focus on foams and coatings.

The chain extender must be sufficiently nucleophilic to resonate the isocyanate group. In this work, the chain extender was 4,4'-methylenebis(2-chloroaniline) (popularly known as MOCA) and also castor oil.[1,9] In practice, the most widely used chain extenders to curing the diphenyl methylene diisocyanate prepolymer is the 1,4-butanediol, this saturated linear chain diol has an equivalent weight of 45 g eq^{-1}. To cured diphenyl toluene diisocyanate is 4,4'-methylenebis(2-chloroaniline) with an equivalent weight of 133 g eq^{-1}.[4] Others diols can be used to cure the urethane prepolymer, such as polyether glycol with a molecular weight between 1000 g mol^{-1} to 2000 g mol^{-1}.[1,2]

EXPERIMENTAL

Materials

The precursors used to obtain the urethanes prepolymers were below, firstly indicated the commercial name and between the parenthesis the chemical name and supplier, respectively.

- Desmodur T-100 (2,4-toluene diisocyanate – "TDI", Covestro);
- Resinol Exp PU 160/10 (castor oil, Azevedo Óleos);
- Terathane 2000 (polytetramethylene ether glycol – "PTMEG 2000", Lycra);
- MOCA (4,4'-methylenebis(2-chloroaniline), Sigma-Aldrich).

Methods

First, it was necessary to calculate the equivalent weight of the polyol or castor oil, as well the amount of the KOH (mg g^{-1}), which is

---

*e-mail: mayara.savioli@unesp.br

the molecule of potassium, oxygen and hydrogen. The KOH content presented in the Resinol Exp PU 160/10 was 160 mg g^{-1}. From this value, the equivalent weight of the castor oil was calculated using the Equation 1. The equivalent weight of castor oil was 350.66 g eq^{-1}. The KOH content presented in PTMEG 2000 was 28 mg g^{-1}, so the equivalent weight using the Equation 1 was 2003.78 g eq^{-1}. The KOH content information can be found in technical datasheet of the commercial materials.

$$W_{eq} = k[KOH]^{-1} \tag{1}$$

where W_{eq} is the equivalent weight (g eq^{-1}), k=56106 (g mol^{-1}) is the sum of the molecular weight of potassium (39.0983 g mol^{-1}), oxygen (15.9999 g mol^{-1}) and hydrogen (1.00784 g mol^{-1}) multiplied by thousand and [KOH] are hydroxyls content in the polyol or castor oil expressed in mg g^{-1}.

Four reactions were performed. The Table 1 shows the raw materials and parameters considered in a pilot reactor Grown Inox (Brazilian manufacture) with 20 liters. The TC6 and TC6* is the same reaction, differentiated by chain extender used. The Desmodur T-100 was loaded at 35 °C and the Resinol Exp PU 160/10 at room temperature. For the reactions TC6, TC6* and TC3.5, firstly the 2,4-toluene diisocyanate was loaded and after 10 minutes castor oil, considering the ratio informed in the Table 1. For reaction TCP3.5, the 2,4-toluene diisocyanate was loaded and after 10 minutes, the castor oil and PTMEG 2000 were loaded in the reactor at the same time.

All reactions temperature was 70 °C for the period of three hours, with a pressure of 2 bar. The maximum temperature due exothermy was 110 °C and ambient humidity was 45%. No difference of exothermic temperature was observed between the reactions. The urethane prepolymers reactions generally occur using an equivalent index from 1.65 NCO:OH to 2.10 NCO:OH. This is the relation of these organic groups will react between each other and form urethane molecule.[1,4] Nitrogenous was add in the recipient after bottling, to avoid any humidity to enter in the prepolymer due the concern of NCO reacting with O_2 from humidity, losing NCO groups and affecting the prepolymer quality and properties.[1]

To recognize the NCO group present in the prepolymer, it was dissolved in a solution of tetrahydrofuran (60%) and n-dibutyl amine (40%), using a blue bromophenol indicator and the mixture was titrated in a 0.1 N hydrochloric acid solution until the blue color turns to yellow.[5] This analysis was performed in the titrator of Metrohm. After the test, the NCO level was measured and calculated using Equation 2.

$$A_{eq} = \frac{10^3}{C}\frac{W}{V_{std} - V} \tag{2}$$

where A_{eq} is the aminic equivalent (dimensionless), W is the weight of the sample in grams, V_{std} and V are the volume obtained in the titrator for the standard and sample, respectively, in millimeter. Finally, C is the concentration of the hydrochloric acid (N).

Using the aminic equivalent was calculated the NCO group present in the prepolymer using the Equation 3.

$$NCO = \frac{4202}{A_{eq}} \tag{3}$$

where NCO is nitrogen, carbon and oxygen present in the prepolymer (%), 4202 is the sum of molecular weight of nitrogen (14.0067 g mol^{-1}), carbon (12.0107 g mol^{-1}) and oxygen (15.9999 g mol^{-1}) multiplied by thousand.

To form a polyurethane part, was necessary to add chain extender to cure the NCO molecules. Figure 1 a) shows the reaction between isocyanate and polyol forming the urethane prepolymer. It is the same of Table 1. Figure 1 b) shows the reaction of curing prepolymer using a chain extender and forming a polyurethane part. For the toluene diisocyanate, the most commonly used chain extender is 4,4'-methylenebis(2-chloroaniline), popularly known as MOCA.

To know the quantity of chain extender used to cure the urethane prepolymer, was necessary to calculate the NCO groups from prepolymer that should react with NH groups from 4,4'-methylenebis(2-chloroaniline) using the Equation 4.

$$X = \frac{NCO}{4202} W_e Sr \tag{4}$$

where X is quantity of chain extender to be add in 100g of urethane prepolymer (g), NCO is nitrogenous, carbon and oxygen present in the prepolymer (%) calculated in the Equation 3, We is chain extender equivalent weight (g eq^{-1}), Sr is the stoichiometric relation (in general used 95% for TDI prepolymers), 4202 is the value of the sum of molecular weight of nitrogenous (14.0067 g mol^{1}), carbon (12.0107 g mol^{-1}) and oxygen (15.9999 g mol^{-1}) multiplied by thousand.

The stoichiometric relation considered in Equation 4 is the percentage of NCO groups reacted with OH or NH groups from diols or amines, respectively. Some researches made by Clemitson (2008) showed that TDI isocyanates based prepolymer have better stoichiometric relation of 95% than 100%, increasing the mechanical properties of final polyurethane[1], that is, 95% of NCO groups from prepolymer would react with OH or NH groups. The Table 2 shows the chain extenders used to cure the prepolymers and to summarize Figure 2 shows the totally of reactions occurred in this research.

The 4,4'-methylenebis(2-chloroaniline) has a melting point of 110 °C.[5] At room temperature this component is solid, so it was necessary to melt using a hot plate. When the chemical achieved the liquid state, it was weighed in the prepolymer using an analytical balance with precision of 0.01 g. The 4,4'-methylenebis(2-chloroaniline) turns liquid physical state for 15 minutes, after that, it is possible to recrystallize. If it occurs 4,4'-methylenebis(2-chloroaniline) should be heated again, but is not recommended due lack of literature information about consequences to material, like loss properties or specifications. The castor oil is liquid at room temperature, even though it was heated until 70 °C. The temperature of prepolymers (TC6, TC3.5, TCP3.5 and STD) were 70 °C, both were heated in the oven. The temperature of 4,4'-methylenebis(2-chloroaniline) liquid

Table 1. Reactions performed using pilot reactor

Reaction Tag	TDI-100 (%)	Castor Oil (%)	PTMEG 2000 (%)	Free NCO Target (%)
TC6	30.54	69.45	0.00	6.00
TC3.5	24.25	75.75	0.00	3.50
TC6*	30.54	69.45	0.00	6.00
TCP3.5	17.36	16.53	66.11	3.50
STD1	14.00	0.00	86.00	3.50

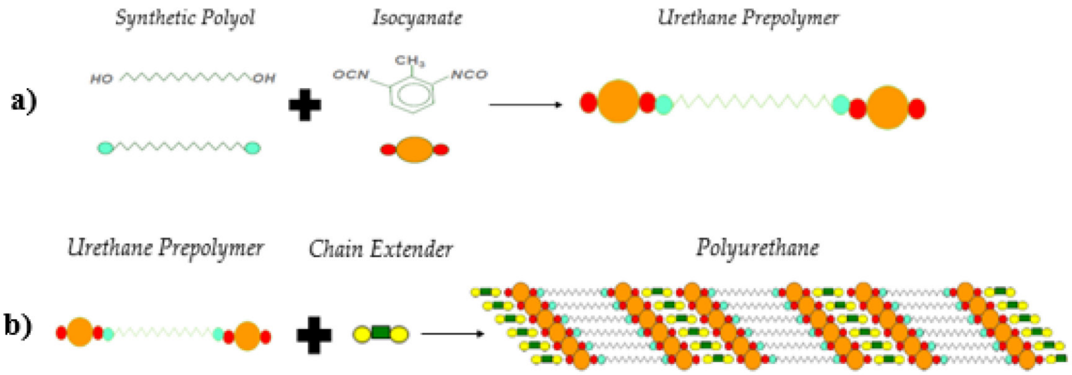

Figure 1. *a) Reaction between isocyanate and polyol forming urethane prepolymer b) Reaction between urethane prepolymer and chain extender forming urethane prepolymer*

Table 2. Chain extenders type and quantity for each reaction

Reaction Tag	Chain Extender	Quantity (g)[a]	Sr (%)[b]
TC6	4,4'-methylenebis(2-chloroaniline)	17.81	95.00
TC3.5	4,4'-methylenebis(2-chloroaniline)	No possible[c]	95.00
TC6*	Castor Oil	45.97	95.00
TCP3.5	4,4'-methylenebis(2-chloroaniline)	10.02	95.00
STD	4,4'-methylenebis(2-chloroaniline)	9.50	95.00

[a]This amount is considering for 100 g of prepolymer. [b]Stoichiometry relation. [c]It was not possible to add chain extender because in this reaction the NCO groups from isocyanate reacted totally with OH groups from castor oil, curing in the pilot reactor.

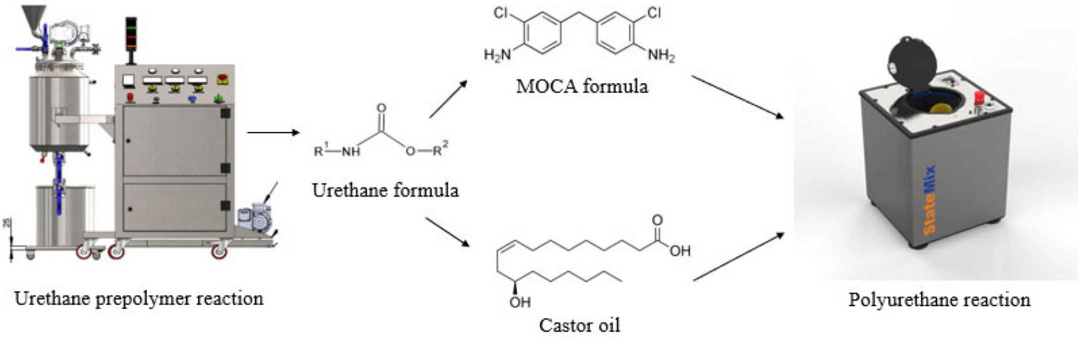

Figure 2. *Sketch of reactions considering urethane prepolymer with MOCA (4,4'-methylenebis(2-chloroaniline) and castor oil*

was around 100 °C to 110 °C. After these steps and immediately the materials were mixture in the vortex mixer VM-200 from StateMix supplier, with 2500 RPM and casted in the aluminum molds, which were in the oven at 70 °C. The materials started the cure some minutes after and stayed in the oven during 24 hours. After this period, it was demolded the specimens and stayed on hold during 7 days to start the mechanical properties tests.

The pot life started when the chain extender was added in the prepolymer. When the polyurethane achieved the pot life time, means it was sticky sufficient and it was not possible to manipulated more and the cure started.[1,4] The Figure 2 shows the sketch of all reactions occurred and the equipment for it.

After 7 days, it was started the mechanical properties tests. The Table 3 shows the tests, standards and equipment.

The Figure 3 shows the measurements of specimens for tensile stress, elongation and tear strength. The tensile stress and elongation must be the same specimen which is (a) and the tear strength is (b). The load cell was 100 kN and was 250 mm min^{-1} of speed. The distance between the claws were 10 mm and all test was made at room temperature.[10]

Table 3. Mechanical properties tests in polyurethanes specimens

Mechanical Tests	Standard	Equipment
Tensile stress	ASTM D-412	Dynamometer from Instron serial 3367
Elongation	ASTM D-412	Dynamometer from Instron serial 3367
Tear Strength	ASTM D-624	Dynamometer from Instron serial 3367
Hardness	ASTM D-2240	Durometer from Zwick & Roll Shore A and D
Rebound Resilience	ASTM D-7121	Resiliometer Schob pendulum from Maqtest
Abrasion Resistance	ASTM D-5963	Abrasimeter from Maqtest

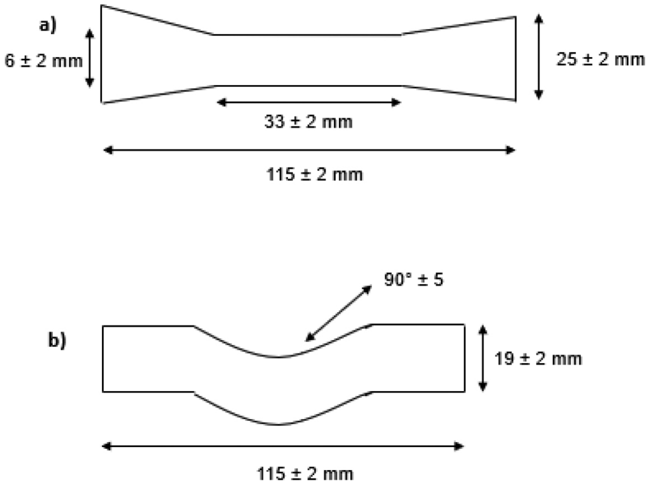

Figure 3. *Measurements of specimens to tensile stress, elongation and tear strength*

Hardness and rebound resilience were same cylindrical specimen with 3.5 cm as longitudinal radius. The abrasion resistance also is cylindrical specimen but 1 cm as longitudinal radius. Both tests performed at room temperature.[10]

Besides of mechanical properties tests, it was performed the Fourier-transform infrared spectroscopy (FTIR) in the spectrophotometer from Thermo Fischer supplier, considering absorbance and ATR (attenuated total reflection) methods. To execute the ATR technique, the polyurethane specimen was supported in the crystal, and through the Nicolet software, the samples were measured. The ATR technique is based on reflections and the sample trajectory depends on the depth of penetration of infrared energy into the sample. In the ATR method, the infrared light energy passes through an optical material (crystal) and through the sample, and with the detector, it is possible to show the wavelengths of the molecules involved in the sample. Each wavelength is characteristic of an organic molecule.[11]

RESULTS AND DISCUSSION

No catalyst was used in the reactions between prepolymers and chain extenders. The isocyanate's reactivity is extremely influenced by positive character of carbon atom between the two π bonds. This is evidenced when observe the isocyanate's resonance, that proves the substitutes bonded in the NCO group influence your reactivity. Aromatic isocyanates are more reactive due aromatic ring in the chemical structure.[4] Another reason that no catalyst was to know the reactivity between the TDI and the components naturally, without any reaction accelerator. Catalysts can be added in future researches focusing to improve the pot life.

All samples made in the pilot reactor were measured the NCO level thought titration analysis described in the methods of this research. The Table 4 shows the NCO results for each sample developed.

The urethane prepolymers reactions occurred using an equivalent index from 1.65 to 2.10.[1] The TC3.5 sample had the relation between NCO:OH equivalent was 1.28, that is, it was a very low index between the two organic components, considering the low NCO level. For this reason, the prepolymer cured within 3 hours directly in the pilot reactor without any chain extender. All NCO present in isocyanate reacted with the OH groups of castor oil. Therefore, it was not possible to cure this prepolymer with the chain extender and did the physical tests.

Table 4. NCO level obtained in the titration analysis

Reaction Sample	Free NCO Level Achieved (%)
TC6	5.90
TC3.5	No possible to measure[a]
TC6*	5.90
TCP3.5	3.32
STD	3.15

[a] It was not possible to measure due in this reaction the NCO groups from isocyanate reacted totally with OH groups from castor oil, curing in the pilot reactor.

The free NCO level achieved were different for free NCO target due to reaction conditions as temperature and pressure, but mostly of the period of reaction. The samples of NCO tests were collected after 3 hours of reaction, but as best practices it was indicated to collect at least 3 samples for each reaction to know the NCO level stabilization. Besides of that, the humidity of raw materials can be affected directly in the prepolymer reaction, decreasing the NCO level achieved and differentiating from free NCO target.

When the prepolymers samples were add in the 4,4'-methylene-bis(2-chloroaniline), it was chronometric the pot life of the reaction between the prepolymer and chain extender. The Table 5 shows the pot life obtained for all samples.

Table 5. Pot life of reaction between prepolymers and chain extenders

Reaction Tag	Pot Life (minutes)
TC6	01:50
TC3.5	No possible to measure[a]
TC6*	15:00
TCP3.5	05:00
STD	15:00

[a] It was not possible to measure because in this reaction the NCO groups from isocyanate reacted totally with OH groups from castor oil, curing in the pilot reactor.

As much shorter was the pot life, more difficult was to cast the materials in the molds. The reaction TC6 was the most difficult to cast in the specimen molds due the short pot life.

It was realized the FTIR characterization of all polyurethane specimens, considering already reacted with chain extenders. Figure 4 shows the consolidation of all graphics in absorbance measurement and ATR method.

Throughout Figure 4 the peaks of these reactions are very similar, proving the possibility to use castor oil as polyol in the urethanes prepolymers formulations.

Figures 5, 6, 7 and 8 below shows the wavenumbers (cm^{-1}) for all samples. It is noted the peaks in 1700 to 1800 cm^{-1} has the ester organic group, originally by castor oil. For STD sample the peak in this wavenumber range is very low, proving the characteristic of this peak for castor oil (ester groups). Other measure to prove is though TC6* sample (Figure 7) used castor oil as polyol and chain extender, which the peak of absorbance is the highest.

Table 6 shows all results obtained for the mechanical properties considering 3 specimens per test and their average. TC3.5 specimens was excluded once it was not possible to complete the prepolymer form in the pilot reactor. For TC6 specimens were not possible to measure the tensile stress, elongation and tear strength, due the high hardness obtained. This high hardness (in Shore D scale) contributed to unless possible to cut the specimens due to the sensitivity of the die cutting.

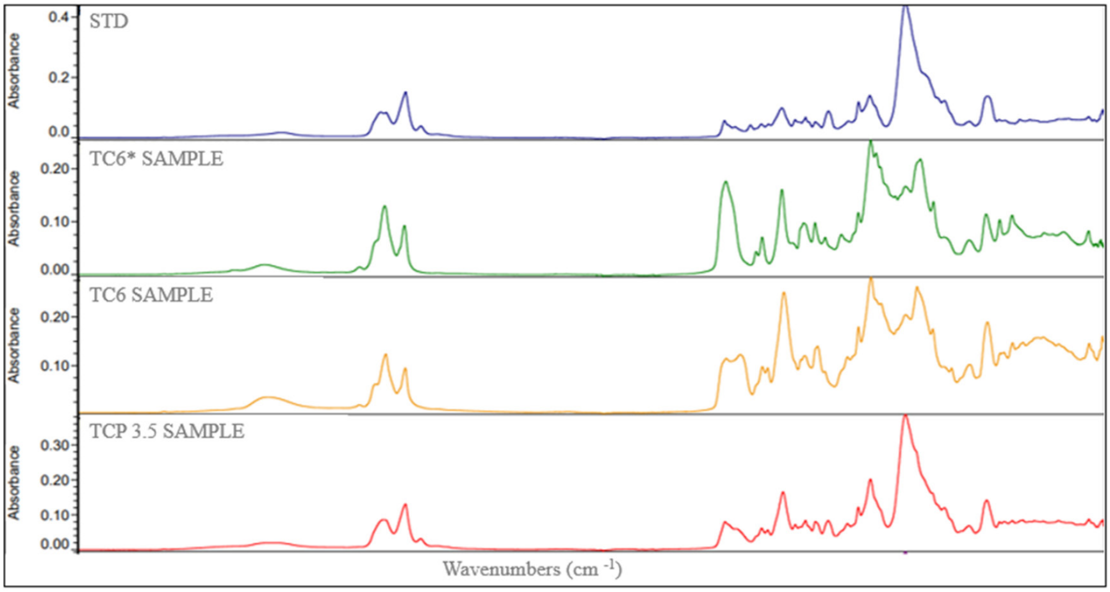

Figure 4. *ATR spectra for STD, TC6**, *TC6 and TCP3.5 samples*

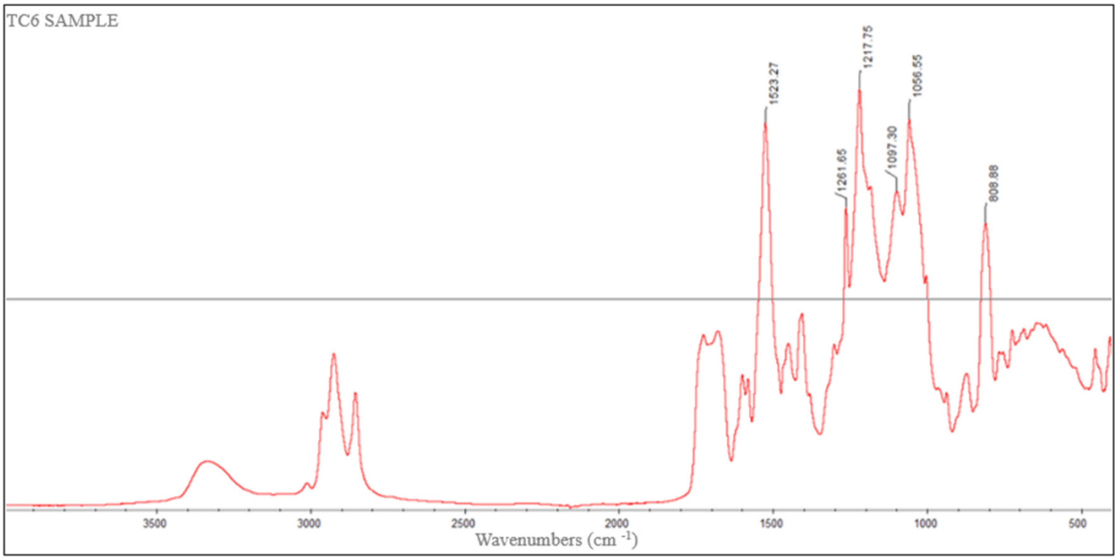

Figure 5. *FTIR graphic from TC6 reaction cured with 4,4'-methylenebis(2-chloroaniline)*

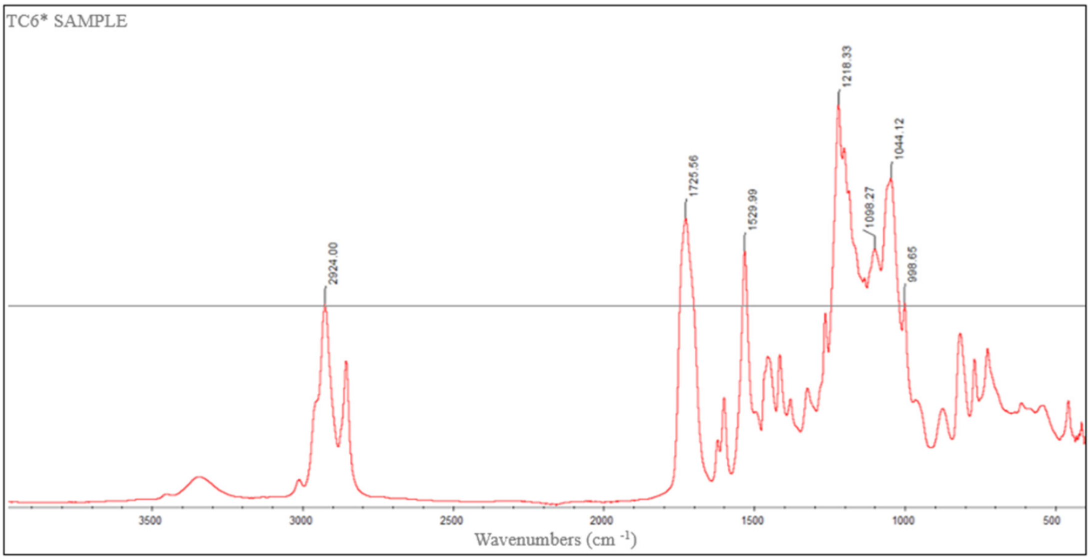

Figure 6. *FTIR graphic from TC6** *reaction cured with castor oil*

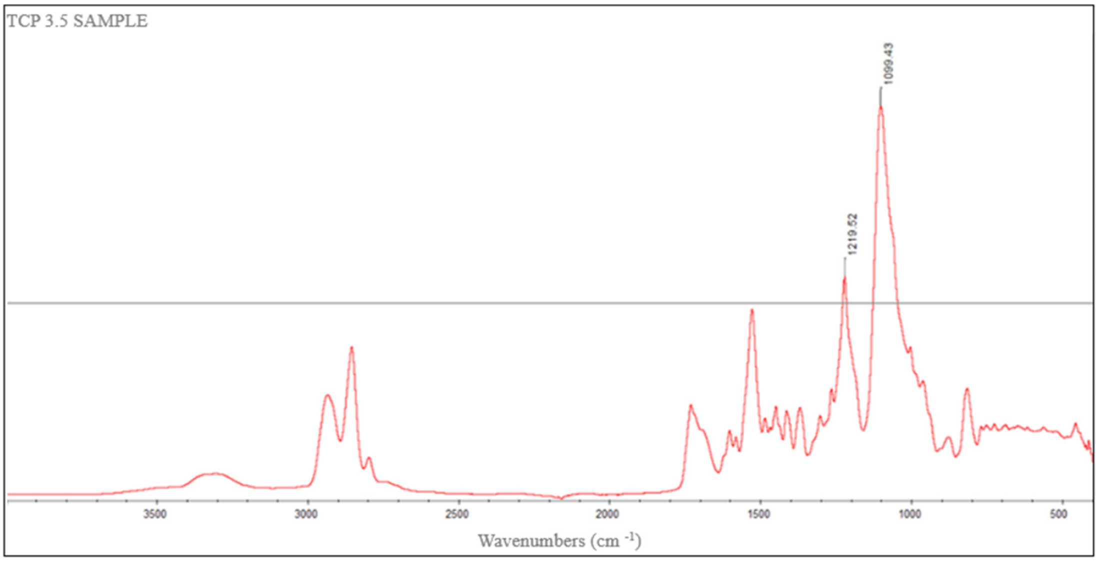

Figure 7. *FTIR graphic from TCP3.5 reaction cured with 4,4'-methylenebis(2-chloroaniline)*

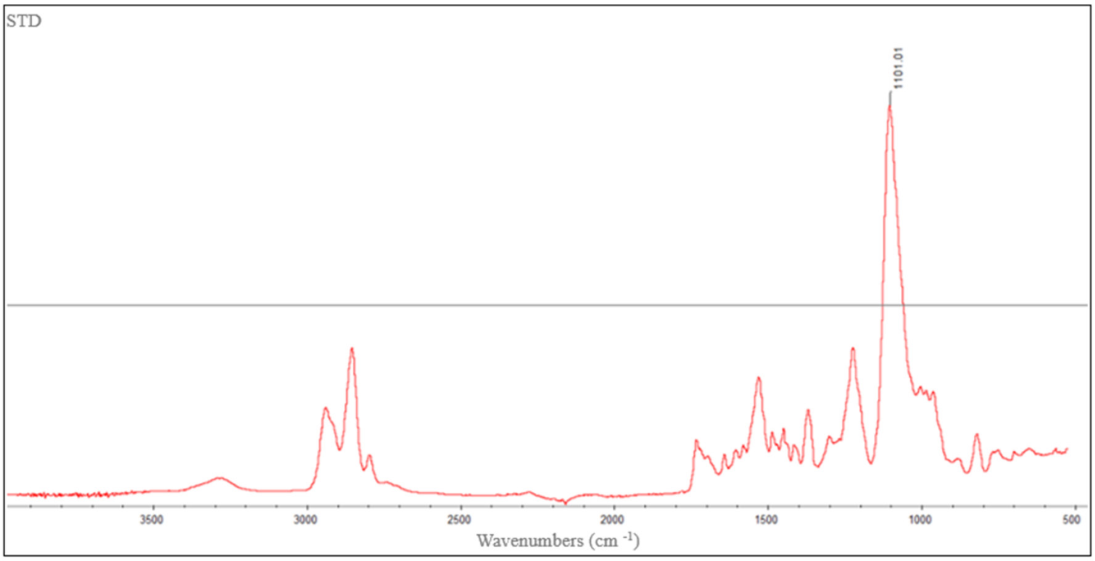

Figure 8. *FTIR graphic from STD reaction cured with 4,4'-methylenebis(2-chloroaniline)*

Through these mechanical tests, it is possible to validate which samples are closer than standard, making possible their replacing. For rebound resilience, the TC6 sample was closest of 55%. The TCP3.5 sample was closer than abrasion resistance, dynamometer tests (tensile stress, elongation and tear strength) and the hardness. There are some differences, mainly for tensile stress, but looking for all samples, the TCP3.5 was the closer than STD sample.

The TC6 sample was not possible to process manually due very short pot life, it is necessary an injector machine. The abrasion resistance did not have good result considering the STD sample. To continue with this sample replacing the synthetic polyol is necessary more researches using some additives to help decrease the value in mm^3 of abrasion resistance, as silicon or plasticizers.

The worst results came from TC6*, which the castor oil was used as polyol and chain extender. These low mechanical properties, mainly for tensile stress, elongation and tear strength shows this chemical material impracticable for polyurethane applications. Moreover, the hardness is very low, proving to be a low performance product. A potential catalyst could be added in the chain extender (castor oil), before to mix with the urethane prepolymer, to decrease the pot life obtained in the Table 5 and to know if it could improve a little bit the mechanical properties.

According with Rocha *et al.,* the MDI (diphenyl methylene diisocyanate) reacted with castor oil had 44 °C as T_g (prepolymer). In their research they reacted it with a propylene glycol ether, which by DMA curves – curve for damping module (E''), the peak was approximately 21 °C. The high T_g result (44 °C) indicated that polymeric chains lost mobility with the addition of castor oil in the prepolymer. Therefore, the researches preferred to produce a copolymer between castor oil and polyol which can provide a better chain mobility to increase the flexible segments.[12]

Castor oil is considered a triol, that is, a component which has three OH groups in the molecule. In general, for urethane prepolymers conventional, the synthetic polyols are considered diols, two OH groups in the molecule, as polytetramethylene ether glycol (PTMEG) or propylene glycol ether (PPG). In terms of crosslinkers density, the diols provide a better chain links to polymer, therefore mechanical properties tend to be better than triols. Even so, need to keep studies about vegetable materials to replace synthetic from petroleum origin.

Table 6. Mechanical properties obtained for each reaction

Reaction Tag	Rebound Resilience, %	Abrasion Resistance, mm3	Tensile Stress, psi	Elongation, %	Tear Strength, kN m-1	Hardness
TC6	50.00	258.00	-	-	-	76 Shore D
	49.00	256.00	-	-	-	
	50.00	257.00	-	-	-	
Σaverage	50.00	257.00	-	-	-	76 Shore D
TC6*	11.50	735.00	181.56	89.08	5.80	55 Shore A
	12.50	730.00	245.50	85.32	5.14	
	12.00	740.00	178.52	70.04	5.41	
Σaverage	12.00	735.70	201.46	81.48	5.45	55 Shore A
TCP3.5	37.00	36.00	475.86	286.14	29.86	65 Shore A
	35.00	37.50	551.41	331.82	31.61	
	35.00	35.16	683.07	358.22	27.11	
Σaverage	35.00	36.22	570.12	325.39	29.53	65 Shore A
STD	54.00	35.00	1967.08	288.21	66.46	85 Shore A
	55.00	38.00	2611.61	366.35	68.82	
	55.00	32.00	2640.69	427.20	69.67	
Σaverage	54.70	35.00	2406.46	360.59	68.32	85 Shore A

CONCLUSIONS

The results show that castor oil can replace the synthetic polyol in the prepolymer polyurethane formulation for cast applications, mainly if is used a blend between the ether and the castor oil in the composition. Fourier-transform infrared spectroscopy (FTIR) method also contributed to this conclusion due the very similar wavenumbers peaks between standard reaction and others, in focus for TCP3.5 sample.

The TCP3.5 reaction presented mechanical properties results closest than standard. There are some differences mainly in rebound resilience and tensile stress. As much lower the resilience rebound, the material is more energy absorber, which can be interesting for some applications as polyurethanes hammers. Regarding the tensile stress, it had an impact in the results, it can be improved changing the ratio in the blend between castor oil and synthetic polyol. Therefore TCP3.5 sample is a potential replacement candidate of vegetable polyol to synthetic polyol and for future studies can be focused on this topic.

REFERENCES

1. Clemitson, I. R.; *Castable polyurethane*, 1st ed., CRC Press: Boca Raton, 2010.
2. Jiang, G. L.; Ren, Z.; Zhao, W.; Liu, W.; Liu, H.; Zhu, C.; *Royal Society Open Science* **2018**, *5*, 4065 [Crossref]
3. Hussain, N. I. A. M.; Bonnia, N. N.; Hirzin, R. S. F. N.; Ali, E. S.; Zawawi, E. Z. E.; *J. Phys.: Conf. Ser.* **2019**, *5-6*, 1349. [Crossref]
4. Zafar, F.; Sharmin, E.; *Polyurethane*; InTech: Rijeka, 2012.
5. Szycher, M.; *Szycher's handbook of polyurethanes*, 2nd ed., CRC Press: Boca Raton, 2012
6. Petrovic, Z. S.; Zhang, W.; Zlatanic, A.; Lava, C. C.; *J. Polym. Environ.* **2002**, *10*, 5. [Crossref]
7. Pfister, D. P.; Xia, Y.; Larock, R. C.; *ChemSusChem* **2011**, *4*, 703. [Crossref]
8. Sonnenschein, M. F.; Koonce, W. A.; *Encyclopedia of Polymer Science and Technology,* 4th ed., **2011**, 26. [Crossref]
9. Cheng, D. and Avtar, S. M. *ACS Sustainable Chemistry & Engineering* **2014**, 2217. [Crossref]
10. American Society for Testing and Materials: "Standard Test Methods for Vulcanized Rubber and Thermoplastics Elastomers – Tension ASTM D 412-98a"; "Standard Test Methods for Tear Strength of Conventional Vulcanized Rubber and Thermoplastics Elastomers ASTM D 624-98"; "Standard Test Methods for Rubber Property – Durometer Hardness ASTM D 2240"; "Standard Test Methods for Rubber Property – Resilience Using Schob Type Rebound Pendulum ASTM D 7121"; "Standard Test Methods for Rubber Property – Abrasion Resistance (Rotary Drum Abrader) ASTM D 5963".
11. Almeida, E. L.; Goulart, G. A. S.; Claro Neto, S.; Chierice, G. O.; Siqueira, A. B.; *Polímeros* **2016**, *26*, 176. [Crossref]
12. Rocha, R. J.; Lima, J. E. S.; Gomes, S. R.; Iha, K.; Rocco, J. A. F. F. *Quim. Nova* **2013**, 793-799. [Crossref]