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1 **Synthesis and characterisation of bio-based polyester materials**
2 **from vegetableoil and short to long chain dicarboxylic acids.**

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10

11 **Abstract**

12 Polyester-type polymers were efficiently prepared from broccoli seed oil and
13 severalcarboxylic diacids. The polyesters were prepared through a simple two-step
14 process including oxidation of the insaturations to oxiranes followed by ring opening
15 with dicarboxylic acids under basic conditions. Eight polymer materials derived from
16 different fatty diacids (from 5C to 16C) and an aromatic diacid were prepared and
17 characterised. Rubber-type crosslinked biobased materials exhibited low Tg values
18 comprised between -5 and +5°C depending on the diacid type and length. These
19 materials could find applications as they are or as plasticizer when blended with other
20 polymers.

21 *Keywords:* Bio-based polyesters; epoxidation; epoxidized vegetable oil; broccoli seed oil

22 **1. Introduction**

23 The production of bio-based material is an increasing field of research that aims
24 to replace non-renewable sourced polymers.(Belgacem and Gandini, 2008; Biermann et
25 al., 2011; Chernykh et al., 2013; Meier, 2014; Meier et al., 2007; Montero de Espinosa

26 and Meier, 2011; Mutlu and Meier, 2010; Stempfle et al., 2014; Xia et al., 2013) Vegetable
27 oils are remarkable renewable resources particularly abundant and cheap. Among them
28 soybean oil is the subject of numerous research topics dealing with applications in
29 polymer material. Indeed, soybean oil finds applications as lubricant, plasticizer or as
30 other types of additives for polymer materials. (Altuna et al., 2011; Chernykh et al., 2013;
31 Montero de Espinosa et al., 2014) Few examples describe also the use of vegetable oil for
32 the preparation of polymer material through direct polymerisation of modified
33 oils. (Maisonneuve et al., 2013; Stemmelen et al., 2011; Tan and Chow, 2010; Winkler
34 and Meier, 2014; Yang et al., 2014) Usually, strategies developed so far for
35 polymerisation of soybean or linseed oils involved multistep triglyceride modification
36 ended by the key polymerisation step. (Biermann et al., 2011; Ma et al., 2013; Stempfle et
37 al., 2014) The most promising strategies involve shorter processes mainly based on
38 anhydride-curing (España et al., 2012; Espinoza-Perez et al., 2011; Ručigaj et al., 2014;
39 Samper et al., 2012) or acid-curing (Shogren et al., 2004; Shogren, 1999) of epoxidised
40 vegetable oil. The present research work focuses on this field with three main goals: 1)
41 Finding new non-food applications for vegetable oils, 2) Developing a polymerisation
42 process leading to potentially biodegradable (Shogren et al., 2004; Shogren, 1999; Yang
43 et al., 2014) polyester-type materials compatible with the use of curing agents of various
44 structures and 3) Determine the influence of the structure of the curing agent used in
45 the polymerisation process. Our choice towards broccoli seed oil (BO) showed up
46 several advantages. This oil is a by-product produced by an extraction process of the food
47 complement industry. (Audic et al., 2014) Its production is actually about 2 tons per year
48 but it could rapidly increase up to 20 tons per year in a near future. The broccoli seed oil
49 is useless for human food industries considering its high erucic acid content (39%).
50 Thus, there is no ethical issue to use such broccoli oil in non-food applications. Broccoli

51 seed oil is also particularly rich in diunsaturated fatty chains such as linoleic and
52 linolenic acid (22%); in addition it contains an average of 3.9 double bonds per
53 triglycerides as determined by NMR in a previous paper. (Audic et al., 2014)

54 The polymerisation process described hereafter involves a two-step procedure: a
55 classical oxidation of the double bonds to epoxides and crosslinking by epoxide-opening
56 with dicarboxylic diacids in basic media. Diacids were preferred to anhydrides because
57 of their high availability at low cost and in various molecular structures. Indeed several
58 carboxylic diacids were evaluated, 7 fatty diacids (C5, C6, C8, C10, C12, C14, C16) and 1
59 aromatic diacid (*o*-phenylene diacetic acid). The efficiency of the chemical reaction
60 involved in the polyester synthesis, i. e. the ring opening reaction of oxirane with
61 carboxylic acid was confirmed by NMR and ATR-FTIR analyses. Corresponding polymer
62 materials were characterised by DMA (Dynamic Mechanical Analysis) demonstrating the
63 potential of these polyester materials and determining the influence of the nature of the
64 diacid (length, structure).

65 **2. Material and methods.**

66 **2.1. Synthesis.**

67 All reagents and solvents were used directly from the supplier without further
68 purification unless noted. Nuclear magnetic resonance spectra were recorded at 400
69 MHz (¹H) and 100 MHz (¹³C). For CDCl₃ solutions, the chemical shifts (δ) are reported as
70 parts per million (ppm) referenced to the appropriate residual solvent peak. Coupling
71 constants are reported in Hertz (Hz). Data are reported as follows: chemical shift
72 (multiplicity, coupling constants where applicable, number of hydrogen atoms,
73 attribution). Abbreviations are as follows: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet),
74 *dd* (doublet of doublet), *dt* (doublet of triplet), *m* (multiplet), *bs* (broad singlet). The
75 NMR peak assignments were determined from 2D NMR experiments such as COSY,

76 HSQC, HMBC. Mass spectra were performed on a MS-ESI spectrometer and are reported
77 as m/z . Masses are reported for the molecular ion $[M+Na]^+$.

78 2.1.1. Epoxidized Broccoli seed oil.

79 BO (300 g, 0.32 mol, 1 equiv.), toluene (1.4 L) and formic acid (24 mL, 0.64 mol, 2
80 equiv.) were mixed into a well-stirred reactor. Hydrogen peroxide (35% wt in water)
81 (143 mL, 1.91 mol, 6 equiv.) was added dropwise to the reaction mixture at 50°C. The
82 reaction mixture was kept at the same temperature and monitored by MS-ESI. After 25h,
83 the aqueous phase was extracted twice with toluene and the combined organic phases
84 were dried ($MgSO_4$). The solvent was then evaporated under reduced pressure affording
85 the EBO (319 g, 99%). 1H NMR ($CDCl_3$, 400 MHz), δ (ppm) 0.79-1.01 (m, 9H, CH_3), 1.18-
86 1.77 (m, 86H, CH_2), 2.22-2.27 (m, 6H, $CH_2-C=O$), 2.82-3.15 (m, 7.8H (3.9 epoxides
87 per/molecule), epoxides), 4.07 (dd, $J = 5.9, 11.9$ Hz, 2H, CH_2-O), 4.22 (dd, $J = 4.4, 11.9$ Hz,
88 CH_2-O), 5.17-5.22 (m, 1H, $CH-O$); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm) 14.0 (CH_3), 22.6
89 (CH_2), 24.8 (CH_2), 26.6 (CH_2), 27.9 (CH_2), 28.9-29.7 (CH_2), 31.9 (CH_2), 34.0 ($CH_2-C=O$),
90 54.1 (epoxides), 56.7-57.2 (epoxides), 62.1 (CH_2-O), 68.9 ($CH-O$), 172.8-173.3 ($C=O$);
91 MS-ESI m/z $[M+Na]^+$: 927.8, 941.8, 955.8, 969.8, 983.8, 997.8, 1011.8, 125.8, 1039.8,
92 1053.8, 1067.9, 1081.9, 1095.8.

93 2.1.2. Reaction of EBO with benzoic acid.

94 EBO (1.0 g, 1.0 mmol, 1 equiv.) was dissolved in toluene (7 mL). Benzoic acid
95 (244 mg, 2.0 mmol, 2 equiv.) and MeONa (5.4 mg, 0.1 mmol, 0.1 equiv.) were added and
96 the reaction mixture was heated to 110°C. After 96h, AcOEt (10 mL) was added and the
97 reaction mixture was washed with NaOH 1M (2x10 mL) and HCl 1M (10 mL). The
98 organic phase was dried over $MgSO_4$ and the solvents were removed under reduced
99 pressure. The product was obtained as a yellow oil (1.2 g) with a benzoic acid
100 incorporation of 1.35 per molecule. 1H NMR ($CDCl_3$, 400 MHz), δ (ppm), 0.77-0.85 (m,

101 9H); 0.97-1.74 (*m*, 95H); 2.22-2.28 (*m*, 6H); 2.83-3.13 (*m*, 3.16H); 3.33-3.50 (*m*,
102 0.42H); 3.53-3.64 (*m*, 1.11H); 3.73-4.02 (*m*, 0.49H); 4.06 (*dd*, *J*=5.9Hz, *J*=11.6Hz, 2H);
103 4.21 (*dd*, *J*=4.4Hz, *J*=11.6Hz, 2H); 5.02 (*m*, 1.15H); 5.17 (*p*, *J*=5.2Hz, 1H); 5.40-5.49 (*m*,
104 0.36H); 7.38 (*t*, *J*=7.2Hz, 3.2H); 7.50 (*t*, *J*=7.2Hz, 1.6H); 7.98 (*d*, *J*=7.6Hz, 3.2H); ¹³C NMR
105 (CDCl₃, 100 MHz), δ (ppm) 14.2, 21.0, 22.5-22.7, 24.8, 25.3, 25.5, 26.6, 27.8, 29.0-29.7,
106 30.7, 31.8, 33.7, 34.0, 34.1, 54.2, 54.3, 57.2, 60.4, 62.1, 68.9, 72.7, 128.4, 129.7, 130.0,
107 133.0, 165.9, 166.4, 172.8, 173.3; MS-ESI *m/z* [M+Na]⁺: 927.8, 941.8, 955.8, 969.8,
108 983.8, 997.8, 1011.8, 1025.8, 1039.8, 1049.8, 1053.8, 1063.8, 1067.9, 1077.8, 1081.8,
109 1091.8, 1095.8, 1105.8, 1119.8, 1133.8, 1147.8, 1161.8, 1171.8, 1175.8, 1185.8, 1189.8,
110 1199.8, 1203.8, 1213.8, 1217.8, 1227.8, 1241.8, 1255.8, 1283.8, 1297.8, 1311.8, 1325.8,
111 1339.8.

112 2.1.3. General Procedure for the reaction of EBO with diacid.

113 EBO (3.0 g, 3.0 mmol, 1 equiv.), diacid (6.0 mmol, 2 equiv.) and MeONa (16 mg,
114 0.3 mmol, 0.1 equiv.) were homogenised at 120°C or at the melting temperature of the
115 diacid. The reaction mixture was poured into an aluminium mould. The aluminium
116 mould was then kept at the same temperature into an oven for 16h. The sample was
117 then characterised by ATR-FTIR and DMA.

118 2.2. Characterisation of polymer materials

119 2.2.1. ATR-FTIR.

120 For IR spectroscopy a Perkin-Elmer Spectrum 100 system infrared spectrometer
121 was used in attenuated total reflectance (ATR) mode using a DTGS detector (4 cm⁻¹
122 resolution) with the spectral range of 650–4000 cm⁻¹. In these measurements 15 scans
123 were applied and the data were collected and analysed using the Spectrum ES 5.0
124 software. The sample is placed onto the surface of a diamond prism and the infrared
125 radiation is collected after total reflection from the diamond–sample interface.

126 2.2.2. DMA.

127 The viscoelastic properties of the cured films were measured with a DMA
128 instrument (Q800, TA Instruments). Rectangular specimens, 18 mm in length, 13 mm in
129 width and 2 mm in thickness, were prepared. The measurements were taken in single
130 cantilever mode at a frequency of 1 Hz and at deformation amplitude of 20 μm . The
131 temperature ranged from -100 to 100°C at scanning rate of 3°C.min⁻¹. The storage
132 modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) of the cured films were measured
133 as a function of the temperature.

134 3. Results and discussion.

135 3.1. Epoxidized broccoli seed oil (EBO)

136 The epoxidation of the broccoli seed oil (BO) has been described by our research
137 group in a previous paper.(Audic et al., 2014)It follows a classical procedure involving
138 the *in situ* formation of performic acid from formic acid and hydrogen peroxide that
139 carried out the epoxidation of the 3.9 double bonds of the triglyceride in toluene
140 (Scheme 1). We further optimised the oxidation process reducing the equivalencies of
141 hydrogen peroxide(6 equiv./BO) and catalytic formic acid (2 equiv./BO). The reaction
142 mixture is kept at 50°C for 24h to reach a complete epoxidation as demonstrated by MS
143 and NMR monitoring.

144 3.2. Model reaction with a monoacid

145 The so-formed epoxidised broccoli seed oil (EBO) was then ready to react with
146 carboxylic acid functions through an epoxide-opening mechanism. This reaction was
147 first evaluated with a monoacid model for establishing the best reaction conditions in
148 terms of reactivity and reduction of side reactions. The EBO was put in reaction with
149 benzoic acid in the presence of a catalyst at 100°C (Scheme 2). A bronsted acid (*p*-
150 toluene sulfonic acid, PTSA), a lewis acid (ZnCl₂) and a base (MeONa) were evaluated

151 and the results are gathered in table 1. NMR analysis permitted to follow both the
152 formation of the new ester bonds and the consumption of the epoxides.

153 When using 4 equivalents of benzoic acid, the bronsted acid gave in 4h (Entry 1) the best
154 conversion in ester derivative (0.40) compared to the lewis acid (Entry 2, 0.30) and the
155 MeONa (Entry 3, 0.20). Concerning the selectivity of the reaction, the sum of ester
156 functions formed and of the remaining epoxide should correspond to the original
157 number of epoxides (3.9) if the desired ester linkage formation is the sole reaction.
158 Otherwise all extra-consumed epoxides result from side reactions. This criterion in
159 mind, the $ZnCl_2$ is considered as the worst catalyst and MeONa as the best one promoting
160 almost no side reaction. Increasing the reaction time to 24h (Entry 4, 5, 6) confirmed the
161 tendency of PTSA to perform side reactions instead of the formation of ester functions
162 both in the presence of 2 or 4 equivalents of benzoic acid. Finally MeONa was found to
163 favour the formation of ester linkages instead of other side reactions. The best results
164 were obtained with MeONa. The use of only 0.1 equiv. of catalyst in the presence of 2
165 equiv. of benzoic acid provided in 24h an average of ester functions of 1.35 (maximum of
166 2) and 2.58 remaining epoxides, corresponding to a conversion of 68%. It is noteworthy
167 that the catalytic amount of MeONa did not lead to methanolysis of the triglyceride as
168 observed on the 1H NMR spectra (fig. 1). The acid-base reaction between MeONa and the
169 benzoic acid is in fact faster than the alcoholysis.

170 Side reactions were noticed when using acidic catalysts. EBO dimers and trimers were
171 observed on SEC chromatograms (data not shown). Their formation was correlated to the
172 formation of ether linkages between triglycerides as determined by 1H NMR
173 experiments. Other research groups dealing with other epoxidized vegetable oils have
174 already described such oligomerisation side reactions. (Shogren, 1999) Note that this
175 acid promoted etherification is also observed in the absence of carboxylic acid.

176 Compared to these previous works, the reaction conditions described herein the
177 presence of catalytic MeONa provide an advantageous esterification process without
178 side reaction.

179 **3.3. Crosslinking with glutaric acid as model dicarboxylic acid**

180 The best reaction conditions obtained with benzoic acid were adapted to the
181 crosslinking step with dicarboxylic acids (Scheme 3). Bulk type polymerisation was
182 selected removing any solvent, homogenisation of the dicarboxylic acid and the MeONa
183 within the EBO being enough to promote a homogeneous crosslinking of the
184 triglycerides.

185 As a starting polymerisation experiment glutaric acid and EBO were engaged.
186 Impacts of the reaction temperature (Table 2, Entries 1-6) and the diacid/EBO ratio
187 (Table 2, Entries 7-12) after 4 or 16h of heating were evaluated. Reaction mixtures
188 incorporating an EBO/glutaric acid molar ratio 1:2 (i.e. COOH/epoxide ratio 1:1) were
189 placed at 60, 80, 100, 120, 140, 160 °C in the presence of 0.1 equiv. of MeONa. After 4h,
190 each sample presented different appearance ranging from colourless liquid to brown
191 hard materials. This study at variable temperature led to the following conclusions: the
192 reaction needs to be performed at temperature over 80°C and a
193 suitable polymerisation in 4h is obtained at 120°C, leading to a yellowish translucent
194 polymer. It is noteworthy that this temperature permitted to fully melt the glutaric acid
195 (Mp = 98°C) facilitating its homogenisation within the EBO. Obviously, the EBO/glutaric
196 acid ratio has also a profound impact on the final appearance of the polymers. At that
197 stage the reaction time was increased to 16h to assure as far as possible a complete
198 polymerisation. Too small quantities (0.25, 0.5 equiv., entries 7-8) of glutaric acid did
199 not provide sufficient crosslinking leading to liquid or partly gel-type materials. One
200 equivalent of diacid (entry 9) provided poor crosslinking and offered a brittle polymer

201 material. Excess of diacid (4 or 6 equiv., entries 11, 12) promoted unsatisfactory
202 crosslinking, the reaction led to a sticky polymer material (4 equiv.) and to a sticky paste
203 (6 equiv.). The excess of carboxylic acid functions limited the crosslinking process to
204 oligomers, keeping most of the acid function untouched. Two equivalents of glutaric acid
205 were finally the best EBO/diacid ratio affording a translucent yellowish polymer (Entry
206 10).

207 At a molecular level, ^1H NMR analysis were carried out for samples obtained with
208 0.5 equiv. of glutaric acid (Table 2, entry 8) the other sample (1, 2, 4, 6 equiv., entries 9-
209 12) being insoluble in any common solvent tried (CHCl_3 , THF, toluene...). The NMR data
210 confirmed both the formation of new ester linkages and subsequent alcohol functions
211 (new signals at 4.9 ppm and 3.5 ppm). It also demonstrated that the integrity of the
212 triglyceride structure is preserved. Quantitatively with 0.5 equiv. of diacid (1 COOH for
213 3.9 epoxides) we observed the formation of 0.74 (maximum of 1) new ester linkages and
214 2.6 remaining epoxides. The other reacted epoxides correspond to side reactions
215 identified by NMR to the formation of ether linkages (ring opening polymerisation of the
216 epoxide). After 16h of heating this side reaction is limited to only 0.56. Not observed for
217 the reaction carried out in solution (scheme 2) the formation of ether linkages is present
218 in bulk conditions. However, these reactions still have a lower rate compared to the
219 preferred polyester formation.

220 The results of the crosslinking step performed with 0.25 to 6 equivalents of
221 glutaric acid (Entry 7-12) were also analysed by ATR-FTIR spectroscopy. The stacked
222 spectra are shown in fig.2. Globally these spectra confirmed the results discussed above.
223 In more details two regions are interesting to discuss 1) the signals related to the
224 epoxide functions around 820 cm^{-1} and 2) the signals related to the carbonyl groups
225 between 1680 and 1750 cm^{-1} . Within the epoxide region, the poorly polymerised

226 material (0.25 equiv.) demonstrated the presence of residual epoxide functions, the
227 spectra being very similar to the original epoxidized oil. Increasing the number of
228 equivalent of diacid, the epoxide band disappears progressively until total
229 disappearance in the presence of 4 or 6 equivalents of diacid. Within the carbonyl region
230 (i.e. 1700 cm^{-1}), several bands are visible corresponding either to acid or ester functions.
231 Again this region is very similar to the EBO spectra for the material prepared with 0.25
232 equivalent of diacid. This band corresponds mainly to the ester function of the
233 triglyceride itself. Excess of diacid (4/6 equiv.) led to the appearance of a band at lower
234 wave numbers corresponding to residual carboxylic acid groups. The polymer material
235 obtained with 2 equiv. of glutaric acid presents two ester bands distinguished by
236 different intensities, which originate from the triglyceride and from the new ester
237 functions formed during the crosslinking process. Thus these ATR-FTIR analyses
238 confirmed the degree of polymerisation obtained as a function of the quantity of diacid
239 involved in the reaction. It also confirmed that our polymers correspond mainly to
240 polyester-type materials.

241 **3.4. Crosslinking with different dicarboxylic acids**

242 The best conditions determined for glutaric acid (2 equiv., 120°C , 0.1 equiv of
243 MeONa) were then applied to longer carboxylic diacids (C5, C6, C8, C10, C12, C14, C16)
244 and to o-phenylene diacetic acid (Scheme 3). The temperature of homogenisation was
245 adjusted for each sample as a function of the melting point of each diacid and all
246 polymerisation were carried out at 120°C for 16h (Table 3). Whatever the diacid used
247 the polymerisation led to a yellowish translucent material (Fig.3) except for the
248 aromatic derivative, which led to a brown translucent material.

249 All polyester materials were then characterised by DMA. Fig.4 shows representative
250 temperature dependence of the storage modulus (E') and loss factor ($\tan \delta$) obtained

251 from the dynamic mechanical analyses (DMA, at a frequency of 1Hz) of networks
252 prepared in this work (EBO/glutaric acid polyester shown). The $\tan \delta$ curve shows two
253 distinct peaks for all polyesters. The lower temperature peak, located at about -75°C , can
254 only be seen at a lower scale. It is associated with the secondary β relaxation, which was
255 already described in epoxy resins cured with anhydride. (Boquillon and Fringant, 2000)
256 This particular secondary relaxation corresponds to the first drop of the storage
257 modulus (fig.4) and can be more easily associated to the low temperature peak observed
258 on fig.5 representing the temperature dependence of loss modulus (E'') of EBO/glutaric
259 acid polyester. This secondary β relaxation can be associated to the motion of the diester
260 segments created between two crosslinks. (Gerbase et al., 2002)

261 The second peak of $\tan \delta$ obtained at higher temperature, between -5 and 5°C (Fig.4),
262 corresponds to the second and biggest decrease of the storage modulus and to a
263 significant second peak of loss modulus just below 0°C . This major transition is
264 correlated to the α relaxation and associated to the glass transition temperature (T_g) of
265 the polymer. The α transition temperature is below 0°C (except for aromatic derivative),
266 indicating that polymers are in a rubbery state at room temperature. All data obtained by
267 DMA for all polyesters materials are gathered in Table 4. α and β relaxation temperatures
268 were recorded for each polyester sample from both $\tan \delta$ peaks and loss modulus peaks.

269 It can be first noticed that increasing diacid length from five to eight carbons first caused
270 a decrease in the α relaxation temperature: determined from $\tan \delta$ peak, this
271 temperature dropped from -1.4 to -4.4°C . From loss modulus data, this temperature also
272 noticeably dropped from -5.7 to -11.4°C . The decrease of the α transition temperature,
273 which corresponds to the glass transition temperature of the polymer could be ascribed
274 to an increase in chain mobility and free volume in the polymer as the diacid length

275 increased. Nevertheless, when the diacid length further increased from eight carbons to
276 sixteen carbons, the α relaxation temperature gradually increased from -4.4°C to $+4.4^{\circ}\text{C}$
277 ($\tan \delta$) or from -11.4°C to -2.6°C (loss modulus). It is well known that the crosslinks
278 length influences glass transition temperature. In the present study, for small diacids
279 with less than 8 carbons, the free volume of the material increased as the crosslinks
280 length increased and the glass transition temperature decreased correspondingly (fig.6).
281 For diacids with more than 8 carbons, the further increase in diacid length caused an
282 increase in glass transition temperature. This could be ascribed to the longer methylene
283 sequences in the diacids, leading to enhanced crystallinity and enhanced London
284 dispersion interactions, resulting in stronger restriction in mobility.(Stempfle et al.,
285 2014)This phenomenon is less clearly observed on the β relaxation temperature, but a
286 minimum was also recorded for suberic (C8) based polyester at -73°C ($\tan \delta$ peak) and -
287 77°C (loss modulus peak). When the polyester is synthesized from *o*-phenylene diacetic
288 acid, its α and β transitions temperature, $+16.2$ and -66°C respectively (from $\tan \delta$) are
289 significantly higher than those observed for previous linear diacids. This could be
290 correlated to the presence of aromatic crosslinks organising themselves into more rigid
291 segments.

292 **4. Conclusion**

293 This research work demonstrates that the polymerisation of vegetable oil can be
294 achieved following a two-step process from an extracted oil and aliphatic diacids. The
295 epoxidation/ring opening sequence was first optimised with benzoic acid and then the
296 best conditions (basic media) were applied to several diacids leading to the crosslinking
297 of the triglycerides. It provides an access to original polyester materials not
298 acquirable with other polymerisation strategies (anhydride curing for instance). The
299 conversion of the useless broccoli seed oil to polymer material constitutes therefore a

300 valuable use of such non-food triglycerides. All polyesters synthesised here were in
301 rubbery state at room temperature because of their relatively low glass transition
302 temperature and they present interesting mechanical properties for numerous
303 applications. It was thus demonstrated that glass transition temperatures (T_g) and also,
304 to a lesser extend, secondary (β) relaxations in the cured polyesters were closely related
305 to the nature and the length of the diacid used in the crosslinking reaction.

306 Such new kind of green polymers could find numerous applications in the
307 manufacture of environmentally friendly soft and flexible materials. For example, they
308 can be blended with some other polymers in order to decrease their T_g through
309 “permanent” plasticization. On the basis of epoxide ring opening reaction described in
310 this paper, it will be possible to prepare new cured polymers involving other bi-
311 functional (or more) crosslinking agents. Some new additives could also be prepared
312 from epoxidised broccoli oil functionalization. Also it must be noticed that all the
313 chemical modifications and polymerisation processes described in this paper can be
314 applied to other type of oil.

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