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## SYNTHESIS AND CHARACTERIZATION OF POLYURETHANE FOAM BASED ON VEGETABLE OIL

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### ABSTRACT

This research shows the production and characterization of the polyurethane foam produced from moringa oil with low energy expenditure. Vegetable oil, polyol and the foam were characterized by hydroxyl, acid and Iodine index, Fourier Transform Infrared Spectroscopy (FTIR), <sup>1</sup>H RMH spectra, Thermo gravimetric analysis (TG), Scanning Electrical Microscopy (SEM), X-Ray Diffractogram (XRD) and Mass Spectroscopy. The physical-chemical results showed the modified oil potential for the polyurethane formation reaction due to the hydroxyl index of 257.52 mg KOH g<sup>-1</sup> and acidity of 2.38 mg KOH g<sup>-1</sup>. FTIR spectra showed the hydroxylation reactions and urethane groups formation in the oil by bands which referring to hydroxyl groups and their NH groups superposition. Foam TG showed a degradation profile between 281 °C and 750 °C, losing half of its mass in temperatures higher than 400 °C. Micrographies showed that foam is composed by opened and closed cells, characteristic of semi-flexibility of the foam.

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## INTRODUCTION

The polyurethanes (PUs) were developed by Otto Bayer in 1937 and it became a material applied in many different industrial areas, with a large applicability in constructions as thermal and acoustic insulator (Członka, Bertino, & Strzelec, 2018). Currently, PUs are the sixth most used polymer in the world, having an annual production of about 16 million tons (Doley & Dolui, 2018). Within this area, flexible foams occupy about 44 % of the world consumption of polyurethanes (Mihail Ionescu, 2005). These foams are formed by the reaction between an isocyanate (di or polyfunctional) and a polyol, besides, it may have some additives such as chain extenders, catalysts, blowing agents, surfactants, fillers or others. The chemical nature and the functions from the reagents must be chosen according to the final properties expected (Akindoyo et al., 2016; Saleh et al., 2019). The synthesis of polyols from renewable sources (biopolyols), represents an alternative to use of mineral sources such as polyols based on polypropylene glycol and polybutadiene (Dhara et al., 2020; Fuensanta & Martin-Martinez, 2019).

Vegetable oils are deeply studied and applied in this process and these materials are composed by fatty acid triglycerides with different structural units and unsaturation proportions (Ghasemlou et al., 2019; Mosiewicki & Aranguren, 2013; Petrovic, 2008). The double bonds act like active sites for reactions that allow their conversion into prepolymers used in production of urethane materials (Zhang, C., Madbouly, S. A., & Kessler, 2015). Moringa *oleifera* Lam. is an example of a plant composed mostly of monounsaturated fatty acids, which can be used in the production of polyols in the polyurethanes area. Its by products, as leaves and seeds, are used like food supplementation and the oil from its seeds – 40 % – is used by pharmacy and cosmetic industries because of its oxidative stability (Viotti et al., 2019). The fatty acids composition in moringa oil ensure that there are some acids such as myristic (0.15 – 0.42 %), palmitic (5.43 – 5.75 %), palmitoleic (1.39 – 1.72 %), stearic (3.95 – 5.40 %), oleic (72.38 – 75.52 %), linoleic (0.61 – 0.69 %), arachidic (2.68 – 3.14 %), gadoleic (2.31 – 3.40 %), bahenium (5.56 – 5.90 %) (Ayerza(h), 2019). The aim of this study was to synthesize and characterize urethane material (foam) through a modification of a

vegetable oil not yet explored in this context. The oil used came from moringa seeds and the methodology applied included the step of modifying the vegetable oil using the in situ peracid hydroxylation, followed by the analysis of polyols and using them as a precursor of polyurethane foams by the one shot methodology. Then, the foam was characterized by thermal, diffraction, microscopic and spectroscopic analysis.

## RESEARCH ELABORATIONS

### MATERIALS

Moringa oil (MO), specifications: iodine value = 133.77 g of I<sub>2</sub>.100 g<sup>-1</sup> of sample, acid value = 0.16 mgKOH.g<sup>-1</sup> of sample) which fatty acids composition is: 0,15 – 0,42 % (C14:0), 5,43 – 5,75 % (C16:0), 1,39 – 1,72 % (C16:1), 3,95 – 5,40 % (C18:0), 72,38 – 75,52 % (C18:1), 0,61 – 0,69 % (C18:2), 2,68 – 3,14 % (C20:1), 2,31 – 3,40 % (C20:2) e 5,56 – 5,90 % (C22:0) [13]. Moringa seeds oil was kindly supplied by Plantus LTDA. During the polyol synthesis formic acid, hydrogen peroxide (35 wt.% aqueous solution), sodium bisulfite and sodium bicarbonate were used. To produce the foams the following materials were used: 4.4-diphenylmethane diisocyanate (MDI) and siloxane surfactant (Polyurethane Industry and Business LTDA, Ibirité – MG, Brazil) and the tertiary amine (Polycat® 41) supplied by Evonik Brasil LTDA, Americana – SP, Brazil.

### METHODS

**Moringa Polyol (MP) Synthesis:** MP was produced from in situ peracid hydroxylation technique applied to Moringa oil (MO), following the 1:3 molar ratio of unsaturation/formic acid, with the addition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in 1:5.5 molar ratio, also related to the amount of unsaturation (Monteavaro, 2005). The mixture was stirred under magnetic agitation (600 rpm) at 60°C for 2 hours. The reactions were stopped with a sodium bisulfite aqueous solution (10 wt.%) to eliminate the hydrogen peroxide excess and with a sodium bicarbonate aqueous solution (15 wt.%) to manage into pH 7 (Veronese *et al.*, 2010).

**Foam production:** The moringa polyurethane foam (MPU) was produced following the One Shot methodology (De Macedo *et al.*, 2017; Zhang *et al.*, 2014)[16,17]. The polyurethanes were formed through the reaction between polyol and diisocyanate (MDI) in a 1.2:1 ratio of NCO/OH and additives such as surfactant and catalysts (siloxane and Polycat 41).

**Physicochemical tests:** The hydroxyl and acid index were made in natura oil and in the polyol according to the ASTM D1957-86 and AOCS Official Method Cd 3a63 (Official Methods and Recommended Practices of the American Oil Chemists' Society, 2004; Standard Test Method for Hydroxyl Value of Fatty Oils and Acids, 2001). Iodine index associated with the unsaturation amount present in the triglyceride was obtained through calculus from integrated areas of Proton Nuclear Magnetic Resonance (NMR <sup>1</sup>H) spectra and performed according to MIYAKE (2001) (Miyake *et al.*, 1998).

**Characterization tests:** The NMR <sup>1</sup>H spectra from oil and polyol samples were obtained in a spectrometer – Varian VNMRs 400 MHz. The samples were dissolved in deuterated chloroform (CDCl<sub>3</sub>) at 25°C. As an intern reference, tetramethylsilane (TMS) was applied. For these analyses a 90° pulse with a repetition time of 5 s, acquisition time of 3.834 s and relaxation time of 1.661 s was used. The thermal analysis was carried out in a Shimadzu DTG-60, between 26 °C and 881 °C, heating rate of 20 °C.min<sup>-1</sup>, with inert atmosphere (N<sub>2</sub>).

SEM analysis of foams were performed in a Vega 3 Scanning Electron Microscope TESCAN A, SE (voltage: 15.00 to 20.0kV).

High angle X-ray diffraction (XDR) used to examine the cells profile of the PU foam was realized in the EDX-720/800HS Energy Dispersive X-Ray Fluorescence Spectrometer, in a range from 5 ° to 60 °; pitch: 0.025 s and angle of incidence: 1°. The diffractograms were obtained with Cu irradiation (k=1.541 Å), 40 kV and 2 mA. Mass spectrometry (MS) analysis was performed in a Solarix T spectrometer (Bruker Daltonics, Bremen, Germany), with gas pressure = 1.5 bar; 16 – 32 lifts; time from 0.600 to 0.850 s; capillary tension = 4.0 – 4.5 Kv and ionic time accumulation from 0.10 to 0.35 s, and the samples were dissolved in 1mL of methanol. The ionization source for an electrospray in positive mode – ESI (+) and a range of m/z (atomic mass and charge ratio) was from 150 to 1500. The Fourier Transform Infrared Spectroscopy (FTIR) analysis of MO and MP were performed by a FTIR System Spectrum GX/Perkin Elmer, range between 4000 – 400 cm<sup>-1</sup>, resolution: 32 cm<sup>-1</sup>. The MPU FTIR analysis was performed in a PRESTIGE 21 IR FTIR (Shimadzu) with Attenuated Total Reflectance (ATR), range between 4000 – 400 cm<sup>-1</sup> and resolution 4 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

The MO modification through hydroxylation led to the formation of three fatty acids, which can be noticed with the increasing in the acid level of the oil to the polyol (0.16 to 2.38 mg KOH.g<sup>-1</sup> of sample, respectively) (Table 1). The increase in acid levels observed in polyol (MP) compared to unmodified oil may be due to the formation of three fatty acids inherent to the polymerization process, due to the temperature of in situ peracid hydroxylation technique in which the oil was submitted; from the possible hydrolysis of vegetable oil or even from the presence of formic acid remaining in the reaction system (Borowicz *et al.*, 2020; Ji *et al.*, 2015; Kurańska *et al.*, 2020). Polyols which acid levels are higher than 5 mg KOH.g<sup>-1</sup> sample cause a delay in the polyurethane reaction, since they can form amide groups together (M Ionescu, 2005). The acid index verified in PM samples is below this value, an indicative factor of the potential to be applied in polyurethane technology.

**Table 1. Results of the physical-chemical and spectra of moringa oil and polyol**

Features	(MO)	(MP)
Acidity Level (AL) (mg KOH.g <sup>-1</sup> sample)	0,16	2,38
Iodine Index (II) (g I <sub>2</sub> .100g <sup>-1</sup> sample)	133,77	19,79
OH Index (OHI) (mg KOH.g <sup>-1</sup> sample)	0,92	257,52

Moringa oil in natura (MO) had a consistent value of hydroxyl according to the reported one in the literature for vegetable oils composed of non-hydroxylated fatty acids (Fernandes *et al.*, 2014; Ourique *et al.*, 2017; Polaczek *et al.*, 2021). The determination of the hydroxyl index showed an increase of 256.6 mg KOH.g<sup>-1</sup> of sample of MO to MP. Polyols with hydroxyl values similar to verified samples of MP were observed in the literature which applied the palm oil epoxidation methodology (Thi *et al.*, 2015). In this case, the oxirane ring was broken using a tetrafluoroboric acid solution as a catalyst, and the hydroxyl index obtained was 223.9 mg KOH.g<sup>-1</sup> (Thi *et al.*, 2015). It's important to note the similarity between the fatty acid composition in palm and moringa oils, predominantly integrated by oleic and palmitic acids with minimal levels of polyunsaturated acids. These indexes, AL and OHI, demonstrate that the *in situ* hydroxylation was effective. Iodine index showed a decrease in the polyol relation to in natura oil, suggesting that there was a break of unsaturation during the hydroxylation reactions (Ghasemlou *et al.*, 2019; Kurańska *et al.*, 2020). The amount of triglyceride double bonds associated with the iodine indexes presented in Table 1 for MO and MP were found according to the math methodology proposed by Miyake (2001) (Miyake *et al.*, 1998) through the curves' integration identified in the RMH <sup>1</sup>H spectra of MO and MP samples (Figures 1 and 3). According to the Miyake (2001) method, the average molecular weights of the samples and its functionalities from moringa's oil and polyol were also determined.

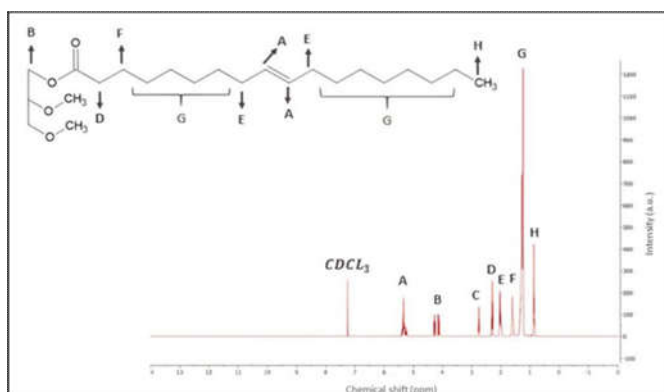
**Table 2. Average molecular weight ( $M_n$ ), hydroxyl index (IOH) e average functionality ( $f_m$ ) from oil and polyol samples**

Sample	$M_n$ ( $g \cdot mol^{-1}$ )	Polyol's IOH ( $mg \text{ KOH} \cdot g^{-1}$ sample)	$f_m$
MO	841,306	0,92	0,01
MP	1079,23	257,52	4,9

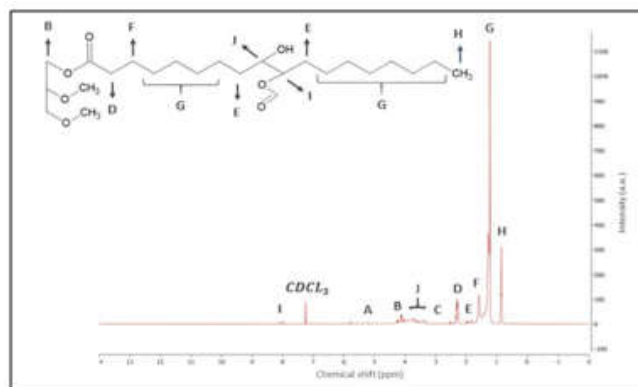
When submitted to the hydroxylation process, the formed polyol showed an increase in its functionality due to the higher values of OH and  $M_n$ , inherent to the polymerization process presented by MP in comparison to MO. NMR  $^1H$  analysis also provided relevant information to the sample's molecular structure, confirming information from physicochemical analysis and later corroborated by the FTIR technique (Ourique *et al.*, 2017). Table 3 shows the most important chemical shifts (ppm) related to the RMH  $^1H$  spectra of MO and MP's samples. Figures 1 and 2 show a relation between moringa oil's RMH  $^1H$  spectra and in natura oleic acid's structure, and between moringa's polyol and hydroxylated oleic acid's structure, respectively, with the proper location and score of chemical shifts mentioned in Table 3.

**Table 3. Chemical shift ranges related to functional groups in triglyceride molecules in the Figures 1 and 2 [28]**

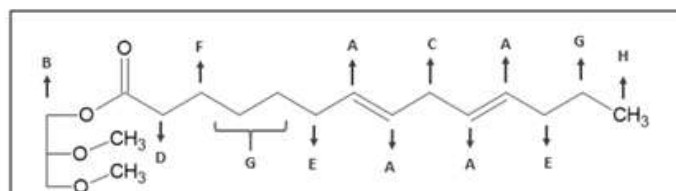
Showed regions	Chemical shifts (ppm)	Functional groups
A	5,30	-CH=CH-
B	4,00 – 4,40	$CH_2OCOR$
C	2,8	=CH- $CH_2$ -CH=
D	2,3	$OCO-CH_2$
E	2,0	$CH_2-CH=CH$
F	1,7	$OCO-CH_2-CH_2$
G	1,3	-( $CH_2$ ) $_n$
H	0,9	- $CH_3$
I	8,01	-CHOO
J	3,6 -3,8	-OH
Solvent	7,35	$CDCl_3$

**Figure 1. Relation between moringa oil's NMR  $^1H$  spectra and in natura oleic acid's structure**

The region in these Figures referenced by letter "C" is not indicated in the schematic representation of oleic acid because it is due to a pertinent structure to polyunsaturated fatty acids present in MO, according to the molecule in Figure 3 (Souza *et al.*, 2012). Therefore, the presence of both structures in the moringa oil analyzed sample is verified. It can be seen from the Figures 1 and 2 that there are the same chemical shifts in moringa's oil and polyol such as the C, D, E, F, G and H regions (Table 3), corresponding to aliphatic hydrocarbons  $CH_2$  and  $CH_3$  (Souza *et al.*, 2012; Thi *et al.*, 2015). On NMR  $^1H$  spectra, in chemical shift between 4.0 – 4.4 ppm there are protons bounded to triglycerides, and between 5.25 – 5.35 ppm there are protons bounded to unsaturated carbons, which intensity decreases in MP in comparison to MO spectrum.

**Figure 2. Relation between moringa oil's polyol NMR  $^1H$  spectra and hydroxylated oleic acid structure**

MP's NMR  $^1H$  spectra (Figure 2) allows the observation of the appearance of characteristic signals of protons bounded to hydroxyl groups around 3.70 ppm and protons bounded to formate groups around 8.01 ppm (Souza *et al.*, 2012). The decreasing of band intensity related to unsaturation in addition to the appearance of OH groups in MP confirms the physicochemical results obtained before.

**Figure 3. Polyunsaturated structure in moringa oil's sample**

The hydroxylated and in natura oleic acid's molecular structure in monomer and dimer forms were confirmed in the MP sample through mass spectrometry analysis (not on). Trimers appeared in a small way in comparison to the other configurations, which is consistent with the proposed polymerization mechanism (Crescentini *et al.*, 2019). The identification of functional groups inherent to the triglyceride molecules in moringa oil and its polyol was made from the evaluation of the MO and MP's FTIR spectra (Figure 4). MO and MP's spectra show characteristic bands of the angular deformation of  $(CH_2)_n$  ( $1457 \text{ cm}^{-1}$  and  $1459 \text{ cm}^{-1}$  respectively) and the symmetrical and asymmetrical stretching of CH bond of the carbonyl (region outlined in the graph –  $2922 \text{ cm}^{-1}$  and  $2855 \text{ cm}^{-1}$ ) (Contreras *et al.*, 2020). There is also the presence of carbonyl's ester groups between  $1700 \text{ cm}^{-1}$  and  $1750 \text{ cm}^{-1}$  and vibrations of the -CO bonds at  $1159 \text{ cm}^{-1}$  (MO) and  $1167 \text{ cm}^{-1}$  (MP), inherent to the triglyceride's molecular structure in natura and modified one (Trovati *et al.*, 2010, 2019). The effectiveness of the in situ peracid hydroxylation reaction which the MO was submitted, was confirmed by the appearance of the -OH group bands at  $3390 \text{ cm}^{-1}$ , associated with the decreasing of the intensity of the double bond band with absorption at  $3009 \text{ cm}^{-1}$  (Contreras *et al.*, 2020; Favero *et al.*, 2019; Kurańska *et al.*, 2020). Figure 5 shows the polyurethane's FTIR spectra, derived from moringa seed oil (MPU). Both bands observed in the spectroscopy at  $2924$  and  $2858 \text{ cm}^{-1}$  were attributed to the symmetrical and asymmetrical stretching of the carbonyl's -CH bond. Other bands at  $1519$ ,  $1305$ ,  $1043$  and  $1205 \text{ cm}^{-1}$  in MPU spectra (Figure 5) represent NH's bending vibration, CN's stretching vibration, CO's stretching and CH's bending, respectively (Contreras *et al.*, 2020). The presence of ester groups between  $1700 \text{ cm}^{-1}$  and  $1750 \text{ cm}^{-1}$  is also checked (Trovati *et al.*, 2010, 2019). The band between  $3200$  and  $3500 \text{ cm}^{-1}$  indicates the superposition of hydroxyls in the polyol by the NH's stretching vibration region, inherent to polyurethane foam. The band at  $2286 \text{ cm}^{-1}$  is attributed to the unreacted isocyanate (Czlonka, Bertino, Košny, *et al.*, 2018). The polyurethane derived from moringa oil (MPU)'s thermogram showed the initial degradation temperature

( $T_{\text{onset}}$ ) at 281 °C, complete degradation at 750 °C, with a mass loss of 50 % at temperatures above 400 °C (Figure 6).

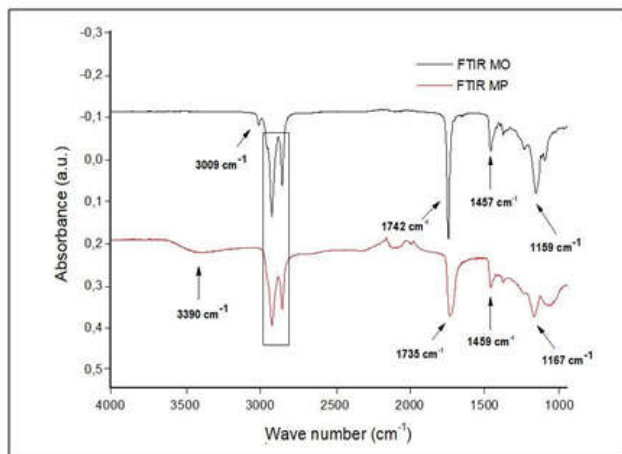


Figure 4. Moringa oil (MO) and moringa's polyol (MP) FTIR spectra

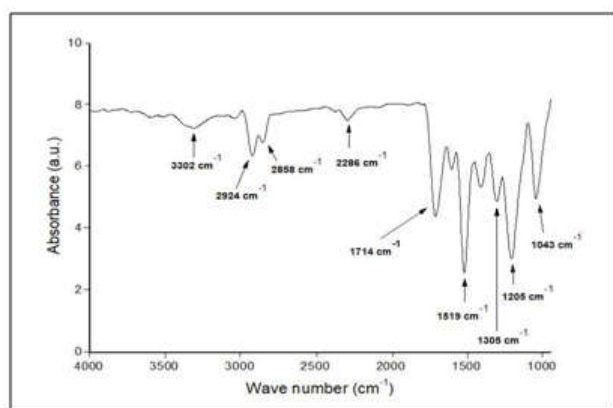


Figure 5. Polyurethane from moringa oil (MPU) FTIR spectra.

The mass loss verified at the temperature range between 50 °C and 192 °C is related to PU dehydration. The event close to 324 °C corresponds to the decomposition of urethane bonds (Marcovich *et al.*, 2017; Trovati *et al.*, 2019) and at 673 °C occurs the emission of decomposition gases (Luiza De Almeida *et al.*, n.d.). In the intermediate range between the last two events (324 °C and 673 °C) the mass loss refers to polyol ester groups' degradation (Prociak *et al.*, 2018).

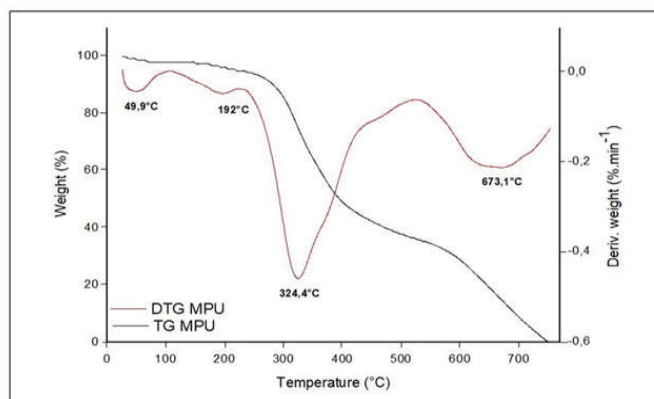


Figure 6. MPU's thermogravimetric analysis

The micrographs in Figure 7, were obtained from the SEM analysis of the MPU samples with an increase of (a) 100x; (b) 500x; (c) 1Kx. From this Figure, its possible to observe small cells which may be

associated to the blowing agents' absence in the foam synthesis (Fawzi *et al.*, 2019). In general, polyurethane foams can have open cells, closed cells or both. The open ones occur when there is communication between the pores, and they usually happen in more flexible foams (M Ionescu, 2005). Closed ones do not communicate with each other and the gas formed for expansion is retained inside, leading to rigid foams, except in some recent works that produced semi-rigid foams with open cells (Członka, Bertino, & Strzelec, 2018; Kurańska *et al.*, 2020). The MPU's micrographs shows open and closed cells, it indicates a semi-flexible profile for the studied foam (Figure 7).

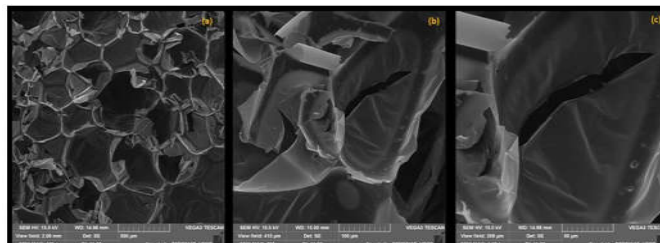


Figure 7. MPU's micrograph using increases of (a) 100x; (b) 500x; (c) 1Kx

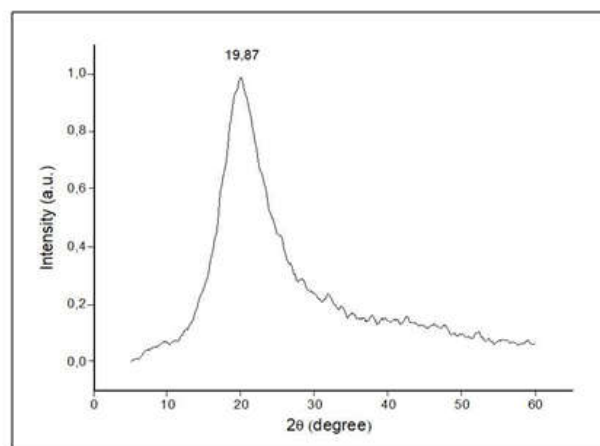


Figure 8. MPU's XRD

The MPU diffractogram shows a broad peak between 11 – 30 ° ( $2\theta$ ) centred at 19.87°  $2\theta$  (Figure 8). The diffractogram presented in this Figure is characteristic of an amorphous material (Ourique *et al.*, 2017). The diffractograms agree with the literature for polyurethanes derived from vegetable oils (Petrovic, 2008; Petrović *et al.*, 2013).

## CONCLUSIONS

This work showed the use of moringa's polyol allows the production of polyurethane foams using a process characterized by a low energy consumption, due to one step methodology applied, under brand reaction conditions. The obtained polyol, as a result of moringa's oil modification presented hydroxyl index of 257.52 mg KOH.g<sup>-1</sup> and acidity of 2.38 mg KOH.g<sup>-1</sup>, suitable parameters for the qualified occurrence of reactions to form urethane products. MPU presented a diffractogram profile consistent to the ones from other vegetable oils' foams. The foam from the polyol studied showed a mass loss about 50 % at temperatures above 400 °C and complete thermal degradation at 750 °C. Its microstructure proved to be composed of open and closed pores. Polyurethane foams from moringa vegetable oil are, therefore, highly thermal and morphologically resistant materials, that can indicate it is a semi-flexible profile.

**Author contributions:** The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Conceptualization, Mariana S.

Gualberto; methodology, Mariana S. Gualberto and Kethory S. B. Rodrigues; formal analysis, Cristiane M. Finzi-Quintão, Mariana S. Gualberto and Kethory S. B. Rodrigues; data curation, Cristiane M. Finzi-Quintão and Mariana S. Gualberto; writing—original draft preparation, Mariana S. Gualberto; writing—review and editing, Eduardo P. Baston, Cristiane M. Finzi-Quintão and Kátia M. Novack. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## REFERENCES

- Akindoyo, J. O., Beg, M. D. H., Ghazali, S., Islam, M. R., Jeyaratnam, N., & Yuvaraj, A. R. (2016). Polyurethane types, synthesis and applications—a review. *RSC Advances*, 6(115), 114453–114482. <https://doi.org/10.1039/c6ra14525f>
- Official methods and recommended practices of the American Oil Chemists' Society, (2004).
- Standard Test Method for Hydroxyl Value of Fatty Oils and Acids, (2001).
- Ayerza(h), R. (2019). Seed characteristics, oil content and fatty acid composition of moringa (*Moringa oleifera* Lam.) seeds from three arid land locations in Ecuador. *Industrial Crops and Products*, 140, 111575. <https://doi.org/10.1016/j.indcrop.2019.111575>
- Borowicz, M., Paciorek-Sadowska, J., & Isbrandt, M. (2020). Synthesis and application of new bio-polyols based on mustard oil for the production of selected polyurethane materials. *Industrial Crops and Products*, 155(May), 112831. <https://doi.org/10.1016/j.indcrop.2020.112831>
- Contreras, J., Valdés, O., Mirabal-Gallardo, Y., de la Torre, A. F., Navarrete, J., Lisperguer, J., Durán-Lara, E. F., Santos, L. S., Nachtigall, F. M., Cabrera-Barjas, G., & Abril, D. (2020). Development of eco-friendly polyurethane foams based on *Lesquerella fendleri* (A. Grey) oil-based polyol. *European Polymer Journal*, 128, 109606. <https://doi.org/10.1016/j.eurpolymj.2020.109606>
- Crescentini, T. M., May, J. C., McLean, J. A., & Hercules, D. M. (2019). Mass spectrometry of polyurethanes. *Polymer*, 181(July), 121624. <https://doi.org/10.1016/j.polymer.2019.121624>
- Czlonka, S., Bertino, M. F., Košny, J., Strąkowska, A., Masłowski, M., & Strzelec, K. (2018). Linseed oil as a natural modifier of rigid polyurethane foams. *Industrial Crops and Products*, 115(January 2018), 40–51. <https://doi.org/10.1016/j.indcrop.2018.02.019>
- Czlonka, S., Bertino, M. F., & Strzelec, K. (2018). Rigid polyurethane foams reinforced with industrial potato protein. *Polymer Testing*, 68. <https://doi.org/10.1016/j.polymertesting.2018.04.006>
- De Macedo, V., Zimmermann, M. V. G., Koester, L. S., Scienza, L. C., & Zattera, A. J. (2017). Flexible polyurethane foams filled with *Pinnus elliotti* cellulose. *Polimeros*, 27, 27–34. <https://doi.org/10.1590/0104-1428.2212>
- Dhara, M., Giri, N., Narasimha Rao, B., Patra, A. K., Sastry, P. U., Ingole, M. S., & Jana, T. (2020). Effect of segmental compatibility imposed over metal based polybutadiene polyurethane. *European Polymer Journal*, 122(October 2019), 109380. <https://doi.org/10.1016/j.eurpolymj.2019.109380>
- Doley, S., & Dolui, S. K. (2018). Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties. *European Polymer Journal*, 102, 161–168. <https://doi.org/10.1016/j.eurpolymj.2018.03.030>
- Favero, D., Marcon, V. R. R., Barcellos, T., Gómez, C. M., Sanchis, M. J., Carsi, M., Figueroa, C. A., & Bianchi, O. (2019). Renewable polyol obtained by microwave-assisted alcoholysis of epoxidized soybean oil: Preparation, thermal properties and relaxation process. *Journal of Molecular Liquids*, 285, 136–145. <https://doi.org/10.1016/j.molliq.2019.04.078>
- Fawzi, T., Yu, L. J., Badri, K. H., Sajuri, Z., Al-Talib, A. A. M., & Eh Noum, S. Y. (2019). Sodium hydrogen bicarbonate and water as blowing agent in palm kernel oil based polyol polyurethane foam. *Materials Today: Proceedings*, 39(xxxx), 993–998. <https://doi.org/10.1016/j.matpr.2020.04.595>
- Fernandes, E., Vicente, J., Cruz, R., Nele, M., Nunes, É., & Costa-Félix, R. (2014). A methodology free of pyridine for measuring hydroxyl value in polymers and oils. *Polymer Testing*, 33, 16–20. <https://doi.org/10.1016/j.polymertesting.2013.10.015>
- Fuensanta, M., & Martin-Martinez, J. M. (2019). Thermoplastic polyurethane pressure sensitive adhesives made with mixtures of polypropylene glycols of different molecular weights. *International Journal of Adhesion and Adhesives*, 88, 81–90. <https://doi.org/10.1016/j.ijadhadh.2018.11.002>
- Ghasemlou, M., Daver, F., Ivanova, E. P., & Adhikari, B. (2019). Polyurethanes from seed oil-based polyols: A review of synthesis, mechanical and thermal properties. *Industrial Crops and Products*, 142, 111841. <https://doi.org/10.1016/j.indcrop.2019.111841>
- Ionescu, M. (2005). *Chemistry and Technology of Polyols for Polyurethanes*. Rapra Technology. <https://books.google.com.br/books?id=TnUGLC604XgC>
- Ionescu, Mihail. (2005). *Chemistry and Technology of Polyols for Polyurethanes*.
- Ji, D., Fang, Z., He, W., Luo, Z., Jiang, X., Wang, T., & Guo, K. (2015). Polyurethane rigid foams formed from different soy-based polyols by the ring opening of epoxidised soybean oil with methanol, phenol, and cyclohexanol. *Industrial Crops and Products*, 74, 76–82. <https://doi.org/10.1016/j.indcrop.2015.04.041>
- Kurańska, M., Polaczek, K., Auguścik-Królikowska, M., Prociak, A., & Ryszkowska, J. (2020). Open-cell rigid polyurethane bio-foams based on modified used cooking oil. *Polymer*, 190(January), 1–7. <https://doi.org/10.1016/j.polymer.2020.122164>
- Luiza De Almeida, E., Alexandre, G., Goulart, S., Neto, S. C., Chierice, G. O., & Buzutti De Siqueira, A. (n.d.). *Preparação e caracterização de poliuretanos contendo diferentes quantidades de óleo de baru Preparation and characterization of polyurethane with different quantities of baru oil*. <https://doi.org/10.1590/0104-1428.2151>
- Marcovich, N. E., Kurańska, M., Prociak, A., Malewska, E., & Kulpa, K. (2017). Open cell semi-rigid polyurethane foams synthesized using palm oil-based bio-polyol. *Industrial Crops and Products*, 102, 88–96. <https://doi.org/10.1016/j.indcrop.2017.03.025>
- Miyake, Y., Yokomizo, K., & Matsuzaki, N. (1998). Rapid determination of iodine value by <sup>1</sup>H nuclear magnetic resonance spectroscopy. *JAOCs, Journal of the American Oil Chemists' Society*, 75(1), 15–19. <https://doi.org/10.1007/s11746-998-0003-1>
- Monteavaro, L. L. (2005). *Poliuretanos a partir de polióis de óleo de soja. 91f. Tese de Doutorado. Universidade Federal do Rio Grande do Sul*. 91.
- Mosiewicki, M. A., & Aranguren, M. I. (2013). A short review on novel biocomposites based on plant oil precursors. *European Polymer Journal*, 49(6), 1243–1256. <https://doi.org/10.1016/j.eurpolymj.2013.02.034>
- Ourique, P. A., Krindges, I., Aguzzoli, C., Figueroa, C. A., Amalvy, J., Wanke, C. H., & Bianchi, O. (2017). Synthesis, properties, and applications of hybrid polyurethane–urea obtained from air-oxidized soybean oil. *Progress in Organic Coatings*, 108, 15–24. <https://doi.org/10.1016/j.porgcoat.2017.04.002>

- Petrovic, Z. S. (2008). Polyurethanes from vegetable oils. *Polymer Reviews*, 48(1), 109–155. <https://doi.org/10.1080/15583720701834224>
- Petrović, Z. S., Hong, D., Javni, I., Erina, N., Zhang, F., & Ilavský, J. (2013). Phase structure in segmented polyurethanes having fatty acid-based soft segments. *Polymer*, 54(1), 372–380. <https://doi.org/10.1016/j.polymer.2012.10.019>
- Polaczek, K., Kurańska, M., Auguścik-Królikowska, M., Prociak, A., & Ryszkowska, J. (2021). Open-cell polyurethane foams of very low density modified with various palm oil-based bio-polyols in accordance with cleaner production. *Journal of Cleaner Production*, 290. <https://doi.org/10.1016/j.jclepro.2021.125875>
- Prociak, A., Malewska, E., Kurańska, M., Bąk, S., & Budny, P. (2018). Flexible polyurethane foams synthesized with palm oil-based bio-polyols obtained with the use of different oxirane ring opener. *Industrial Crops and Products*, 115. <https://doi.org/10.1016/j.indcrop.2018.02.008>
- Saleh, S., Yunus, N. Z. M., Ahmad, K., & Ali, N. (2019). Improving the strength of weak soil using polyurethane grouts: A review. *Construction and Building Materials*, 202, 738–752. <https://doi.org/10.1016/j.conbuildmat.2019.01.048>
- Souza, V. H. R. De, Silva, S. A., Ramos, L. P., & Zawadzki, S. F. (2012). Synthesis and characterization of polyols derived from corn oil by epoxidation and ozonolysis. *JAACS, Journal of the American Oil Chemists' Society*, 89(9), 1723–1731. <https://doi.org/10.1007/s11746-012-2063-5>
- Thi, T., Hoang, K., & Kim, I. (2015). Epoxidation and Ring-Opening of Palm Oil to Produce High-Functionality Polyols. *Australian Journal of Basic and Applied Sciences*, 9(8), 89–93.
- Trovati, G., Natali Suman, M. V., Sanches, E. A., Campelo, P. H., Neto, R. B., Neto, S. C., & Trovati, L. R. (2019). Production and characterization of polyurethane castor oil (*Ricinus communis*) foam for nautical fender. *Polymer Testing*, 73(July 2018), 87–93. <https://doi.org/10.1016/j.polymertesting.2018.11.010>
- Trovati, G., Sanches, E. A., Neto, S. C., Mascarenhas, Y. P., & Chierice, G. O. (2010). Characterization of polyurethane resins by FTIR, TGA, and XRD. *Journal of Applied Polymer Science*, 115(1), 263–268. <https://doi.org/10.1002/app.31096>
- Veronese, V., Menger, R. K., C., F. M. M. de, & Petzhold, C. L. (2010). Rigid Polyurethane Foam Based on Modified Vegetable Oil. *Journal of Applied Polymer Science*, 120(5), 530–537. <https://doi.org/10.1002/app.33185>
- Viotti, P. V., Moreira, W. M., Santos, O. A. A. dos, Bergamasco, R., Vieira, A. M. S., & Vieira, M. F. (2019). Diclofenac removal from water by adsorption on *Moringa oleifera* pods and activated carbon: Mechanism, kinetic and equilibrium study. *Journal of Cleaner Production*, 219, 809–817. <https://doi.org/10.1016/j.jclepro.2019.02.129>
- Zhang, C., Madbouly, S. A., & Kessler, M. R. (2015). *Biobased Polyurethanes Prepared from Different Vegetable Oils*.
- Zhang, L., Zhang, M., Hu, L., & Zhou, Y. (2014). Synthesis of rigid polyurethane foams with castor oil-based flame retardant polyols. *Industrial Crops and Products*, 52, 380–388. <https://doi.org/10.1016/j.indcrop.2013.10.043>

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