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Spectroscopic characterization and thermal behavior of baru nut and macaw palm vegetable oils and their epoxidized derivatives

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Abstract

The ability to produce new and renewable, epoxidized Brazilian vegetable oils from baru nut (*Dipteryx alata Vogel*) and macaw palm (*Acrocomia aculeata)* oil*,* using a fast and clean heterogeneous catalytic method, was investigated. The Wijs method and Proton Nuclear Magnetic Resonance (^{1}H-NMR) analysis were utilized, and compared to one another, to calculate the iodine value (IV), average number of double bonds (DB_{average}) and fatty acid content, and thus degree of epoxidation, for both vegetable oils. This analysis indicated that alkene conversions of 100 and 95.3% were obtained for baru nut oil and macaw palm oil, respectively; which is an excellent result when compared with some works in literature. The epoxidized Baru nut oil is a solid at room temperature, which was related to the percentage of mono-unsaturated fatty acids present in its structure. Epoxide samples were also analyzed via mid-Infrared Spectroscopy and ^{13}C NMR analysis. Thermogravimetry-differential thermal analysis (TG-DTA) was used to determine the thermal stability of these epoxidized oils. Differential Scanning Calorimetry (DSC) also provided information about their crystallization, melting and solid-solid transition processes.

Keywords: Epoxidation; thermal properties; solid epoxy oil; fatty acid content; renewable monomers; mid-infrared spectroscopy

1. Introduction

Epoxides are currently used worldwide in resins used in paints, adhesives and coatings (Elmore *et al.,* 2002). They are also often used in polymerizations, by catalytically promoting cleavage of the epoxide ring at high temperatures. The most frequently used polymerization method is to first create a binary mixture, where the epoxides are blended with polyamines, polyalcohols or polyacids/anhydrides, and are then heated at high temperatures, or left for a long time at room temperatures, to give the final polymer (Mohan, 2013; Wurm *et al.*, 2008; Ding *et al.*, 2015). Furthermore, some authors have investigated the use of dyes, and ultraviolet or visible light, in order to catalyze epoxide polymerization. These processes commonly trigger the polymerization of acrylate/methacrylate compounds; but often require onium salts to form the desired product (Decker *et al.*, 2001; Branciforti *et al.*, 2019).

Although the use of epoxy resins has been improving, most binary mixtures are limited to using bisphenol A diglycidyl ether (BADGE or DGEBA). However, DGEBA is a petrochemically derived monomer and is therefore not considered a green or renewable compound. Some studies have also raised concerns about its toxic effect on human health and wildlife such as endocrine disruption and reproductive disorders (Vandenberg *et al.*, 2009; Maffini *et al.*, 2006; Flint *et al.*, 2012). Thus, to avoid the use of DGEBA, some authors have reported the synthesis of epoxides using more renewable monomers, such as cinnamic acid (Xin *et al.*, 2014), resveratrol (Tian *et al.*, 2020), syringaresinol (Janvier *et al.*, 2017), eugenol (Santiago *et al.*, 2020), vanillin (Fache *et al.*, 2015), quercetin (Kristufek *et al.*, 2016), furan (Hu *et al.*, 2015) and vegetable oils (Kumar *et al.*, 2017).

Vegetable oils are one of the most attractive alternative and renewable compounds compared to other materials used in epoxide polymerization studies. The natural epoxide-containing vegetable oil (vernolic acid) was first investigated in 1986.

However, due to its expense, its use has since declined (Perude *et al.*, 1986; Samuelsson *et al.*, 2004; Thompson *et al.*, 1994). More recently, research using epoxidized soybean and linseed oil has gained more attention, as these materials have multiple unsaturated fatty acid chains and thus produce monomers containing multiple epoxides which have high viscosity (Panchal *et al.*, 2017). Consequently, these two vegetable oils have been researched extensively in the literature. However, there is still a need to find more renewable and green oils to use to prepare epoxides, in order to alleviate the demand for soybean and linseed oil. Research into using new and alternative unsaturated vegetable oils is therefore of high importance. Moreover, increasing the percentage of unsaturation, and using different fatty acids in the triglyceride composition, can provide epoxidized vegetable oils that can be used in lubricants (Adhvaryu and Erhan, 2002; Campanella *et al.*, 2010).

As a result, vegetable oil from baru nut (*Dipteryx alata Vogel*) and macaw palm (*Acrocomia aculeata)* were selected and analysed in this study. Baru and macaw are drupes grown on trees and palms, respectively, in the Cerrado region of Brazil; the baru nut is normally cropped in little communities which is incentive by Brazil's Government to improve the use of renewable resources from Cerrado; in addition the baru tree is very productive and about 100 baru trees can produce 19.4 ton of nuts and only one Brazil state can produce about 20,000 ton of nuts, as consequence 8,000 ton of vegetable oil (Batista and Sousa, 2019; Sano *et al.*, 2004). The macaw palm fruit contains a high quantity of vegetable oil, which produces 4,000 L of oil per hectare, much higher than the soybean which produces only 500 L per hectare (Oliveira, 2016; Pires *et al.*, 2013); Brazil's government has been encouraging its crop to biodiesel production and as a renewable resource (Grupioni *et al.*, 2020). Furthermore, these vegetable oils can be also consumed by humans and animals and are often used in healthcare products (Bravo *et al.*, 2020; Moraes *et al.*, 2018). Baru oil (BO) can be used as an antioxidant, a hepatoprotective agent and as a lubricant (Albs and Betruger, 2019; Reis *et al.*, 2018). The baru vegetable oil has about 78.5% of unsaturation, provided by 47.2% of oleic acid (C18:1), 28.2% of linoleic acid (C18:2), 0.1% of linolenic acid (C18:3), 2.7% of eicosenoic acid (C20:1) and 0.3% of erusic acid (C22:1). In addition, the baru vegetable oil has palmitic acid (C16:0) and stearic (C18:0) acid as saturated fatty acids in its structure (Oliveira-Alves *et al.*, 2020). The macaw oil (MO) contains about 81.7% of unsaturation, with 74.2% of oleic acid, 4.8% of linoleic acid and 2.7% of linolenic acid (Ribeiro *et al.*, 2017). These percentages of saturation and unsaturation can vary, depending on the extraction process employed to obtain these oils (Coimbra and Jorge, 2011).

The epoxidation of baru or macaw vegetable oils have never been fully investigated. Research has been published describing the modification of baru oil by ozonolysis and polyurethane production, and it has been used to make biodiesel (Kogawa *et al.*, 2012; Almeida *et al.*, 2016; Batista *et al.*, 2012). Macaw oil has also been widely used in biodiesel production (Ribeiro *et al.*, 2017; da Conceição *et al.*, 2019; Silva *et al.*, 2014; Ramos *et al.*, 2016) and in starch-based thermoplastics (Schlemmer *et al.*, 2010). In this work, we therefore decided to investigate the possibility of epoxidizing both baru nut and macaw palm vegetable oil.

Epoxidized oils often show different properties, in particular thermal properties, compared to non-modified vegetable oils. The starting oils also greatly affect the properties of the final products, as no two epoxidized oils show the same properties. Techniques such as thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC) are therefore fundamental to elucidating and comparing the thermal behaviors of the initial oil and final epoxidized products. DSC is an extremely important technique that provides useful information about melting and crystallization temperatures, glass transitions and solid-solid transitions. Furthermore, mid-infrared spectroscopy (MIR) and nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) are extremely useful techniques to study structural modifications and the conversion of alkenes (C=C) into epoxide rings. The epoxidized materials produced in this report are therefore studied by these techniques, in order to analyze their thermal properties and, most importantly, to understand the appropriate storage conditions required to transport these materials. This will, in particular, reduce problems that are often encountered in scale up, when these materials are used in industrial production lines.

2. Materials and Methods

Baru nut oil (batch code: BA006/19, leaking data: 06/2019) and macaw palm oil (batch code: MAO073/18; leaking data: 03/2019) were purchased from Mundo dos óleos (Brasília - DF, 70673-642, Brazil); in addition, soybean oil (SO, Liza® batch code: L08P) was purchased in a local market and epoxidized soybean oil with 6.8 wt% of epoxy (SO-E, Drapex 6.8, batch code: 610601; leaking data: 07/10/2019) was kindly provided by INBRA Chemical industry Ltd. (Diadema-SP, 09950-300, Brazil), both were used as a control in DSC experiment. Wijs solution (iodine monochloride in glacial acetic acid, 0.1 mol L^{-1}) was purchased from Dinâmica Química Contemporânea Ltd. (Indaiatuba-SP, 13347-060, Brazil). Hydrogen peroxide (30% H_2O_2), Amberlite IR120, glacial acetic acid (≥99%), perchloric acid (70%), sodium carbonate, tetraethylammonium bromide (TEAB; 99%) were purchased from Sigma-Aldrich and used without further purification.

2.1. Epoxidation of baru and macaw palm vegetable oil

The synthetic route employed followed the literature procedure reported by Park *et al.* in 2004. Firstly, 100.0 g of baru nut vegetable oil, 25.0 g of glacial acetic acid and 25.0 g of Amberlite IR120 (catalyst) were settled into a round bottomed flask with a magnetic bar, and then stirred for 30 minutes at 60 ºC use a magnetic stirrer-hotplate with aluminum base insulation. Afterwards, 79.0 g of hydrogen peroxide (30%) was added dropwise (1 mL min^{-1}). Thereafter, the reaction was kept at 60 ºC for 6 hours with a reflux apparatus. After 6 hours, the crude product was filtered (recovering the catalyst) and then extracted with 50 mL of ethyl acetate. The organic layer was then washed with 30.0 mL of sodium carbonate solution (0.1 mol L^{-1}) three times, until the water layer reached a neutral pH of 7.0 using a universal pH paper. The organic layer was then concentrated *in vacuo* to afford the final product (102.0 g) as a colorless liquid, which solidifies at room temperature to give a white, greasy compound.

The same procedure was employed in the epoxidation of 100.0 g of macaw palm oil, to afford the final product as a light-yellow liquid at room temperature (99.0 g).

2.2 Iodine Value and Epoxide content

The iodine value (IV) was calculated using the Wijs method, a titration process which measures the average quantity of alkenes (C=C), and thus the degree of unsaturation, in triglyceride or vegetable oil samples. This method works by saturating all of the double bonds in the compound with iodine, using iodine chloride, and then measuring the total iodine consumed by titrating with sodium thiosulfate solution (0.1 mol L^{-1}). The IV determined via this method is defined as grams of iodine (I_2) absorbed by 100 g of vegetable oil. For this procedure, a standard method (ASTM D5554-15; ASTM, 2015) was followed and used to study the baru vegetable oil (BO) and macaw vegetable oil (MO).

The epoxide content in the both epoxidized vegetable oils (BO-E and MO-E) were determined following a standard titration method for epoxide content of epoxy resins (ASTM D1652-11; ASTM, 2019). This method describes the reaction between TEAB and perchloric acid ($HClO_4$), resulting in hydrogen bromide (HBr) formation *in situ*. Consequently, the HBr reacts 1:1 with the epoxide ring, forming a bromo alcohol. Thereafter, the acidic solution is titrated against potassium hydrogen phthalate (0.1 mol L^{-1}) to determine the residual amount of HBr left in the solution. It is then possible to calculate the epoxide content. The method uses a blank to compare the results with, as a solution but with no sample present is titrated under the same conditions.

2.3 Mid-Infrared Spectroscopy (MIR)

Infrared spectra were obtained using a Bruker Vertex 70 FT-IR spectrometer, with a resolution of 4 cm^{-1} in the region of 4000-400 cm^{-1}. This spectrometer uses a Fourier transform spectrophotometer, with attenuated total reflectance (ATR) using a diamond crystal.

2.4. ^{1}H-NMR and ^{13}C-NMR analyses

To determine the principal signal of BO, MO, BO-E and MO-E, as well as to quantify alkene conversion, ^{1}H-NMR and ^{13}C-NMR analysis were performed, using a Jeol 400 MHz spectrometer. Samples were solubilized in deuterated chloroform ($CDCl_3$, 99.8% D, Sigma-Aldrich).

In addition, the average number of alkene double bonds ($DB_{average}$) in a triglyceride molecule was calculated using the ^{1}H-NMR spectrum and Eq. 1 (Nicolau *et al.*, 2012).

$$DB_{average} = K/_{2Nf} \qquad (1)$$

K is the integration area of the vinyl hydrogens at 5.3 ppm. The *Nf* value is the area of the double quartet, associated with the four methylene hydrogens of the glycerol backbone at 4.1 ppm and 4.2 ppm, divided by the number of related hydrogens. To integrate these areas correctly, it was necessary to relate these environments to a normalized area such as the methylene hydrogens of the α-carbonyl in the acyl chain at 2.3 ppm (six hydrogens).

The IV can be also calculated via ^{1}H-NMR analysis, using the integrations of the vinyl hydrogens (*K*) and Eq. 2 (Guillén and Ruiz, 2003).

$$IV = 12691 * K/(120 + 701.3 + 6.006 * K) \qquad (2)$$

Furthermore, the percentage of each fatty acid (saturated, oleic, linoleic and linolenic acids) in both vegetable oils were calculated by ^{1}H-NMR spectroscopy following the literature (Guillén and Ruiz, 2003).

2.5 Simultaneous Thermogravimetry-Differential Thermal Analysis (TG-DTA) and Differential Scanning Calorimetry (DSC)

Simultaneous TG-DTA curves were obtained using a Netzsch thermal analysis system, model STA 449 F3. Approximately 40 mg of sample was placed in a 200-µL α-alumina open crucible. The samples were then heated from 30.0 ºC to 800.0 ºC, at a heating rate of 10.0 ºC min^{-1}, whilst a dry air atmosphere, at a flow rate of 50 mL min^{-1}, was flowed through the system. To better visualize the thermal transitions measured, DTG (Derivative Thermogravimetry) analysis of the TG curves was performed. The obtained curves are shown together with the TG-DTA curves.

DSC analysis and images were obtained on a Mettler-Toledo DCS machine, model DSC 1 Star^e System, in conjunction with a SC30 digital camera with 3.3

megapixels and 6.5x magnification. Approximately 10 mg of sample were placed in a 40 μL closed aluminium crucible with a perforated lid. The samples were heated from -35.0 ºC to 120.0 ºC at 10 ºC min^{-1}, whilst under a flow rate of 50 mL min^{-1} of dry air. When images were taken during the DSC analysis, the same experimental conditions were used, except the analysis was performed in a 40 μL open alumina crucible. Another DSC analysis was performed following the same experimental conditions except using an atmosphere of N_2 (99.9%). This analysis was carried out to understand better the thermal behavior of BO-E.

3 Results and Discussion

3.1 Iodine Value and epoxide content

Baru vegetable oil (BO) is a liquid at room temperature (25.0 ºC) and has a yellowish golden colour (Fig. 1-a), with an IV of 103.5±0.9 grams of I_2 per 100 g of vegetable oil. After epoxidation, the formed product (BO-E) did not record an iodine value, indicating a conversion of all, or the majority, of alkenes into epoxide rings. In addition, BO-E turned into a white greasy solid compound (Fig. 1-b) at room temperature. This solidification occurs due to the presence of epoxide ring hydrogen bonds and molecular conformation, which restrict the mobility of the fatty acid chain. Similar findings have been presented in the literature for 100% epoxidized soybean and linseed vegetable oils. These oils were found to be a semi-solid with high viscosity at 10.0 ºC (Muturi *et al.*, 1994). In comparison, BO-E is a solid at room temperature, melts above 40.0 ºC and forms a colourless liquid (Fig.1-c). The epoxide content for BO-E was equal to 5.98±0.03 wt% of oxygen. In other words, BO-E has 5.98 g of epoxy oxygen atoms per 100 g of epoxidized oil. Dividing this value by 16 (the atomic mass of oxygen) makes it possible to obtain the molar quantity of oxygen as 0.37375 mol (Kousaalya *et al.*, 2018), which is an important parameter to know in polymer chemistry. Different quantities of epoxide can provide different physical properties in the final polymer. Normally, commercial epoxidized soybean and linseed oils have a value equal to 6.8 wt% of oxygen (0.42500 mol) and 8.9 wt% of oxygen (0.55625 mol), respectively (Bähr and Mülhaupt, 2012).

The macaw vegetable oil (MO) has an orange-reddish colour and is liquid at room temperature (Fig. 1-d), possessing an IV of 116.0±0.6 grams of I_2 per 100 g of vegetable oil. After epoxidation, MO turned into a slightly yellow colour compound (MO-E) with an iodine value of 14.7±1.73 g of I_2 per 100 g of vegetable oil, which indicates the presence of residual alkenes. Unlike BO-E, the MO-E sample is not a solid at room temperature. The oxygen epoxide content in the MO-E is equal to 5.39±0.07 wt% and thus has 5.39 g of epoxide oxygen atoms per 100 g of epoxidized oil (and 0.33687 mol of oxygen).

<Figure 1>

3.2 Mid-Infrared Spectroscopy (MIR) and ^{1}H-NMR and ^{13}C-NMR analysis

Mid-Infrared (MIR) spectra for BO and BO-E are illustrated in Fig. 2. The region between 2000 cm^{-1} and 2700 cm^{-1} is omitted, as no peaks of interest were detected. The two principal bands in BO relate to an alkene functional group at 1656.9 cm^{-1} (highlighted in blue), consistent with C=C stretches from oleic and linoleic acid, and to C-H stretching of the alkene at 3005.1 cm^{-1} (highlighted in red). As expected, after the epoxidation reaction, the aforementioned bands vanish and two new bands at low intensity can be observed at 826.8 cm^{-1} and 844.4 cm^{-1}. These correlate to the C-O-C stretching of an epoxy ring (highlighted in green, Mahendran *et al.*, 2012). In addition, the absence of a large and intense band at 3500.0 cm^{-1}, often related to an O-H stretch, prove that the reaction occurred without any by-product formation. It is often typical in these reactions that alcohol formation occurs, due to a reaction between the epoxy ring and acetic acid or water.

<Figure 2>

MIR spectra for MO and MO-E can be seen in Fig. A.1 (supplementary material). As expected, the spectra for both samples are similar to BO and BO-E, except the C=C stretches appears as two bands at 1653.9 cm^{-1} and 1712.8 cm^{-1}. After the epoxidation process, the C-H stretch of the alkene at 3010.9 cm^{-1} (highlighted in red, Fig. S1-b) vanishes. The shoulder peak at 1712.8 cm^{-1} may however indicate that some C=C bonds remain (highlighted in blue, Fig. A.1-b). Overall, these results suggest that 100% epoxidation was achieved in the formation of BO-E and just under 100% epoxidation in the formation MO-E.

For further analysis of the epoxidised samples, ^{1}H and ^{13}C NMR analysis was also performed. The ^{1}H-NMR spectra for BO and BO-E can be seen in Fig. 3. The vinyl hydrogens [-C**H**=C**H**-] in BO appear as a multiplet signal at 5.32 ppm close to a low intensity multiplet signal at 5.1 ppm associated with the hydrogen attached to the secondary carbon of the glycerol backbone [-C**H**-O]; in addition, the triplet at 2.75 ppm is associated with α-hydrogens between the two alkenes [-C=C-C**H**$_2$-C=C-] in the linoleic acid. These signals are fundamental in evaluating the efficiency of the epoxidation of oils (Lathi and Mattiasson, 2007; Fernandes *et al.*, 2017). By using Eq. 1 to calculate the average double bond value ($DB_{average}$) per triglyceride molecule, a value of 3.5 was obtained. Using Eq. 2, an IV value of 102.9 g of I_2 per 100 g of vegetable oil was also obtained. This result is very similar to the result obtained by Wijs method (103.5±0.9 grams of I_2 per 100 g of vegetable oil). The ^{1}H-NMR spectrum for BO-E (Fig.1-b) shows that the signals related to the vinyl and α-hydrogens disappear, with the addition of four new signals at 1.46, 2.85, 2.94 and 3.06 ppm. The signal at 1.46 ppm relates to the α-hydrogens between two epoxide rings, while the three other signals are related to the epoxide ring hydrogens (Lathi and Mattiasson, 2007; Fernandes *et al.*, 2017), as expected the signal at 5.1 ppm relating to the hydrogen attached to the secondary carbon of the glycerol backbone remained. This result also confirms 100% conversion of all the alkene bonds into epoxy rings.

<Figure 3>

The ^{1}H-NMR spectrum for MO is shown in Fig. A.2 (supplementary material) and the same hydrogen signals are seen as reported for BO. NMR analysis of MO, in conjunction with Eq. 1 and Eq 2, reported a double bond average ($DB_{average}$)value of 4.0 per triglyceride molecule and an IV of 108.2 g of I_2 per 100g of vegetable oil. This IV result reported a difference of 7.8 g of I_2 when compared to Wijs method (116.0±0.6 grams of I_2 per 100 g of vegetable oil). The MO-E spectrum (Fig. A.3, supplementary material) shows signals corresponding to the epoxide ring hydrogens and to the α-hydrogens between two epoxide rings. However, the double bonds were not totally converted in epoxide rings, because it is possible to see a signal with low intensity at 5.34 ppm, due to some residual alkene hydrogens. Therefore, the epoxidation reaction did not reach 100% conversion. Using the ^{1}H NMR spectrum and Eq.1 and Eq.2, it was possible to calculate an alkene conversion of 95.3% and the IV= 4.2 g of I_2/100g.

Alkene conversions obtained for both vegetable oils in this study, using Amberlite IR120 as reaction catalyst were clean and fast with an excellent conversion in comparison with other methods in the literature. Park *et al.*, 2004 used the same reaction route for soybean oil and castor oil, but did not reach 100% alkene conversion for these vegetable oils. A tungsten-based phase-transfer catalyst was used in the epoxidation of castor oil, obtaining an epoxide conversion of only 60% (Chakrapani and Crivello, 1998). Sulfuric acid has also been employed as a catalyst in the epoxidation of perilla oil (Kousaalya *et al.*, 2018). After 8 hours at 60.0 °C, the reaction reached a reasonable conversion of 88%. Furthermore, the use of *Candida antarctica* Lipase B (CALB) as an epoxidation catalyst for linseed oil was shown by Mahendran *et al.* in 2012, achieving a maximum conversion of 96% using 20 wt% of catalyst. The principal advantage of this method is the heterogeneous catalyst employed, as it can be recovered at the end of the reaction. Furthermore, the washing step in the workup is easier and faster to do, because acid catalysts (normally sulfuric or phosphoric acids) are homogeneous and therefore require more washings.

The different fatty acid chains present in BO and MO were calculated via ^{1}H NMR analysis (Table 1) and were found to include saturated acid (S), oleic acid (O), linoleic acid (L) and linolenic acid (Ln). The quantity of mono-unsaturated fatty acid chains in BO is almost double that of MO. The greater quantity of mono-unsaturated fatty acid chains in BO may explain why BO-E is a solid at room temperature. The epoxidized oleic acid (C18:1) chain can have a strong fatty chain physical interaction with other oleic acid chains, as oleic acid is almost linear in structure. On the other hand, poly-unsaturated chains such as linoleic (C18:2) and linolenic acid (C18:3) are not linear, which interferes with fatty chain physical interaction. This non-linearity of the alkyl chains is preserved after epoxidation; therefore, MO-E is a liquid at room temperature due to its greater quantity of poly-epoxidized chains than BO-E.

Furthermore, the BO used in this study possessed a fatty acid content similar to that reported in the literature (Oliveira-Alves *et al.*, 2020) with only a small variation in the amounts of mono-unsaturated fatty acid and saturated fatty acid (Table 1). However, the MO used in this work had a high amount of linoleic acid whilst the literature describes a greater mono-unsaturated fatty acid content and a lower quantity of linoleic acid (Ribeiro *et al.*, 2017). However, the saturated fatty acid content is similar to that reported in the literature.

<Table 1>

The ^{13}C-NMR spectrum for BO and BO-E samples are shown in Fig. 4. In the spectrum for BO, five signals were observed in the range of 125-135 ppm, which are related to the alkene carbons. The two first signals at 127.96 ppm and 128.18 ppm are associated with carbons in the oleic chain (C18:1), whilst the signals at 129.80, 130.09 and 130.30 ppm are associated with the alkene carbons in the linoleic acid chain (C18:2, Salih *et al.*, 2015). After the epoxidation reaction, these alkene carbon signals were not observed and five new signals were detected in the 53-58 ppm region. The signals at 54.27 ppm and 54.41 ppm can be associated with the epoxide ring carbons present in the oleic acid chain and the signals at 56.72, 57.06 and 57.26 ppm can be associated with epoxide carbons in the linoleic acid chain (Salih *et al.*, 2015). In addition, the ^{13}C-NMR results for MO and MO-E are illustrated in Fig. A.4 and Fig. A.5 (supplementary material), respectively, showing similar results to both BO and BO-E, as previously discussed.

<Figure 4>

Considering the average double bond by ^{1}H-NMR for BO ($DB_{average} = 3.5$) and MO ($DB_{average} = 4.0$) together with the fatty acid content (Table 1) is possible to suggest the main structure for both vegetable oils (Figure 5).

<Figure 5>

3.3 TG/DTG-DTA and DSC

The TG/DTG-DTA curves for BO are illustrated in Fig. 6. Using the TG and DTG curves, it was possible to determine the thermal stability of BO (260.8 ºC). The first step of mass loss occurs in the range of 260.8 ºC to 488.4 ºC, with a mass loss (*Δm)* of 96.3%, and is associated with the exothermic peak at 384.3 ºC in the DTA curve. This mass loss is related to the degradation and oxidation of unsaturated fatty acid chains, which degrade by radical processes with O_2 causing a dehydrogenation process resulting in total degradation of all the fatty chains (saturated and unsaturated) (Pires *et al.*, 2019; Gaglieri *et al.*, 2019). Furthermore, it was possible to calculate the maximum degradation rate (MDR) of this step, using the DTG curve, which was equal to 14.7 % min^{-1}. The second mass loss step (*Δm* = 3.7%) can be associated with the oxidation and degradation of carbonaceous matter formed in the first step, which occurred in the temperature range of 490.8 to 600.6 ºC and was associated with an exothermic peak at 502.9 ºC, as shown by the DTA curve.

BO-E (Fig. 6-b) is stable only up to 220.6 ºC. This lower thermal stability in comparison with BO can be associated with epoxide thermal cleavage, resulting in a faster fatty acid chain degradation due to radical dehydrogenation. This behavior was previously reported for epoxidized soybean oil (Yang *et al.*, 2008). Although the first step of mass loss (220.6 ºC to 488.4 ºC) appears as a single and well-defined step, with a *Δm* of 93.4% (TG curve) and an associated exothermic peak at 382.6 ºC (DTA curve), the DTG curve showed two overlapped peaks during this step. This illustrates that this transition is related to a complicated and consecutive degradation. This behavior was similar to trends reported in the literature for other modified vegetable oils (Alarcon *et al.*, 2020). The MDR for the first DTG peak was equal to 8.7% min^{-1}. The second mass loss step (488.4 ºC to 623.3 ºC) was also related to carbonaceous matter oxidation and degradation (*Δm* = 6.6%) with a peak in the DTA curve at 525.7 ºC.

The TG curve for MO (Fig. 6-c) shows two mass loss steps. The first step is an overlapped and complex transition, as can be seen in the DTG curve, occurring from its thermal stability at 217.3 ºC to 480.1 ºC, with a *Δm* of 93.7% and is associated with an exothermic peak at 382.2 ºC. The second mass loss step occurs between 480.1 ºC and 578.9 ºC (*Δm* = 6.3%) and is associated with an exothermic peak at 504.7 ºC, related to the oxidation of carbonaceous matter. MO-E has a similar thermal curve profile (Fig. 6-d) when compared to MO, showing a complex and overlapped first mass loss event (217.9-488.0 ºC, *Δm* = 91.9%) related to an exothermic peak at 378.5 ºC. In addition, the second mass loss step is related to oxidation of carbonaceous matter (*Δm* = 8.1%) occurring in a temperature range of 488.0 ºC to 625.9 ºC, with an exothermic peak at 523.7 ºC. Unlike BO and its epoxidised derivative, MO and MO-E have the same thermal stability. Epoxidized vegetable oils often have the same or inferior thermal stability seen for vegetable oils without modification (Yang *et al.*, 2008; Kim and Sharma, 2012). Then, as the amount of unsaturated fatty acids in MO is high (81.7%, Table 1) the presence of epoxides do not interfere in its thermal stability. This may explain why there are no significant changes in MDR values for MO and MO-E, which are 9.9% min^{-1} and 9.6% min^{-1}, respectively. It is also known that increasing the amount of unsaturated fatty acids in vegetable oil leads to a decrease in its thermal stability.

<Figure 6>

As previously mentioned, BO is a liquid at room temperature. Interestingly, BO crystallizes when undergoing a cooling process, as shown as by the small exothermic peak at -29.5 ºC in the DSC curve (Fig. 7-a). Afterwards, a melting process occurs whilst heating. This process appears as a large endothermic event between - 28.3 ºC and - 5.0 ºC, with a peak at -13.3 ºC. Furthermore, the DSC curve for MO (Fig. 7-b) seems to be identical to the BO curve, with the first and second heating processes showing an endothermic peak at -13.4 ºC, relating to a melting process. The first cooling step exhibits two exothermic peaks at -11.7 ºC and 19.9 ºC, which are associated with a crystallization process. The DSC curve for SO (supplementary material Fig. A-7a) shows a similar thermal behavior as discussed to BO and MO. In the first cooling is possible to see an exothermic peak at -22.3 ºC and the first and second heating steps exhibit an endothermic event due to melting process at -14.4 ºC and -12.6 ºC, respectively.

<Figure 7>

Unlike BO, BO-E is a white greasy solid at room temperature. BO-E was first cooled to -35.0 ºC, to study its complete thermal behavior in the first heating process (Fig.8-a). As expected, the thermal behavior for BO-E is totally different to BO, as previously described. The first two endothermic events at -6.5 ºC and 14.1 ºC have enthalpy values (*ΔH)* equal to 21.4 J g^{-1} and 2.8 J g^{-1}, respectively; furthermore, these events were associated with a melting process of the non-intersoluble triglycerides, in particular those with more quantity of saturated fatty acid chains. This process has been previously reported for other modified vegetable oils (Alarcon *et al.*, 2020). The third thermal event was an endothermic peak at 43.5 ºC (ΔH = 45.4 J g^{-1}), which was related to the total melting process of the epoxidized oil. In addition, this melting process occurred at higher temperatures compared to BO (Fig. 7-a). This may be associated with the difference in intermolecular interaction forces between the epoxide rings, which is stronger than C=C interactions (Yang *et al.*, 2008). The first cooling cycle showed an intense exothermic peak at -30.5 ºC, associated with a crystallization process.

Subsequently, a second heating process was executed on the same sample and appeared totally different to the results obtained during the first heating. The non-intersoluble melting process had a slight temperature change and occurred as a single step at -2.4 ºC. In addition, a different thermal event transpired as an exothermic peak at 3.2 ºC, which could be associated with a solid transition between two different forms (Yan *et al.*, 2018; Adhvaryu *et al.*, 2003). This process occurs when the material is cooled quickly, causing a new solid form which is less stable than the solid formed when BO-E solidified at room temperature. This event was not observed in the first heating step as the material was already a solid. The solidification process at room temperature causes another solid structure, probably a more stable solid form. Finally, BO-E melted at 31.6 ºC, with a difference of 11.9 ºC between the first and second heating cycle. The ΔH values of each event during the second heating were not possible to obtain, due to the events overlapping during the sequence. A DSC analysis under a N_2 atmosphere was performed (supplementary material; Fig. A.6) and showed the same thermal behavior as reported when under a dry air atmosphere, proving that these thermal events are physical changes (crystallization and melting processes).

The DSC curve for MO-E is exhibited in Fig. 8-b and is less complex compared to BO-E. In the first cooling stage, an exothermic peak with low intensity is observed at -16.0 ºC, due to a crystallization process. The first and second heating steps are identical showing only an exothermic peak at -14.2 ºC and -14.1 ºC, respectively. The DSC curve is simpler than BO-E, which showed two different thermal processes due to being a solid. As previously mentioned, BO has more oleic acid (C18:1) than linoleic acid (C18:2), at 60.7% and 25.4%, respectively. The proportion of acids in the MO used in this work is completely different, with 33.0% and 46.5% of oleic acid (C18:1) and linoleic acid (C18:2), respectively. Therefore, there are more conjugated bonds in MO compared to BO and consequently more epoxide rings in the same chain, in MO-E compared to BO-E (3.5 and 4.0, respectively). As a result, BO-E has a more linear structure than MO-E, resulting in a higher chain interaction and requiring more energy for the whole sample to melt (three melting steps) compared to MO-E (one melting step), which presents less physical interaction between chains due to the higher quantity of linoleic acid (C18:2), resulting in a liquid sample (Kim and Sharma, 2012).

The DSC curve for SO-E can be seen in the supplementary material (Fig. A-7b) and seems almost equal to MO-E, probably due to the similar fatty acid content with high quantity of linoleic acid (Kim and Sharma, 2012). In the first cooling step a small exothermic peak (-13.2 ºC) is observed due to SO-E solidification; in addition, an endothermic peak in the first heating at -3.5 ºC and at -3.8 in the second heating step are related to melting process.

<Figure 8>

In order to obtain better visualizations of these thermal transitions, DSC analysis for BO-E and MO-E were performed and recorded simultaneously via video footage. These videos can be seen in the supplementary material (Video A.1 and Video A.2). Images obtained from these videos are presented in Fig. 9. In the first heating cycle of BO-E, it was not possible to notice a difference in the sample before and after the first two thermal endothermic events, at-6.5 ºC and 14.2 ºC (Fig. 9-b to 9-d). In the third endothermic melting process, it was possible to observe a difference in the sample, during the start (42.0 °C, Fig. 9-e) and end (45.0 °C, Fig. 9-f) of the melting process. In the cooling cycle, the solidification process started at -18.0 °C (Fig. 9-i) as shown in the DSC curve. The solidification process starts in the center of the sample, then the rest of the sample gradually starts to solidify (Fig. 9-l). This can be observed by the change in brightness of the images, especially in the bottom left corner. Consequently at -35.0 °C, the BO-E sample was totally solidified, showing less brightness than when in its liquid state. Furthermore, in the second heating cycle the solid-solid transition was observed (Fig. 9-n and 9-o), as shown by the difference in brightness and opaqueness of the sample after the transition, as can be seen in the middle of the image. Melting of the sample begins in Fig. 9-p, with the sample melting totally by Fig.9-r (at 40.0 °C).

<Figure 9>

4 Conclusions

The epoxidation of BO and MO using the heterogeneous catalyst Amberlite IR120 was successful, obtaining alkenes into epoxy rings conversions of 100% and 95.3%, respectively. The main modifications can be seen in the ^{1}H-NMR, ^{13}C-NMR and MIR spectra, supporting that this reaction occurred in a fast and clean manner. Moreover, BO-E was a solid greasy compound at room temperature, due to its greater mono-epoxidized fatty acid content. This trend was not observed for MO-E, which had a greater quantity of poly-epoxidized fatty acids.

Firstly, the iodine value (IV) for BO and MO were determined by Wijs method, to obtain a value of 103.5±0.9 g of I_2 per 100 g for BO and 116.0±0.6 g of I_2 per 100 g for MO. For a precise result, the IV for both samples were also calculated by ^{1}H-NMR, which resulted in a value of 102.9 for BO and 108.2 for MO. In addition, the average double bond (DB_{average}) and fatty acid content were also calculated for BO and MO by

^{1}H-NMR using the IV results previously obtained. The BO has a greater quantity (60.7%) of monounsaturated fatty acid chain (mostly oleic acid) compared to MO, which shows a 33.0% of monounsaturated fatty chain, but a greater quantity of polyunsaturated fatty acid chains (46.5%).

Differences in thermal stability were observed between BO and BO-E via TG/DTG curves. On the other hand, similar thermal stability was observed when comparing MO and MO-E. DSC analysis was used to determine the crystallization and melting process of each sample. Furthermore, BO-E had a complex thermal behavior, showing a melting process and solid-solid transition. These processes were further confirmed by the microscopy-DSC images and video.

In summary, the epoxidation of both Brazilian renewable vegetable oils was successful and could be performed in a rapid and green manner. Each epoxidized material contained different fatty acid content and consequently different thermal and physical proprieties. In future work, these epoxidized vegetable oils will be further studied and tested in their ability to use as lubricants and as monomers for polymer synthesis.

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Figures captions

Fig.1. (a) BO, (b) BO-E, (c) melted BO-E, (d) MO and (e) MO-E.

Fig. 2. MIR spectra for (a) BO and (b) BO-E.

Fig. 3. ^{1}H-NMR spectra for (a) BO and (b) BO-E.

Fig. 4. ^{13}C-NMR spectra for (a) BO and (b) BO-E.

Fig. 5. Possible main chemical structures for BO and MO.

Fig. 6. TG/DTG-DTA curves for (a) BO, (b) BO-E, (c) MO and MO-E (d).

Fig. 7. DSC curves for (a) BO and (b) MO.

Fig. 8. DSC curves for (a) BO-E and (b) MO-E.

Fig. 9. Microscopic images for BO-E in heating and cooling cycles by DSC analyses. (a-f) First heating, (g-h) first cooling and (m-r) second heating.