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Maëlle Gobin,[a,b]**Patrick Loulergue,**[a,b]**Jean-Luc Audic,***[a,b] **and Loïc Lemiègre***[a,b]

a) Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France.

b) Université Européenne de Bretagne, France.

[*] Corresponding author. Tel. : +33 223238160 ; Fax. +33 223238199

E-mail adress: jean-luc.audic@univ-rennes1.fr

Abstract

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

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

1. Introduction

The production of bio-based material is an increasing field of research that aims to replace non-renewable sourced polymers.(Belgacem and Gandini, 2008; Biermann et 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 renewableresourcesparticularly 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 promisingstrategiesinvolve shorter processesmainly 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 researchwork focuseson this field with threemain goals: 1)

41 Finding new non-food applicationsfor vegetable oils, 2) Developinga polymerisation

42 process leading topotentially biodegradable(Shogren et al., 2004; Shogren, 1999; Yang

43 et al., 2014)polyester-type materialscompatible with the use ofcuring 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-productproducedbyan 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 richin diunsaturated fatty chains such as linoleic and

52 linolenic acid (22%); in addition it contains an average of 3.9double 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 (^{1}H) and 100 MHz (^{13}C). For CDCl$_3$ 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%). ^{1}H 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, CH2-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. ^{1}H 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); ^{13}C NMR

105 (CDCl$_3$, 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 δ) 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 (ZnCl$_2$) 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 onepromoting

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 ^{1}H NMR spectra (fig. 1). The acid-base reaction between MeONa and the

169   benzoic acid is in fact faster than the alcoholysis.

170   Side reactionswere noticed when using acidic catalysts. EBO dimers and trimers were

171   observed on SEC chromatograms(data not shown). Their formation was correlatedto the

172   formation of ether linkages between triglycerides as determined by ^{1}H NMR

173   experiments. Other research groups dealing with other epoxidized vegetable oils have

174   already describedsuch 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 EBOwere 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 appearanceranging 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 suitablepolymerisationin 4his 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, ^{1}H 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 showsrepresentative

250 temperature dependence of the storage modulus (E') and loss factor (tan δ) 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 δ 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 βrelaxation, which was

255 already described in epoxy resins cured with anhydride.(Boquillon and Fringant, 2000)

256 This particular secondary relaxationcorresponds 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. Thissecondary 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 δ 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 (Tg) 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 materialsaregathered in Table 4. α and β relaxation temperatures

268 were recorded for each polyester sample from both tan δ 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 δ 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°C

277 (tan δ) 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 cristallinity 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 δ peak) and -

287 77°C (loss modulus peak). When the polyester is synthetized from *o*-phenylene diacetic

288 acid, its α and β transitions temperature, +16.2 and -66°C respectively (from tan δ) 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 acquirablewith 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 (Tg) 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 Tg through

309   "permanent" plasticization. On the basis of epoxide ring opening reaction descried 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.

315   **Acknowledgements**

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