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

3 *Rafael T. Alarcon¹, Caroline Gaglieri¹, Katie J. Lamb², Michael North², Gilbert*
4 *Bannach^{*1}*

5 ¹UNESP- São Paulo State University, School of Sciences, Department of Chemistry, Bauru,
6 17033-260, SP, Brazil.

7 ² The University of York, Green Chemistry Centre of Excellence, Department of Chemistry,
8 Heslington, York YO10 5DD, UK.

9 * michael.north@york.ac.uk, gilbert.bannach@unesp.br

10 **Abstract**

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

25

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

28

29 **1. Introduction**

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

41 Although the use of epoxy resins has been improving, most binary mixtures are
42 limited to using bisphenol A diglycidyl ether (BADGE or DGEBA). However, DGEBA
43 is a petrochemically derived monomer and is therefore not considered a green or
44 renewable compound. Some studies have also raised concerns about its toxic effect on
45 human health and wildlife such as endocrine disruption and reproductive disorders
46 (Vandenberg *et al.*, 2009; Maffini *et al.*, 2006; Flint *et al.*, 2012). Thus, to avoid the use
47 of DGEBA, some authors have reported the synthesis of epoxides using more
48 renewable monomers, such as cinnamic acid (Xin *et al.*, 2014), resveratrol (Tian *et al.*,
49 2020), syringaresinol (Janvier *et al.*, 2017), eugenol (Santiago *et al.*, 2020), vanillin
50 (Fache *et al.*, 2015), quercetin (Kristufek *et al.*, 2016), furan (Hu *et al.*, 2015) and
51 vegetable oils (Kumar *et al.*, 2017).

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

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

67 As a result, vegetable oil from baru nut (*Dipteryx alata Vogel*) and macaw palm
68 (*Acrocomia aculeata*) were selected and analysed in this study. Baru and macaw are
69 drupes grown on trees and palms, respectively, in the Cerrado region of Brazil; the baru
70 nut is normally cropped in little communities which is incentive by Brazil's
71 Government to improve the use of renewable resources from Cerrado; in addition the
72 baru tree is very productive and about 100 baru trees can produce 19.4 ton of nuts and
73 only one Brazil state can produce about 20,000 ton of nuts, as consequence 8,000 ton
74 of vegetable oil (Batista and Sousa, 2019; Sano *et al.*, 2004). The macaw palm fruit
75 contains a high quantity of vegetable oil, which produces 4,000 L of oil per hectare,
76 much higher than the soybean which produces only 500 L per hectare (Oliveira, 2016;
77 Pires *et al.*, 2013); Brazil's government has been encouraging its crop to biodiesel
78 production and as a renewable resource (Grupioni *et al.*, 2020). Furthermore, these
79 vegetable oils can be also consumed by humans and animals and are often used in

80 healthcare products (Bravo *et al.*, 2020; Moraes *et al.*, 2018). Baru oil (BO) can be used
81 as an antioxidant, a hepatoprotective agent and as a lubricant (Albs and Betruger, 2019;
82 Reis *et al.*, 2018). The baru vegetable oil has about 78.5% of unsaturation, provided by
83 47.2% of oleic acid (C18:1), 28.2% of linoleic acid (C18:2), 0.1% of linolenic acid
84 (C18:3), 2.7% of eicosenoic acid (C20:1) and 0.3% of erusic acid (C22:1). In addition,
85 the baru vegetable oil has palmitic acid (C16:0) and stearic (C18:0) acid as saturated
86 fatty acids in its structure (Oliveira-Alves *et al.*, 2020). The macaw oil (MO) contains
87 about 81.7% of unsaturation, with 74.2% of oleic acid, 4.8% of linoleic acid and 2.7%
88 of linolenic acid (Ribeiro *et al.*, 2017). These percentages of saturation and unsaturation
89 can vary, depending on the extraction process employed to obtain these oils (Coimbra
90 and Jorge, 2011).

91 The epoxidation of baru or macaw vegetable oils have never been fully
92 investigated. Research has been published describing the modification of baru oil by
93 ozonolysis and polyurethane production, and it has been used to make biodiesel
94 (Kogawa *et al.*, 2012; Almeida *et al.*, 2016; Batista *et al.*, 2012). Macaw oil has also
95 been widely used in biodiesel production (Ribeiro *et al.*, 2017; da Conceição *et al.*,
96 2019; Silva *et al.*, 2014; Ramos *et al.*, 2016) and in starch-based thermoplastics
97 (Schlemmer *et al.*, 2010). In this work, we therefore decided to investigate the
98 possibility of epoxidizing both baru nut and macaw palm vegetable oil.

99 Epoxidized oils often show different properties, in particular thermal properties,
100 compared to non-modified vegetable oils. The starting oils also greatly affect the
101 properties of the final products, as no two epoxidized oils show the same properties.
102 Techniques such as thermogravimetry-differential thermal analysis (TG-DTA) and
103 differential scanning calorimetry (DSC) are therefore fundamental to elucidating and
104 comparing the thermal behaviors of the initial oil and final epoxidized products. DSC

105 is an extremely important technique that provides useful information about melting and
106 crystallization temperatures, glass transitions and solid-solid transitions. Furthermore,
107 mid-infrared spectroscopy (MIR) and nuclear magnetic resonance ($^1\text{H-NMR}$ and $^{13}\text{C-}$
108 NMR) are extremely useful techniques to study structural modifications and the
109 conversion of alkenes ($\text{C}=\text{C}$) into epoxide rings. The epoxidized materials produced in
110 this report are therefore studied by these techniques, in order to analyze their thermal
111 properties and, most importantly, to understand the appropriate storage conditions
112 required to transport these materials. This will, in particular, reduce problems that are
113 often encountered in scale up, when these materials are used in industrial production
114 lines.

115

116 **2. Materials and Methods**

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

129

130

131 **2.1. Epoxidation of baru and macaw palm vegetable oil**

132 The synthetic route employed followed the literature procedure reported by Park
133 *et al.* in 2004. Firstly, 100.0 g of baru nut vegetable oil, 25.0 g of glacial acetic acid and
134 25.0 g of Amberlite IR120 (catalyst) were settled into a round bottomed flask with a
135 magnetic bar, and then stirred for 30 minutes at 60 °C use a magnetic stirrer-hotplate
136 with aluminum base insulation. Afterwards, 79.0 g of hydrogen peroxide (30%) was
137 added dropwise (1 mL min⁻¹). Thereafter, the reaction was kept at 60 °C for 6 hours
138 with a reflux apparatus. After 6 hours, the crude product was filtered (recovering the
139 catalyst) and then extracted with 50 mL of ethyl acetate. The organic layer was then
140 washed with 30.0 mL of sodium carbonate solution (0.1 mol L⁻¹) three times, until the
141 water layer reached a neutral pH of 7.0 using a universal pH paper. The organic layer
142 was then concentrated *in vacuo* to afford the final product (102.0 g) as a colorless liquid,
143 which solidifies at room temperature to give a white, greasy compound.

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

146

147 **2.2 Iodine Value and Epoxide content**

148 The iodine value (IV) was calculated using the Wijs method, a titration process
149 which measures the average quantity of alkenes (C=C), and thus the degree of
150 unsaturation, in triglyceride or vegetable oil samples. This method works by saturating
151 all of the double bonds in the compound with iodine, using iodine chloride, and then
152 measuring the total iodine consumed by titrating with sodium thiosulfate solution (0.1
153 mol L⁻¹). The IV determined via this method is defined as grams of iodine (I₂) absorbed
154 by 100 g of vegetable oil. For this procedure, a standard method (ASTM D5554-15;
155 ASTM, 2015) was followed and used to study the baru vegetable oil (BO) and macaw
156 vegetable oil (MO).

157 The epoxide content in the both epoxidized vegetable oils (BO-E and MO-E)
158 were determined following a standard titration method for epoxide content of epoxy
159 resins (ASTM D1652-11; ASTM, 2019). This method describes the reaction between
160 TEAB and perchloric acid (HClO₄), resulting in hydrogen bromide (HBr) formation *in*
161 *situ*. Consequently, the HBr reacts 1:1 with the epoxide ring, forming a bromo alcohol.
162 Thereafter, the acidic solution is titrated against potassium hydrogen phthalate (0.1 mol
163 L⁻¹) to determine the residual amount of HBr left in the solution. It is then possible to
164 calculate the epoxide content. The method uses a blank to compare the results with, as
165 a solution but with no sample present is titrated under the same conditions.

166

167 **2.3 Mid-Infrared Spectroscopy (MIR)**

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

172

173 **2.4. ¹H-NMR and ¹³C-NMR analyses**

174 To determine the principal signal of BO, MO, BO-E and MO-E, as well as to
175 quantify alkene conversion, ¹H-NMR and ¹³C-NMR analysis were performed, using a
176 Jeol 400 MHz spectrometer. Samples were solubilized in deuterated chloroform
177 (CDCl₃, 99.8% D, Sigma-Aldrich).

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

181

$$182 \quad DB_{average} = K/2Nf \quad (1)$$

183

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

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

192

$$193 \quad IV = 12691 * K / (120 + 701.3 + 6.006 * K) \quad (2)$$

194

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

198

199 *2.5 Simultaneous Thermogravimetry-Differential Thermal Analysis (TG-DTA) and* 200 *Differential Scanning Calorimetry (DSC)*

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

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

210 megapixels and 6.5x magnification. Approximately 10 mg of sample were placed in a
211 40 μL closed aluminium crucible with a perforated lid. The samples were heated from
212 $-35.0\text{ }^{\circ}\text{C}$ to $120.0\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$, whilst under a flow rate of 50 mL min^{-1} of dry air.
213 When images were taken during the DSC analysis, the same experimental conditions
214 were used, except the analysis was performed in a $40\text{ }\mu\text{L}$ open alumina crucible.
215 Another DSC analysis was performed following the same experimental conditions
216 except using an atmosphere of N_2 (99.9%). This analysis was carried out to understand
217 better the thermal behavior of BO-E.

218

219 **3 Results and Discussion**

220 ***3.1 Iodine Value and epoxide content***

221 Baru vegetable oil (BO) is a liquid at room temperature ($25.0\text{ }^{\circ}\text{C}$) and has a
222 yellowish golden colour (Fig. 1-a), with an IV of 103.5 ± 0.9 grams of I_2 per 100 g of
223 vegetable oil. After epoxidation, the formed product (BO-E) did not record an iodine
224 value, indicating a conversion of all, or the majority, of alkenes into epoxide rings. In
225 addition, BO-E turned into a white greasy solid compound (Fig. 1-b) at room
226 temperature. This solidification occurs due to the presence of epoxide ring hydrogen
227 bonds and molecular conformation, which restrict the mobility of the fatty acid chain.
228 Similar findings have been presented in the literature for 100% epoxidized soybean and
229 linseed vegetable oils. These oils were found to be a semi-solid with high viscosity at
230 $10.0\text{ }^{\circ}\text{C}$ (Muturi *et al.*, 1994). In comparison, BO-E is a solid at room temperature, melts
231 above $40.0\text{ }^{\circ}\text{C}$ and forms a colourless liquid (Fig.1-c). The epoxide content for BO-E
232 was equal to 5.98 ± 0.03 wt% of oxygen. In other words, BO-E has 5.98 g of epoxy
233 oxygen atoms per 100 g of epoxidized oil. Dividing this value by 16 (the atomic mass
234 of oxygen) makes it possible to obtain the molar quantity of oxygen as 0.37375 mol
235 (Kousaalya *et al.*, 2018), which is an important parameter to know in polymer

236 chemistry. Different quantities of epoxide can provide different physical properties in
237 the final polymer. Normally, commercial epoxidized soybean and linseed oils have a
238 value equal to 6.8 wt% of oxygen (0.42500 mol) and 8.9 wt% of oxygen (0.55625 mol),
239 respectively (Bähr and Mülhaupt, 2012).

240 The macaw vegetable oil (MO) has an orange-reddish colour and is liquid at
241 room temperature (Fig. 1-d), possessing an IV of 116.0 ± 0.6 grams of I_2 per 100 g of
242 vegetable oil. After epoxidation, MO turned into a slightly yellow colour compound
243 (MO-E) with an iodine value of 14.7 ± 1.73 g of I_2 per 100 g of vegetable oil, which
244 indicates the presence of residual alkenes. Unlike BO-E, the MO-E sample is not a solid
245 at room temperature. The oxygen epoxide content in the MO-E is equal to 5.39 ± 0.07
246 wt% and thus has 5.39 g of epoxide oxygen atoms per 100 g of epoxidized oil (and
247 0.33687 mol of oxygen).

248
249
250
251

<Figure 1>

252 ***3.2 Mid-Infrared Spectroscopy (MIR) and 1H -NMR and ^{13}C -NMR analysis***

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

263 typical in these reactions that alcohol formation occurs, due to a reaction between the
264 epoxy ring and acetic acid or water.

265

266

<Figure 2>

267

268 MIR spectra for MO and MO-E can be seen in Fig. A.1 (supplementary
269 material). As expected, the spectra for both samples are similar to BO and BO-E, except
270 the C=C stretches appears as two bands at 1653.9 cm^{-1} and 1712.8 cm^{-1} . After the
271 epoxidation process, the C-H stretch of the alkene at 3010.9 cm^{-1} (highlighted in red,
272 Fig. S1-b) vanishes. The shoulder peak at 1712.8 cm^{-1} may however indicate that some
273 C=C bonds remain (highlighted in blue, Fig. A.1-b). Overall, these results suggest that
274 100% epoxidation was achieved in the formation of BO-E and just under 100%
275 epoxidation in the formation MO-E.

276 For further analysis of the epoxidised samples, ^1H and ^{13}C NMR analysis was
277 also performed. The ^1H -NMR spectra for BO and BO-E can be seen in Fig. 3. The vinyl
278 hydrogens [-CH=CH-] in BO appear as a multiplet signal at 5.32 ppm close to a low
279 intensity multiplet signal at 5.1 ppm associated with the hydrogen attached to the
280 secondary carbon of the glycerol backbone [-CH-O]; in addition, the triplet at 2.75 ppm
281 is associated with α -hydrogens between the two alkenes [-C=C-CH₂-C=C-] in the
282 linoleic acid. These signals are fundamental in evaluating the efficiency of the
283 epoxidation of oils (Lathi and Mattiasson, 2007; Fernandes *et al.*, 2017). By using Eq.
284 1 to calculate the average double bond value ($\text{DB}_{\text{average}}$) per triglyceride molecule, a
285 value of 3.5 was obtained. Using Eq. 2, an IV value of 102.9 g of I₂ per 100 g of
286 vegetable oil was also obtained. This result is very similar to the result obtained by Wijs
287 method (103.5 ± 0.9 grams of I₂ per 100 g of vegetable oil). The ^1H -NMR spectrum for
288 BO-E (Fig.1-b) shows that the signals related to the vinyl and α -hydrogens disappear,

289 with the addition of four new signals at 1.46, 2.85, 2.94 and 3.06 ppm. The signal at
290 1.46 ppm relates to the α -hydrogens between two epoxide rings, while the three other
291 signals are related to the epoxide ring hydrogens (Lathi and Mattiasson, 2007;
292 Fernandes *et al.*, 2017), as expected the signal at 5.1 ppm relating to the hydrogen
293 attached to the secondary carbon of the glycerol backbone remained. This result also
294 confirms 100% conversion of all the alkene bonds into epoxy rings.

295

296

<Figure 3>

297

298 The ^1H -NMR spectrum for MO is shown in Fig. A.2 (supplementary material)
299 and the same hydrogen signals are seen as reported for BO. NMR analysis of MO, in
300 conjunction with Eq. 1 and Eq 2, reported a double bond average ($\text{DB}_{\text{average}}$) value of
301 4.0 per triglyceride molecule and an IV of 108.2 g of I_2 per 100g of vegetable oil. This
302 IV result reported a difference of 7.8 g of I_2 when compared to Wijs method (116.0 \pm 0.6
303 grams of I_2 per 100 g of vegetable oil). The MO-E spectrum (Fig. A.3, supplementary
304 material) shows signals corresponding to the epoxide ring hydrogens and to the α -
305 hydrogens between two epoxide rings. However, the double bonds were not totally
306 converted in epoxide rings, because it is possible to see a signal with low intensity at
307 5.34 ppm, due to some residual alkene hydrogens. Therefore, the epoxidation reaction
308 did not reach 100% conversion. Using the ^1H NMR spectrum and Eq.1 and Eq.2, it was
309 possible to calculate an alkene conversion of 95.3% and the IV= 4.2 g of I_2 /100g.

310

311

312

313

314

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

315 epoxidation of castor oil, obtaining an epoxide conversion of only 60% (Chakrapani
316 and Crivello, 1998). Sulfuric acid has also been employed as a catalyst in the
317 epoxidation of perilla oil (Kousaalya *et al.*, 2018). After 8 hours at 60.0 °C, the reaction
318 reached a reasonable conversion of 88%. Furthermore, the use of *Candida antarctica*
319 Lipase B (CALB) as an epoxidation catalyst for linseed oil was shown by Mahendran
320 *et al.* in 2012, achieving a maximum conversion of 96% using 20 wt% of catalyst. The
321 principal advantage of this method is the heterogeneous catalyst employed, as it can be
322 recovered at the end of the reaction. Furthermore, the washing step in the workup is
323 easier and faster to do, because acid catalysts (normally sulfuric or phosphoric acids)
324 are homogeneous and therefore require more washings.

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

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

340 literature describes a greater mono-unsaturated fatty acid content and a lower quantity
341 of linoleic acid (Ribeiro *et al.*, 2017). However, the saturated fatty acid content is
342 similar to that reported in the literature.

343

344 <Table 1>

345

346 The ^{13}C -NMR spectrum for BO and BO-E samples are shown in Fig. 4. In the
347 spectrum for BO, five signals were observed in the range of 125-135 ppm, which are
348 related to the alkene carbons. The two first signals at 127.96 ppm and 128.18 ppm are
349 associated with carbons in the oleic chain (C18:1), whilst the signals at 129.80, 130.09
350 and 130.30 ppm are associated with the alkene carbons in the linoleic acid chain (C18:2,
351 Salih *et al.*, 2015). After the epoxidation reaction, these alkene carbon signals were not
352 observed and five new signals were detected in the 53-58 ppm region. The signals at
353 54.27 ppm and 54.41 ppm can be associated with the epoxide ring carbons present in
354 the oleic acid chain and the signals at 56.72, 57.06 and 57.26 ppm can be associated
355 with epoxide carbons in the linoleic acid chain (Salih *et al.*, 2015). In addition, the ^{13}C -
356 NMR results for MO and MO-E are illustrated in Fig. A.4 and Fig. A.5 (supplementary
357 material), respectively, showing similar results to both BO and BO-E, as previously
358 discussed.

359

<Figure 4>

360

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

364

365

<Figure 5>

366

367

368

3.3 TG/DTG-DTA and DSC

369
370 The TG/DTG-DTA curves for BO are illustrated in Fig. 6. Using the TG and
371 DTG curves, it was possible to determine the thermal stability of BO (260.8 °C). The
372 first step of mass loss occurs in the range of 260.8 °C to 488.4 °C, with a mass loss (Δm)
373 of 96.3%, and is associated with the exothermic peak at 384.3 °C in the DTA curve.
374 This mass loss is related to the degradation and oxidation of unsaturated fatty acid
375 chains, which degrade by radical processes with O₂ causing a dehydrogenation process
376 resulting in total degradation of all the fatty chains (saturated and unsaturated) (Pires *et*
377 *al.*, 2019; Gaglieri *et al.*, 2019). Furthermore, it was possible to calculate the maximum
378 degradation rate (MDR) of this step, using the DTG curve, which was equal to 14.7 %
379 min⁻¹. The second mass loss step ($\Delta m = 3.7%$) can be associated with the oxidation and
380 degradation of carbonaceous matter formed in the first step, which occurred in the
381 temperature range of 490.8 to 600.6 °C and was associated with an exothermic peak at
382 502.9 °C, as shown by the DTA curve.

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

393 loss step (488.4 °C to 623.3 °C) was also related to carbonaceous matter oxidation and
394 degradation ($\Delta m = 6.6\%$) with a peak in the DTA curve at 525.7 °C.

395 The TG curve for MO (Fig. 6-c) shows two mass loss steps. The first step is an
396 overlapped and complex transition, as can be seen in the DTG curve, occurring from
397 its thermal stability at 217.3 °C to 480.1 °C, with a Δm of 93.7% and is associated with
398 an exothermic peak at 382.2 °C. The second mass loss step occurs between 480.1 °C
399 and 578.9 °C ($\Delta m = 6.3\%$) and is associated with an exothermic peak at 504.7 °C, related
400 to the oxidation of carbonaceous matter. MO-E has a similar thermal curve profile (Fig.
401 6-d) when compared to MO, showing a complex and overlapped first mass loss event
402 (217.9-488.0 °C, $\Delta m = 91.9\%$) related to an exothermic peak at 378.5 °C. In addition,
403 the second mass loss step is related to oxidation of carbonaceous matter ($\Delta m = 8.1\%$)
404 occurring in a temperature range of 488.0 °C to 625.9 °C, with an exothermic peak at
405 523.7 °C. Unlike BO and its epoxidised derivative, MO and MO-E have the same
406 thermal stability. Epoxidized vegetable oils often have the same or inferior thermal
407 stability seen for vegetable oils without modification (Yang *et al.*, 2008; Kim and
408 Sharma, 2012). Then, as the amount of unsaturated fatty acids in MO is high (81.7%,
409 Table 1) the presence of epoxides do not interfere in its thermal stability. This may
410 explain why there are no significant changes in MDR values for MO and MO-E, which
411 are $9.9\% \text{ min}^{-1}$ and $9.6\% \text{ min}^{-1}$, respectively. It is also known that increasing the amount
412 of unsaturated fatty acids in vegetable oil leads to a decrease in its thermal stability.

413

414

<Figure 6>

415

416

417

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

418 peak at -29.5 °C in the DSC curve (Fig. 7-a). Afterwards, a melting process occurs
419 whilst heating. This process appears as a large endothermic event between - 28.3 °C
420 and - 5.0 °C, with a peak at -13.3 °C. Furthermore, the DSC curve for MO (Fig. 7-b)
421 seems to be identical to the BO curve, with the first and second heating processes
422 showing an endothermic peak at -13.4 °C, relating to a melting process. The first
423 cooling step exhibits two exothermic peaks at -11.7 °C and 19.9 °C, which are
424 associated with a crystallization process. The DSC curve for SO (supplementary
425 material Fig. A-7a) shows a similar thermal behavior as discussed to BO and MO. In
426 the first cooling is possible to see an exothermic peak at -22.3 °C and the first and
427 second heating steps exhibit an endothermic event due to melting process at -14.4 °C
428 and -12.6 °C, respectively.

429

430

<Figure 7>

431

432 Unlike BO, BO-E is a white greasy solid at room temperature. BO-E was first
433 cooled to -35.0 °C, to study its complete thermal behavior in the first heating process
434 (Fig.8-a). As expected, the thermal behavior for BO-E is totally different to BO, as
435 previously described. The first two endothermic events at -6.5 °C and 14.1 °C have
436 enthalpy values (ΔH) equal to 21.4 J g⁻¹ and 2.8 J g⁻¹, respectively; furthermore,
437 these events were associated with a melting process of the non-intersoluble
438 triglycerides, in particular those with more quantity of saturated fatty acid chains. This
439 process has been previously reported for other modified vegetable oils (Alarcon *et al.*,
440 2020). The third thermal event was an endothermic peak at 43.5 °C ($\Delta H = 45.4$ J g⁻¹),
441 which was related to the total melting process of the epoxidized oil. In addition, this
442 melting process occurred at higher temperatures compared to BO (Fig. 7-a). This may

443 be associated with the difference in intermolecular interaction forces between the
444 epoxide rings, which is stronger than C=C interactions (Yang *et al.*, 2008). The first
445 cooling cycle showed an intense exothermic peak at -30.5 °C, associated with a
446 crystallization process.

447 Subsequently, a second heating process was executed on the same sample and
448 appeared totally different to the results obtained during the first heating. The non-
449 intersoluble melting process had a slight temperature change and occurred as a single
450 step at -2.4 °C. In addition, a different thermal event transpired as an exothermic peak
451 at 3.2 °C, which could be associated with a solid transition between two different forms
452 (Yan *et al.*, 2018; Adhvaryu *et al.*, 2003). This process occurs when the material is
453 cooled quickly, causing a new solid form which is less stable than the solid formed
454 when BO-E solidified at room temperature. This event was not observed in the first
455 heating step as the material was already a solid. The solidification process at room
456 temperature causes another solid structure, probably a more stable solid form. Finally,
457 BO-E melted at 31.6 °C, with a difference of 11.9 °C between the first and second
458 heating cycle. The ΔH values of each event during the second heating were not possible
459 to obtain, due to the events overlapping during the sequence. A DSC analysis under a
460 N₂ atmosphere was performed (supplementary material; Fig. A.6) and showed the same
461 thermal behavior as reported when under a dry air atmosphere, proving that these
462 thermal events are physical changes (crystallization and melting processes).

463 The DSC curve for MO-E is exhibited in Fig. 8-b and is less complex compared
464 to BO-E. In the first cooling stage, an exothermic peak with low intensity is observed
465 at -16.0 °C, due to a crystallization process. The first and second heating steps are
466 identical showing only an exothermic peak at -14.2 °C and -14.1 °C, respectively. The
467 DSC curve is simpler than BO-E, which showed two different thermal processes due to

468 being a solid. As previously mentioned, BO has more oleic acid (C18:1) than linoleic
469 acid (C18:2), at 60.7% and 25.4%, respectively. The proportion of acids in the MO used
470 in this work is completely different, with 33.0% and 46.5% of oleic acid (C18:1) and
471 linoleic acid (C18:2), respectively. Therefore, there are more conjugated bonds in MO
472 compared to BO and consequently more epoxide rings in the same chain, in MO-E
473 compared to BO-E (3.5 and 4.0, respectively). As a result, BO-E has a more linear
474 structure than MO-E, resulting in a higher chain interaction and requiring more energy
475 for the whole sample to melt (three melting steps) compared to MO-E (one melting
476 step), which presents less physical interaction between chains due to the higher quantity
477 of linoleic acid (C18:2), resulting in a liquid sample (Kim and Sharma, 2012).

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

484

485 <Figure 8>

486

487 In order to obtain better visualizations of these thermal transitions, DSC
488 analysis for BO-E and MO-E were performed and recorded simultaneously via video
489 footage. These videos can be seen in the supplementary material (Video A.1 and Video
490 A.2). Images obtained from these videos are presented in Fig. 9. In the first heating
491 cycle of BO-E, it was not possible to notice a difference in the sample before and after
492 the first two thermal endothermic events, at -6.5 °C and 14.2 °C (Fig. 9-b to 9-d). In the

493 third endothermic melting process, it was possible to observe a difference in the sample,
494 during the start (42.0 °C, Fig. 9-e) and end (45.0 °C, Fig. 9-f) of the melting process. In
495 the cooling cycle, the solidification process started at -18.0 °C (Fig. 9-i) as shown in the
496 DSC curve. The solidification process starts in the center of the sample, then the rest of
497 the sample gradually starts to solidify (Fig. 9-l). This can be observed by the change in
498 brightness of the images, especially in the bottom left corner. Consequently at -35.0 °C,
499 the BO-E sample was totally solidified, showing less brightness than when in its liquid
500 state. Furthermore, in the second heating cycle the solid-solid transition was observed
501 (Fig. 9-n and 9-o), as shown by the difference in brightness and opaqueness of the
502 sample after the transition, as can be seen in the middle of the image. Melting of the
503 sample begins in Fig. 9-p, with the sample melting totally by Fig.9-r (at 40.0 °C).

504

505

<Figure 9>

506

507 **4 Conclusions**

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

515 Firstly, the iodine value (IV) for BO and MO were determined by Wijs method, to
516 obtain a value of 103.5±0.9 g of I₂ per 100 g for BO and 116.0±0.6 g of I₂ per 100 g for
517 MO. For a precise result, the IV for both samples were also calculated by ¹H-NMR,
518 which resulted in a value of 102.9 for BO and 108.2 for MO. In addition, the average
519 double bond (DB_{average}) and fatty acid content were also calculated for BO and MO by

520 ¹H-NMR using the IV results previously obtained. The BO has a greater quantity
521 (60.7%) of monounsaturated fatty acid chain (mostly oleic acid) compared to MO,
522 which shows a 33.0% of monounsaturated fatty chain, but a greater quantity of
523 polyunsaturated fatty acid chains (46.5%).

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

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

536

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541

542 **References**

543

544 Adhvaryu, A., Erhan, S.Z., 2002. Epoxidized soybean oil as a potential source of high-
545 temperature lubricants. *Ind. Crop. Produc.* 15, 247-254.

546

- 547 Adhvaryu, A., Erhan, S.Z., Perez, J.M., 2003. Wax appearance temperatures of vegetable oils
548 determined by differential scanning calorimetry: effect of triacylglycerol structure and its
549 modification. *Thermoc. Acta.* 395, 191-200.
550
- 551 Alarcon, R.T., Gaglieri, C., de Souza, O.A., Rinaldo, D., Bannach, C., 2020. Microwave-
552 Assisted Syntheses of Vegetable Oil-Based Monomer: A Cleaner, Faster, and More Energy
553 Efficient Route. *J. Polym. Envir.* 28, 1265-1278.
554
- 555 Almeida, E.L., Goulart, G.A.S., Claro-Neto, S., Chierice, G.O., de Siqueira, A.B., 2016.
556 Preparation and characterization of polyurethane with different quantities of baru oil. *Polim.*
557 26,176-184.
558
- 559 ASTM D1652-11, 2019. Standard test method for epoxy content of epoxy resins.
560
- 561 ASTM D5554-15, 2015. Standard test method for determination of the iodine value of fats and
562 oils.
563
- 564 Bähr, M., Mülhaupt, R., 2012. Linseed and soybean oil-based polyurethanes prepared via the
565 non-isocyanate route and catalytic carbon dioxide conversion. *Green Chem.* 14, 483-489.
566
- 567 Bathista, A.AB. 2019. NMR Study of Cumbaru Oil to Apply as Mechanical Engineering
568 Lubricant. *Evo. Mechan. Eng.* 2.
569
- 570 Batista, A.C.F., Rodrigues, H.S., Pereira, N.R., Hernandez-Terrone, M.G., Vieira, A.T., de
571 Oliveira, M.F., 2012. Use of baru oil (*dipteryx alata vog.*) to produce biodiesel and study of the
572 physical and chemical characteristics of biodiesel/petroleum diesel fuel blends. *Chem. Tech.*
573 *Fuels Oils.* 48, 13-16.
- 574 Batista, F.O., Sousa, R.S., 2019. Bioactive compounds in fruits pequi (*caryocar brasiliense*
575 *comb.*) E baru (*dipteryx alata vogel*) and their potential uses: a review. *Braz. J. Develop.* 5,
576 9259-9270.
577
- 578 Branciforti, D.S., Lazzaroni, S., Milanese, C., Castiglioni M., Auricchio, F., Pasini, D., Dondi,
579 D., 2019. Visible light 3D printing with epoxidized vegetable oils. *Addit. Manufac.* 25, 317-
580 324.
581

- 582 Bravo, K., Quintero, C., Agudelo, C., García, S., Bríñez, A., Osorio, E., 2020. CosIng database
583 analysis and experimental studies to promote Latin American plant biodiversity for cosmetic
584 use. *Ind. Crop. Prod.* 144, 112007.
- 585
- 586 Campanella, A., Rustoy, E., Baldessari, A., Baltanás, M.A., 2010. Lubricants from chemical
587 modified vegetable oils. *Biosourc. Technol.* 101, 245-254.
- 588
- 589 Chakrapani, S., Crivello, J.V., 1998. synthesis and photoinitiated cationic polymerization of
590 epoxidized castor oil and its derivatives. *Pure Appl. Chem.* A35, 1-20
- 591
- 592 Coimbra, M.C., Jorge, N., 2011. Characterization of the Pulp and Kernel Oils from *Syagrus*
593 *oleracea*, *Syagrus romanzoffiana*, and *Acrocomia aculeata*. *J. Food Sci.* 76, C1156-61.
- 594
- 595 da Conceição, L.R., Reis, C.R., de Lima, R., Cortez, D.V., de Castro, H.F., 2019. Keggin-
596 structure heteropolyacid supported on alumina to be used in trans/esterification of high acid
597 feedstocks. *RSC Adv.* 9, 23450-23458.
- 598
- 599 Decker, C., Viet, T.N.T., Thi, H.P., 2001. Photoinitiated cationic polymerization of epoxides.
600 *Polym. Inter.* 50,986-997.
- 601
- 602 Ding, C., Shuttleworth, P.S., Makin, S., Clark, J.H., Matharu, A.S., 2015. New insights into the
603 curing of epoxidized linseed oil with dicarboxylic acids. *Green Chem.* 17, 4000-4008.
- 604
- 605 Elmore, J.D., Kincaid, D.S., Komar, P.C., Nielsen, J.E., 2002. Waterbone epoxy protective
606 coatings for metal. *J. Coat.Tech.* 74, 63-72.
- 607
- 608 Fache, M., Auvergne, R., Boutevin, B., Caillol, S., 2015. New vanillin-derived diepoxy
609 monomers for the synthesis of biobased thermosets. *Euro. Polym. J.* 67, 527-538.
- 610
- 611 Flint, S., Markle, T., Thompsom, S., Wallace, E., 2012. Bisphenol A exposure, effects and
612 policy: a wildlife review. *J Environ. Manag.* 104, 19-34.
- 613
- 614 Fernandes, F.C., Kirwan, K., Lehane, D., Coles, S.R., 2017. Epoxy resin blends and composites
615 from waste vegetable oil. *Euro. Polym. J.* 89, 449-460.
- 616
- 617 Fouassier, J.P., Lalevee J., 2012. Photoinitiators for polymer synthesis: scope, reactivity and
618 efficiency. (1st ed). Wiley., Weinhein.

619

620 Gaglieri, C., Alarcon, R.T., de Moura, A., Mendes, R.A., Caires, F.J., 2019. Is
621 Thermogravimetry an efficient alternative to gas chromatography in degree of biodiesel
622 conversion?. *J. Therm. Anal. Calorim.* 135, 2591-2597.

623

624 Guillén, M.D., Ruiz, A., 2003. Rapid simultaneous determination by proton NMR of
625 unsaturation and composition of acyl groups in vegetable oils. *Eur. J. Lipid. Sci. Technol.* 105,
626 688-696.

627

628 Grupioni, C.M.F., Santos, F.L., Velloso, N.S., Valente, D.S.M., Pinto, F.A.C., 2020. Macaw
629 palm supply chain: Evaluation of a semi-mechanized fruit harvesting system. *Ind. Crop. Prod.*
630 151, 112444.

631

632 Hu, F., Yadav, S.K., La Scala, J.J., Sadler, J.M., Palmese, G.R., 2015. Preparation and
633 Characterization of Fully Furan - Based Renewable Thermosetting Epoxy - Amine Systems.
634 *Macromol. Chem. Phys.* 216, 1441-1446.

635

636 Janvier, M., Hollande, L., Jaufurally, A.S., Pernes, M., Ménard, R., Grimaldi, M., Beaugrand,
637 J., Balaguer, P., Ducrot, P., Allais, F., 2017. Syringaresinol: A Renewable and Safer Alternative
638 to Bisphenol A for Epoxy-Amine Resins. *ChemSusChem.* 10, 738-746.

639

640 Kim, J.R., Sharma, S., 2012. The development and comparison of bio-thermoset plastics from
641 epoxidized plant oils. *Ind. Crop. Prod.* 36, 485-499.

642

643 Kristufek, S.L., Yang, G., Link, L.A., Rohde, B.J., Robertson, M.L., Wooley, K.L., 2016.
644 Synthesis, Characterization, and Cross-Linking Strategy of a Quercetin-Based Epoxidized
645 Monomer as a NaturallyDerived Replacement for BPA in Epoxy Resins. *ChemSusChem.* 9,
646 2135-2142.

647

648 Kogawa, N.R.A., Arruda, E.J., Micheletti, A.C., Matos, M.F.C., de Oliveira, L.C.S., de Lima,
649 D.P., Carvalho, N.C.P., de Oliveira, P.D., Cunha, M.C., Ojeda, M., Beatriz, A., 2015. Synthesis,
650 characterization, thermal behavior, and biological activity of ozonides from vegetable oils. *RSC*
651 *adv.* 5, 65427-65436.

652

- 653 Kousaalya, A.B., Beyene, S.D., Gopal, V., Ayalew, B., Pilla, S., 2018. Green epoxy synthesized
654 from *Perilla frutescens*: A study on epoxidation and oxirane cleavage kinetics of high-linolenic
655 oil. *Ind. Crops Prod.* 123, 25-34.
656
- 657 Kumar, S., Samal, S.K., Mohanty, S., Nayak, S.K., 2017. Epoxidized Soybean Oil-Based
658 Epoxy Blend Cured with Anhydride Based Cross-Linker: Thermal and Mechanical
659 Characterization. *Ind. Eng. Chem. Res.* 56, 687-698.
660
- 661 Lathi, P.S., Mattiasson, B., 2007. Green approach for the preparation of biodegradable lubricant
662 base stock from epoxidized vegetable oil. *Appl. Catal.* 69, 207-212.
663
- 664 Maffini, V.M., Rubin, B.S., Sonneschein, C., Soto, A.M., 2006. Endocrine disruptors and
665 reproductive health: The case of bisphenol-A. *Molec. Cellu. Endocr.* 254, 179-186.
666
- 667 Mahendran, A.R., Aust, N., Wuzella, G., Kandelbauer, A., 2012. Synthesis and characterization
668 of a bio-based resin from linseed oil. *Macromol. Symp.* 311, 18-27.
669
- 670 Mohan, P., 2013 A critical review: The modification, properties, and applications of epoxy
671 resins. *Polym. Plast. Tech. Engin.* 52, 107-125.
672
- 673 Moraes, C., Anjos, J.L.V., Maruno, M., Alonso, A., Rocha-Filho, P., 2018. Development of
674 lamellar gel phase emulsion containing baru oil (*Dipteryx alata* Vog.) as a prospective delivery
675 system for cutaneous application. *Asian J. Pharm. Sci.* 13, 183-190.
676
- 677 Muturi, P., Wang, D., Dirlikov, S., 1994. Epoxidized vegetable oils as reactive diluents I.
678 Comparison of vernonia, epoxidized soybean and epoxidized linseed oils. *Progres. Polym.*
679 *Coat.* 25, 85-94.
680
- 681 Nicolau, A., Samios, D., Piatnick, C.M.S., Reiznautt, Q.B., Martini, D.D., Chagas, A.L., 2012.
682 On the polymerization of the epoxidized biodiesel: The importance of the epoxy rings position,
683 the process and the products. *Euro. Poly. J.* 48, 1266-1278.
684
- 685 Oliveira, M., 2016. Óleo para o biodiesel. *Pesquisa FAPESP.* 245, 68-71. 2016
686
- 687 Oliveira-Alves, S.C., Pereira, R.S., Pereira, A.B., Ferreira, A., Mecha, E., Silva, A.B., Serra,
688 A.T., Bronze, M.R., 2020. Identification of functional compounds in baru (*Dipteryx alata* Vog.)

- 689 nuts: Nutritional value, volatile and phenolic composition, antioxidant activity and
690 antiproliferative effect. *Food. Res. Inter.* 131, 109026.
- 691
- 692 Panchal, T.M., Patel, A., Chauhan, D.D., Thomas, M., Patel, J.V., 2017. A methodological
693 review on bio-lubricants from vegetable oil based resources. *Renew. Sust. Energ. Review.* 70,
694 65-70.
- 695
- 696 Park, S., Jin, F., Lee, J., 2004. Synthesis and Thermal Properties of Epoxidized Vegetable Oil.
697 *Macromol. Rapid Commun.* 25, 724-727.
- 698
- 699 Perdue, R.E., Carlson, K.D., Gilbert, M.G., 1986. *Vernonia galamensis*, Potential New Crop
700 Source of Epoxy Acid. *Econom. Botan.* 40, 54-68.
- 701
- 702 Pires, O.A.B., Alarcon, R.T., Gaglieri, C., Silva-Filho, L.C., Bannach, G., 2019. Synthesis and
703 characterization of a biopolymer of glycerol and macadamia oil. *J. Therm. Anal. Calorim.* 137,
704 161-170.
- 705
- 706 Pires, T.P., Souza, E.S., Kuki, K.N., Motoike, S.Y., 2013. Ecophysiological traits of the macaw
707 palm: A contribution towards the domestication of a novel oil crop. *Ind. Crops Prod.* 44, 200-
708 210.
- 709
- 710 Ramos, L., Martin, L.S., Santos, J.C., de Castro, H.F., 2016. Combined Use of a Two-Stage
711 Packed Bed Reactor with a Glycerol Extraction Column for Enzymatic Biodiesel Synthesis
712 from Macaw Palm Oil. *Ind. Eng. Chem. Res.* 56, 1-7.
- 713
- 714 Reis, M.A., Novaes, R.D., Baggio, S.R., Viana, A.L.M., Salles, B.C.C., Duarte, S.M.S.,
715 Rodrigues, M.R., Paula, F.B.A., 2018. Hepatoprotective and Antioxidant Activities of Oil from
716 Baru Almonds (*Dipteryx alata* Vog.) in a Preclinical Model of Lipotoxicity and Dyslipidemia.
717 *Evid. Complem. Alter. Med.* 2018, 83766081.
- 718
- 719 Ribeiro, J.S., Celante, D., Simões, S.S., Bassaco, M.M., da Silva, C., de Castilhos, F., 2017.
720 Efficiency of heterogeneous catalysts in interesterification reaction from macaw oil
721 (*Acrocomia aculeata*) and methyl acetate. *Fuel.* 2017, 499-505.
- 722
- 723 Salih, A.M., Ahmad, M.B., Ibrahim, N.A., Dahlan, K.Z.H.M., Tajau, R., Mahmood, M.H.,
724 Yunus, W.M.Z.W., 2015. Synthesis of Radiation Curable Palm Oil-Based Epoxy Acrylate:
725 NMR and FTIR Spectroscopic Investigations. *Molec.* 20, 14191-14211.

726

727 Samuelsson, J., Sundell, P., Johansson, M., 2004. Synthesis and polymerization of a radiation
728 curable hyperbranched resin based on epoxy functional fatty acids. *Progres. Organ. Coat.* 50,
729 193-198.

730

731 Sano, S.M., Ribeiro, J.F., Brito, M.A., 2004. *Baru: biologia e uso*, first ed. EMBRAPA
732 Cerrados-Brazil. Planaltina.

733

734 Santiago, D., Guzman, D., Ramis, X., Ferrando F., Serra, A., 2020. New Epoxy Thermosets
735 Derived from Clove Oil Prepared by Epoxy-Amine Curing. *Polym.* 12, 44.

736

737 Schelemmer, D., Sales, M.J.A., 2010. Thermoplastic starch films with vegetable oils
738 of Brazilian Cerrado. *J. Therm. Anal. Calorim.* 99, 675-679.

739

740 Silva, W.C., Teixeira, L.F., Carvalho, A.K.F., Mendes, A.A., de Castro, H.F., 2014. Influence
741 of feedstock source on the biocatalyst stability and reactor performance in continuous biodiesel
742 production. *J. Ind. Eng. Chem.* 20, 881-886.

743

744 Thompson, A.E., Dierig, D.A., Kleiman, R., 1994. Variation in *Vernonia galamensis* flowering
745 characteristics, seed oil and vernolic acid contents. *Ind. Crops Prod.* 3, 175-183.

746

747 Tian, Y., Wang, Q., Shen, L., Cui, Z., Kou, L., Cheng, J., Zhang, J., 2020. A renewable
748 resveratrol-based epoxy resin with high T_g, excellent mechanical properties and low
749 flammability. *Chem. Engin. J.* 383, 123124.

750

751 Vandenberg, L.N., Maffini, V.M., Sonnenschein, C., Rubin, B.S., Soto, A.M., 2009. Bisphenol-
752 A and the Great Divide: A Review of Controversies in the Field of Endocrine Disruption.
753 *Endocr.Review.* 30, 75-95.

754

755 Xin, J., Zhang, P., Huang, K., Zhang, J., 2014. Study of green epoxy resins derived from
756 renewable cinnamic acid and dipentene: synthesis, curing and properties. *RSC Adv.* 4, 8525-
757 8532.

758

759 Wurm, F., Niebrle, J., Frey, H., 2008. Synthesis and characterization of poly(glyceryl-glycerol)
760 block copolymers. *Macromol.* 41, 1909-1911.

761

762 Yan, M., Frank, E.M., Cochran, E.R., 2018. Effects of Vegetable Oil Composition on
763 Epoxidation Kinetics and Physical Properties. *J. Am. Oil Chem. Soc.* 95, 209-216.

764

765 Yang, L., Dai, H., Yi, A., Lin, B., Li, G., 2008. Structure and properties of partially epoxidized
766 soybean oil. *J. Therm. Anal. Calorim.* 93, 875-879.

767

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769 **Figures captions**

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

771

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

773 **Fig. 3.** ¹H-NMR spectra for (a) BO and (b) BO-E.

774 **Fig. 4.** ¹³C-NMR spectra for (a) BO and (b) BO-E.

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

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

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

778

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

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

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