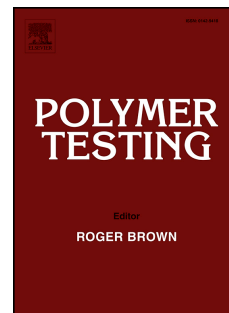


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Curing behavior and properties of high biosourced epoxy resin blends based on a triepoxy monomer and a tricarboxylic acid hardener from 10-undecenoic acid

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1 **Curing behavior and properties of high biosourced epoxy resin blends based on a**
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ABSTRACT

Renewable propane-1,2,3-triyl tris(9-(oxiran-2-yl) nonanoate) (EGU, 100 wt.% biogenic) and a tricarboxylic acid triglyceride (CGTU) hardener (85.7wt.% biogenic) were synthesized from 10-undecenoic acid (10-UDA) and used to produce epoxy resins with 52 – 92 wt.% biobased carbon. CGTU was prepared by thermally activated thiol-ene coupling of thioglycolic acid onto propane-1,2,3-triyl tris(undec-10-enoate), (GUD) in the absence of solvent. The characterized CGTU was used as a green hardener of blends based on EGU and a conventional bisphenol A-based epoxy pre-polymer (DGEBA) at various mass percentages (0 to 100 wt.%) with an stoichiometric epoxy/acid equivalent ratio. Calorimetric studies revealed higher peak temperature, lower reaction heats, and longer gelation times in resins with high EGU proportion, evidencing the lower reactivity of aliphatic EGU compared with aromatic DGEBA. Cured resins were yellowish transparent rubber-like materials with glass transition temperatures (T_g) varying from $-14\text{ }^\circ\text{C}$ to $-42\text{ }^\circ\text{C}$ and tensile strength in the range of 1750 kPa to 790 kPa, for 0 and 100 wt. % EGU, respectively. The soluble fraction of all resins was less than 4.3%, reflecting a high level of crosslinking. Thermosets with high biobased content showed both UV-light protection and visible light transparency.

KEYWORDS: EPOXY RESIN; 10-UNDECENOIC ACID; BIOMASS; CURING BEHAVIOR; PROPERTIES.

32 1. Introduction

33 Epoxy resins are one of the most versatile class of thermosetting polymers with a wide
34 range of industrial applications, such as coatings, adhesives and structural composites, owing
35 to their enhanced mechanical properties, excellent thermal resistance, and good processability
36 [1]. Epoxy thermosets account for almost 70 % of the thermosetting polymer market [2], and
37 their global market share was forecasted at USD 7.1 billion in 2014, and is projected to reach
38 USD 10.5 billion by 2020 [3]. Most of the commercially available bisphenol A-based epoxy
39 resins (BPA) are suspected of having potential health risks [4]. As a consequence, current
40 research is focused on the synthesis of building blocks derived from readily renewable
41 sources, including epoxidized oils, terpenes, itaconic acids, natural polyphenols, and sugars.
42 Progress in this area has extensively been reviewed [2,5–7].

43 Most of these green epoxy precursors are usually crosslinked with a variety of synthetic
44 curing agents. The traditional amine and anhydride-based crosslinking strategy has provided a
45 powerful tool to tailor the physical properties of epoxy resins [2,8–10]. Nonetheless, the
46 suspected toxicity of certain amines [11] and the potential skin sensitization and asthma
47 induced by some anhydrides [5,12] have brought their intensive use into question. Then
48 efforts have been concentrated in formulating biobased and more benign epoxy curing agents
49 [5,12–16]. Compared to renewable amines [13,17] and anhydrides [18,19], the use of
50 poly(carboxylic acids) as hardeners has been less explored, probably due to their secondary
51 reactions such as esterification, hydrolysis, and transesterification, as postulated by Matějka et
52 al., [20] in their seminal work. So far, few studies have dealt with the combination of
53 biobased epoxy and poly(carboxylic acid) hardeners. Naturally occurring citric acid (CA) has
54 been used as a curing agent of several vegetable oils including jatropha oil (JO) [21],
55 epoxidized cottonseed oil (ECS), and epoxidized algae oil (EAO) [22]. The curing reaction of
56 blends of bisphenol A-based epoxy pre-polymer (DGEBA) and epoxidized soybean oil (ESO)

57 cured with sebacic acid (SA) resulted slower than that of this same system with an amino-
58 based hardener, evidencing the lower reactivity of the carboxylic acid [23]. Epoxidized
59 linseed oil (ELO) was converted to flexible and transparent thermosets by crosslinking with
60 renewable dicarboxylic acids (DCAs) of different chain length, having the shorter diacid-
61 cured resin the higher T_g and better mechanical properties [24]. Zeng and coworkers [14–16]
62 produced a series of high performance sustainable epoxy resins based on ESO using
63 crystalline dicarboxyl-terminated oligomeric poly(butylene succinate), OPBS [14] and
64 polyamida 1010, NYL [15,16] as sustainable curing agents. Thermosets based on ESO/OPBS
65 and ESO/NYL (acid/epoxy equivalent ratio of 0.7 : 1) were crystalline, and crystallization and
66 crosslinking density were influenced by the chain length of the harder, resulting in bioresins
67 with enhanced thermal resistance, tensile strength, Young modulus and elongation at break
68 due to the restricted crosslinking density. By varying the acid/epoxy equivalent ratio (R-
69 value) between NYL 1010 oligomer and ESO, authors produced thermosets with controlled
70 chemical structures and tuned physical properties [16]. Epoxidized sucrose soyate is cured
71 with “blocked” naturally occurring dicarboxylic acids such as succinic, azelaic, 2,5-
72 furandicarboxylic and brassylic acid affording 100% biobased thermosets with excellent
73 adhesion and tunable hardness [25]. A polyacid achieved by the thiol-ene coupling (TEC) of
74 thioglycolic acid (THGA) onto soybean oil (SBO) demonstrated higher reactivity toward
75 DGEBA than other carboxylic acids did since the presence of sulfur atoms in β -position
76 increased proton activity, thereby reducing the curing time [26]. Similarly, poly(carboxylic
77 acid) monomers were prepared by UV-light mediated TEC of 3-mercaptopropionic acid onto
78 oleic acid, 10-undecenoic acid, and propane-1,2,3-triyl tris(undec-10-enoate) (GUD) and used
79 to afford fast degrading polyanhydride precursors [18].

80 In the present work, 10-undecenoic acid (10-UDA), a fatty acid derived from castor oil by
81 pyrolysis of its main constituent, ricinoleic acid [27], was selected as a valuable platform able

82 to provide monomers for epoxy precursors and hardeners with high biobased content. As
83 illustrated in Scheme 1, 10-UDA was first transformed into GUD by direct esterification with
84 glycerol. This ω -unsaturated triene precursor was converted into the three functional ω -epoxy
85 derivative, propane-1,2,3-triyl tris(9-(oxiran-2-yl)nonanoate (EGU) by treatment with
86 peracetic acid formed *in situ* [28] (Scheme 1). Epoxy resins based on EGU have previously
87 been reported, but in all cases, EGU was cured with synthetic amino or anhydride-based
88 crosslinking agents such as 4,4'-methylenedianiline (MDA) and phthalic anhydride (PA)
89 [8,28] or isophoronediamine (IPA) [10]. In this contribution and as an attempt to provide a
90 more environmentally sound hardener, a novel tricarboxylic acid-functionalized triglyceride
91 was prepared by introducing carboxylic acid moieties via TEC onto GUD (Scheme 1).
92 Furthermore, the renewable hardener was applied according to a stoichiometric epoxy/COOH
93 ratio to cure blends of EGU with variable amounts of synthetic DGEBA to produce high
94 renewable content epoxy resins. The influence of the precursors' structures on curing
95 behavior, thermal, mechanical and optical properties of the resin blends was investigated.

96 **Insert Scheme 1**

97

98 **2. Experimental section**

99 **2.1. Chemicals**

100 Bisphenol A-based epoxy pre-polymer, i.e., diglycidyl ether of bisphenol A (DGEBA)
101 (epoxide equivalent weight, EEW= 180 g/eq) was provided by Distraltec (Buenos Aires,
102 Argentina). 10-undecenoic acid (10-UDA, 95%), thioglycolic acid (THGA, >98%), glacial
103 acetic acid (>99%), p-toluene sulfonic acid (PTS, 99%), and toluene (99.8%) were all
104 purchased from Sigma-Aldrich (St. Louis, USA). Sodium bicarbonate (NaHCO_3), sodium
105 carbonate (Na_2CO_3), glycerol (Gly), hydrogen peroxide and anhydrous magnesium sulfate
106 (MgSO_4) were all p.a. grade and purchased from Anedra (Buenos Aires, Argentina).

107 2.2. Characterization.

108 Fourier Transform Infrared (FTIR) spectra (NaCl window or KBr pellet, depending on the
109 sample) of the precursors were registered using a Thermo-Scientific Nicolet 6700 (Wisconsin,
110 USA) spectrometer at room temperature, at a resolution of 1 cm^{-1} and between 4000 and 400
111 cm^{-1} .

112 Nuclear Magnetic Resonance (^1H and ^{13}C NMR) spectra were recorded using a Bruker AM
113 500 MHz spectrometer (Billerica, MA) at room temperature using CDCl_3 as solvent.
114 Chemical shifts (δ) are quoted in parts per million (ppm) downfield from tetramethylsilane
115 (TMS) as an internal reference. The heteronuclear single quantum coherence (HSQC) method
116 was used for spectral correlation with the structures.

117 Differential Scanning Calorimetry (DSC) measurements were performed using a differential
118 calorimeter Pyris (Perkin Elmer, Boston, USA) under nitrogen atmosphere (20 ml/min).
119 Reacting mixtures of EGU with appropriate amounts of DGEBA and stoichiometric amounts
120 of CGTU were mixed by hand at room temperature until homogeneous, immediately poured
121 into aluminum pans and subjected to a programmed temperature cycle: heating from -60 to
122 200 °C, rapid cooling and re-heat from -60 to 200 °C. Both heating cycles were run at 10
123 °C/min. Curing reaction parameters such as total enthalpy of curing (ΔH_c) and the peak
124 temperature of the exothermic peak (T_p) were calculated in the first run, while glass transition
125 temperature (T_g) was determined from the second heating.

126 Dynamic thermo-gravimetric analysis (TGA) was carried out using a thermo-balance TGA
127 Mettler Toledo SDTA 851 (Greifensee, Switzerland) from room temperature up to 900 °C at
128 10 °C/min and under nitrogen atmosphere (20 ml/min) to avoid oxidative reactions.

129 The soluble fraction was determined for specimens of the cured resins accurately weighed
130 using an analytical balance ($\pm 0.0001\text{ g}$, Ohaus, USA), placed in a pre-weighed cellulose
131 extraction thimble (obtained from Whatman) and sited in a Soxhlet extractor using toluene as

132 solvent. Extraction was performed for 24 h at a rate of five extractions/h. The resulting
133 solution was concentrated by the rotary evaporation of the solvent (Büchi, Switzerland). The
134 solid residue was collected by filtration and dried at reduced pressure for several hours before
135 being weighed in an analytical balance (± 0.0001 g, Ohaus, USA). Results are the average of
136 three measurements.

137 The approximate value of gelation time (t_{GEL}) was determined at different temperatures (80-
138 130 °C) using reactive mixtures contained in glass vials fitted with a thin wire thermocouple
139 and placed in a thermostat. Gel time was fixed as the time necessary for the wire to become
140 immobile [29].

141 Tensile tests were determined according to an ASTM D882 standard method at room
142 temperature using a miniature material tester MiniMat 2000 (Rheometric Scientific, NJ-
143 USA), provided with a load cell of 200 N and 30 mm between gaps. Strips (30 mm x 5 mm x
144 1 mm in thickness) were prepared and tested at room temperature (25 ± 2 °C) at a constant
145 crosshead speed of 3 mm/min. Young's modulus (E), tensile strength (TS) and elongation at
146 break (ϵ) were determined from the experimental stress-strain curves. At least nine specimens
147 were tested for each set of samples, and the average values are reported.

148 Mean thickness was measured for each specimen at five random locations with ± 0.001 mm
149 precision using a Vernier manual micrometer (Guangdong, China), and averaged.

150 Color parameters were assessed for 1 mm-thick films obtained in a similar fashion as those
151 for tensile testing using a portable Lovi Bond Colorimeter RT 500 (Amesbury, United
152 Kingdom), with a measuring area of 8 mm in diameter and recorded in a Hunter Lab color
153 scale.

154 Total transmittance (%) of the produced biobased resins (5 x mm x 5 mm x 1 mm) films was
155 examined using an Agilent 8453 UV-visible spectrophotometer (Shanghai, China).

156 The acid value (AV), iodine value (IV), hydroxyl value (OHV), and epoxy equivalent weight
157 (EEW) were assessed using AOCS CD 3D-63, AOCS JA 14-91 reapproved 2017, AOCS CD
158 13-60 reapproved 2017 and AOCS Cd 9-57 standard methods, respectively.

159 **2.3. Statistics**

160 One-way analysis of variance (ANOVA), along with the Tukey test for pair comparison, was
161 employed to examine differences between groups, with a significance of the difference set at
162 $\alpha < 0.05$.

163

164 **2.4. Synthetic procedures**

165 **2.4.1. Propane-1,2,3-triyl tris(9-(oxiran-2-yl)nonanoate (EGU)**

166 *Esterification step.* GUD was obtained by direct esterification of glycerol and 10-undecenoic
167 acid using a previously reported procedure [30,31]. Purified GUD was obtained as a yellowish
168 oily product (yield: 95 %, AV <0.5 meq/g sample, melting point: 3-5 °C).

169 *Epoxidation step.* Epoxidized GUD (propane-1,2,3-triyl tris(9-(oxiran-2-yl)nonanoate, EGU)
170 was prepared according to Milchert *et al.* (2009) [32], with variations. The peroxyacid reagent
171 was prepared by mixing glacial acetic acid (10 mol) and sulfuric acid (0.5 mol) in a three-
172 necked round-bottomed reaction flask equipped with a thermometer, a reflux condenser, and a
173 glass dropping-funnel. The reactor was placed in a cryostat at 4 °C. Then 30 wt.% hydrogen
174 peroxide solution (1 mol) was added drop-wise to the gently stirred mixture using a dropping-
175 funnel to prevent system overheating. After neutralizing with sodium acetate solution and
176 separation, the obtained solution was transferred to a dropping funnel connected to a four-
177 necked round-bottomed glass reactor equipped with a reflux condenser, a thermometer, an
178 inlet for collecting samples and containing GUD dissolved in toluene (100 mL) maintained at
179 0 °C in a cryostat. Freshly prepared peroxyacid was added drop-wise at a continuous flow rate
180 in order to prevent oxirane ring opening. The reaction temperature was monitored and

181 adjusted to $0\text{ }^{\circ}\text{C}\pm 1\text{ }^{\circ}\text{C}$. The course of the reaction was followed by iodine value (IV) on a
182 small fraction of the sample extracted at different times. After about 9 h, the reaction mixture
183 was cooled to ambient temperature and the organic layer was separated, washed with 10 %
184 w/V Na_2CO_3 solution until pH 7 and dried over anhydrous MgSO_4 . After filtering the
185 desiccant off, toluene was eliminated in a rotary evaporator. The EGU was recovered as light
186 yellow oil (yield: 89 %, melting point: $-10\text{ }^{\circ}\text{C}$, epoxy equivalent weight (EEW): 227 g/eq,
187 $\text{EEW}_{\text{theoretical}} = 213\text{ g/eq}$ and average epoxy functionality: 2.82, IV: 0.21).

188

189 **2.4.2. Propane-1,2,3-triyl tris(11-((carboxy-2-ylmethyl)thio)undecanoate (CGTU)**

190 The biobased hardener was obtained by thermally activated TEC, based on the strategy
191 reported elsewhere [26] with variations. GUD (20 g, 0.033 mol) was dissolved in a minimum
192 amount of chloroform and placed in a round-bottomed reaction flask previously purged with
193 dry nitrogen to eliminate oxygen during TEC. In parallel, THGA (12.4 mL, 0.116 mol) that
194 was also under dry nitrogen, was added to the GUD solution. The reaction mixture was
195 homogenized by magnetic stirring at 500 rpm, and the reactor was placed in a thermostat at 70
196 $^{\circ}\text{C}$. The reaction progress was followed by monitoring the evolution of the reaction heat with
197 time by DSC. After eight hours, no residual reaction heat was observed indicating the
198 completion of the reaction. Crude CGTU was recrystallized in acetone. Yield: 98%, AV: 3.36
199 meq KOH/g, average functionality: 2.94

200

201 **2.5. Preparation of cured resins**

202 Several blends were prepared by replacing EGU with synthetic DGEBA at different mass
203 ratios (10, 20, 50, 70, 100 % w/w). The weight of the epoxy components was calculated using
204 the EEW of EGU and DGEBA, and the amount of cross-linker required for a stoichiometric
205 ratio (ca. epoxy/COOH equivalent ratio = 1) was estimated from the acid equivalent weight

206 (AEW) of CGTU. All samples were prepared via a catalyst and solvent-free procedure. A
207 typical EGU-DGEBA 50:50 (w/w) was prepared by mixing manually EGU (1 g, 4.54 meq)
208 and DGEBA (1 g, 5.56 meq) in a thermostat held at 60 °C. Then the stoichiometric amount of
209 CGTU (2.93 g, 10.1 meq) was added, and the mixture was maintained at 60 °C (10 min
210 approx.). All formulations were transferred into molds manufactured from a rubber gasket
211 material (1 mm thick) sandwiched between two glass plates coated with anti-adherent paper.
212 The assembly positioned vertically was placed in a vacuum oven (Cole Palmer, Chicago,
213 USA) at 60 °C to eliminate the air bubbles entrapped in the bulk during mixing. Subsequently,
214 the reactive mixture was subjected to a two-step curing process selected according to
215 preliminary calorimetric studies: 80 °C for 1 h and then 130 °C for 4 h.

216

217 **3. Results and discussion**

218 **3.1. Characterization of biobased precursors**

219 Scheme 1 illustrates the synthetic pathway and the chemical structures of the biobased GUD,
220 EGU, and CGTU. All reactions were carried out under mild conditions, and the precursors'
221 structures were confirmed by chemical as well as spectroscopic analysis.

222

223 *3.1.1. GUD and EGU*

224 The conversion of 10-UDA into GUD was established by FTIR (Fig. 1, curves a and b). The
225 spectrum of 10-UDA exhibited characteristic absorption bands at 1710 cm⁻¹ (C=O stretching)
226 and 3500 cm⁻¹ (O-H stretching), specific to the carboxylic acid moiety, and at 1650 cm⁻¹ due
227 to terminal alkene stretching (Fig. 1, curve a). The reaction with glycerol resulted in the
228 formation of a new strong absorption band at 1740 cm⁻¹ (C=O stretching) related to the ester
229 group due to triglyceride formation and the loss of the bands associated with the carboxylic
230 acid group.

231 Insert Fig. 1

232 The HSQC of GUD (Figure 2 a) was characterized by the signals at δ 5.8 ppm and 4.9 ppm
233 representing the vinyl methyne and methylene protons, and those at δ 5.3 ppm and 4.1-4.3 due
234 to methyne and methylene protons of glycerol backbone, respectively, with a ratio of 1/3, in
235 accordance with data reported by others [9,33–35]. A complete resolution of ^1H NMR and
236 ^{13}C NMR spectra of GUD is available in the supplementary file. The signals at 62 and 68 ppm
237 in ^{13}C NMR (Fig. 2a) were assigned to the carbons of glycerol in a triglyceride structure. The
238 small but detectable signal at 65 ppm evidenced the presence of about 3 % of 1,3-diglyceride.
239 No monoglycerides were detected, as verified by the absence of signals at 70 ppm (Fig 2 a
240 and Fig. 2S) [35]. The resonances at 114 and 128 ppm indicated the presence of vinyl
241 carbons, while C=O due to glycerol esterification were found at 172-173 ppm.

242 Insert Fig. 2a and Fig. 2b

243 The conversion of the carbon-carbon double bonds to oxirane rings was achieved within 9 h at
244 0 °C [31]. The afforded product had the highest conversion of double bonds to oxirane, while
245 the opening of the newly formed epoxy (with the formation of glycols) was minimized.
246 Iodine number and hydroxyl index attained negligible values after purification (Table 1). The
247 disappearance of the peak at 1650 cm^{-1} due to C=C double bond, along with the appearance of
248 a new band at 846 cm^{-1} attributable to terminal epoxy groups [36], provides evidence for the
249 epoxidation reaction. In the HSQC of EGU (Fig. 2 b), the characteristic peaks due to
250 resonances of methyne and methylene protons of glycerol (5.3 ppm and 4.1-4.3 ppm, Fig. 2 a)
251 were preserved. The intensity of the peaks assigned to vinyl protons (5.8 ppm and 4.9 ppm,
252 Fig. 2 a) decreased significantly while new resonances appeared at 2.9 ppm and 2.7 ppm due
253 methyne and methylene protons bonded directly to the epoxy ring [28,34,37]. The presence of
254 vinyl protons suggested the presence of unconverted double bonds. After a second
255 purification step, the ^{13}C NMR spectrum of EGU evidenced the absence of vinyl protons and

256 new signals emerged at 52 ppm and 47 ppm, respectively, associated with carbons bonded to
257 oxirane rings [34]. Epoxidation also preserved C=O resonances (Fig. 4S, supplementary file).
258 Experimental EEW_{EGU} was 227 g/eq, near the theoretical value of 213 g/eq, and functionality
259 was 2.82 (Table 1).

260 **Insert Table 1**

261 *3.1.2. CGTU*

262 The synthesis of CGTU involved the thiol-ene coupling of TGA onto the ω -unsaturated GUD
263 at a stoichiometric ene/thiol ratio without the addition of any catalyst. Reaction proceeded
264 with quantitative conversion of the double bonds after 8 h at 70 °C, in accordance with the
265 results reported for the TEC of THGA onto soybean oil (SBO) catalyzed by azo
266 bis(isobutyronitrile) [26] and the photo-initiated TEC of 3-mercaptopropionic acid onto 10-
267 UDA, oleic acid and GUD [38]. The reaction conditions used in this work were milder than
268 those reported to functionalize SBO (24 h, 80 °C, evidencing the higher reactivity of the
269 terminal carbon-carbon double bonds of GUD in comparison with the hindered internal
270 instaurations in SBO [26].

271 The FTIR spectrum of CGTU (Fig. 1, curve d) exhibited the presence of a broad absorption
272 band at 3400-2500 cm^{-1} (O-H stretching) and a new sharp shoulder peak at 1705 cm^{-1} (C=O
273 stretching), both specific to carboxylic acid moiety, along with the concomitant loss of bands
274 associated with the terminal carbon-carbon double bond. The main features in the ^1H NMR
275 spectrum of CGTU (Figure 3), was given by the signals of protons belonging to glycerol at
276 5.1 ppm (H_f) and 4.45 ppm (H_g), and those representing protons linked to carbonyl (H_c), and
277 the appearance of resonances at 3.3 ppm (H_a , s, 3H) and 2.6 ppm (H_b , t, 6H) (Fig. 3),
278 corresponding to the new carbon-sulfur bond [26,38], and the loss of vinyl proton signals at
279 5.8 ppm and 4.9 ppm. The acid value obtained by titration was 3.36 meq KOH/g, which is

280 equivalent to 188 mg KOH/g, giving a hydrogen equivalent weight of 257 g/eq. According to
281 acid and iodine values (Table 1), the conversion was as high as 98%.

282 **Insert Fig. 3**

283

284 **3.2. Biobased content of cured resins**

285 The biobased content is defined by the United States Department of Agriculture as “the
286 amount of biobased carbon in the material or product as a percent of the weight (mass) of the
287 total organic carbon in the product”. EGU and CGTU, upon which the thermosets are
288 prepared, are considered as fully bio-derived, while DGEBA is defined as petroleum-based.
289 Since GUD and glycerol are both biobased, every carbon atom of EGU is from biomass. As a
290 consequence, EGU is 100 wt.% bio-derived. In the case of CGTU, the contribution of
291 methylenecarboxy moieties from THGA, reduces its biomass content to 85.7 wt.%. The bio-
292 derived content of cured resins varied from 52 wt.% to 92 wt.% for DGEBA and EGU neat
293 resins, respectively (Table 2). Accordingly, all the thermosets developed can be considered as
294 highly biobased materials.

295 **Insert Table 2**

296

297 **3.3. Study of the curing process**

298 The synthesized acid hardener was formulated with EGU-DGEBA mixtures at the different
299 mass ratios and with the stoichiometric epoxy/acid ratio. Since EGU is slightly soluble in
300 DGEBA at room temperature due to differences in solubility parameters ($20.6 \text{ MPa}^{1/2}$ vs. 16.7
301 $\text{MPa}^{1/2}$), respectively, calculated by group contribution method [39], all blends were kept at 60
302 °C for 10 min before being poured into DSC pans to get initially homogeneous reactive
303 mixtures. Figure 4(a) shows the dynamic thermograms of EGU-DGEBA/CGTU reactive
304 mixtures in the range of -60 °C to 250 °C. Curing parameters are listed in Table 2. Neat

305 EGU/CGTU system exhibited a single exothermic peak between 115 °C and 200 °C with a
306 maximum around 164 °C associated with the epoxy–carboxylic acid curing reaction, which
307 was 40 °C higher than that of the DGEBA/CGTU counterpart (124 °C) indicating the lower
308 reactivity of the biobased epoxy precursor. Such difference was attributed to the poorer
309 polarizability of the oxirane ring in EGU, because its long methylene chains affect the
310 neighboring epoxy ring less than the CH₂OPh group of DGEBA through an electron
311 withdrawing effect [40]. The T_p value of EGU cured with CGTU was higher than that of EGU
312 cured with phthalic anhydride (141 °C) and 4,4'-methylenedianiline (MDA, 186 °C) [28],
313 4,4'-diaminodiphenylamine (DDM, 170 °C) [9], and isophoronediamine (IPDA)-based curing
314 agent, Ancamine 2423 (129 °C) [8]. In the case of DGEBA/CGTU resin, T_p was lower than
315 the values found for DGEBA/sebacic acid (187 °C), [23] and DGEBA/ASBO (150 °C) [26],
316 determined under similar conditions, evidencing the higher reactivity of CGTU due to its
317 increasing acidity induced by the presence of a sulfur atom [26].

318 For intermediate EGU-DGEBA formulations, two partially convoluted reaction peaks were
319 visible, becoming pronounced for DGEBA ≥ 30 wt.% (Fig. 4a). This behavior was attributed
320 to the polymerization of EGU at higher temperatures compared with that of DGEBA, as
321 already stated. The T_p of the blends showed a downtrend with increasing DGEBA proportion
322 accompanied by a gradual increment in the reaction enthalpy (Table 2), indicating the highest
323 reactivity of the aromatic epoxy compared with an aliphatic one against the same hardener in
324 a stoichiometrically balanced polymerization. A similar trend was observed for DGEBA
325 blends with epoxidized oils cured with carboxylic acids [41]. Total enthalpy values (ΔH_T),
326 were calculated from the calorimetric curves (Fig. 4a) by the integration of the exothermic
327 peak, and are expressed in kilojoules per equivalent, taking into account the EEW involved in
328 the epoxy–carboxylic acid reaction. Comparisons on the total heat of curing reaction
329 confirmed the higher reactivity of DGEBA resin (Table 2), ranging from 39 kJ/ee to 47 kJ/ee,

330 for 0 to 100 wt.% DGEBA. The values obtained in this study were lower than those reported
331 for EGU cured with IPDA (61 kJ/ee), 3-DCM (54 kJ/ee) and MTHPA-BDMA systems (48
332 kJ/ee) [10]. The endothermic event observed at low temperature in the thermograms of the
333 reacting mixtures (i.e., 48 °C) was ascribed to the melting of the synthesized CGTU.

334 **Inset Fig. 4 a and 4 b**

335 The final glass transition temperature, T_g , was determined during the second DSC run to
336 ensure the complete curing of the system (Fig. 4 b). CGTU-cross-linked resins displayed
337 single T_g values below 0 °C, from -14 °C up to -42 °C, for neat DGEBA and neat EGU,
338 respectively (Figure 4 b). This trend is explained by the predominant effect of the more
339 flexible aliphatic segments between crosslinking points over the higher functionality of EGU,
340 that contribute to increasing chain mobility, and hence to reduce T_g . Similar behavior was
341 reported for ELO cured with a series of dicarboxylic acids with varying chain length [24] and
342 ESO cured by OPBS [14]. Curing EGU with hardeners having greater rigidity than CGTU
343 leads to higher T_g values as reported for phthalic anhydride (64 °C) and MDA (56 °C) [28],
344 IPA (19 °C) [38], 3-DCM (17 °C), MTHPA (34 °C) [10], and NYL (-10 to 3.5 °C, depending
345 on the average molecular weight of NYL and the acid/epoxy equivalent ratio) [15,16]. The
346 presence of only one T_g in the temperature range studied (Fig. 4 b), provides experimental
347 evidence of the homogeneous nature of the blends.

348 Gelation time of the reactive mixtures was assessed in a temperatures temperature range
349 where the reaction occurs, based on DSC results. Neat DGEBA/CGTU resin displayed the
350 shortest gel time for all the temperatures evaluated (Fig. 5). According to the
351 Flory–Stockmayer theory for step-growth polymerization [42] (considering the average
352 functionality of each monomer and that esterification and transesterification reactions do not
353 occur), the predicted critical gel conversion (x_{gelc}) for DGEBA/CGTU and EGU/CGTU resins
354 were 0.718 and 0.532, respectively. The partially biobased resin reached higher conversion

355 before the fully biobased counterpart did, because the high functionality of EGU could not
356 compensate for its low reactivity, as discussed above.

357 **Insert Fig. 5**

358 DSC results showed that the curing of mixtures occurred over a rather broad temperature
359 range, the lowest temperature being around 78 °C for the neat DGEBA/CGTU system. For
360 that reason, EGU-DGEBA resins were prepared through a two-step curing process with two
361 pre-curing stages. In the first pre-curing step, the components were manually mixed at 60 °C
362 for 10-15 min to yield homogeneous mixtures. Subsequently, blends were treated for 10 min
363 at 60 °C in a vacuum oven to eliminate entrapped bubbles (second pre-curing step). Finally,
364 all mixtures were cured at 80 °C for 1h followed by 130 °C for 4 h. The low-temperature stage
365 ensured the dissolution of the hardener in the mixture. Besides, during that time, all
366 formulations were far from gelation (Fig. 5). The stage at 130 °C was used to increase the rate
367 of monomer conversion while restricting the thermal degradation of the biobased precursors.
368 DSC analysis by successive heat-cool-heat scans on the cured samples evidenced the absence
369 of residual reaction heat at least within the instrumental level of detection. This implies that
370 samples were wholly cured under the conditions imposed. Interestingly, when resins were
371 cured without the aid of the anti-adherent paper, they firmly adhered to the glass surface,
372 thereby suggesting that resins have potential as adhesive components.

373

374 **3.3. Performance of cured resins**

375 **3.3.1. Soluble fraction**

376 The soluble fraction of the wholly cured resins after 24 h of reflux in toluene decreased with
377 the amount of DGEBA (Table 3). The soluble content was less than 4.3% for all cured resins,
378 indicating the high degree of cross-linking achieved (Table 3). The higher rate of soluble for
379 EGU resin could be ascribed to the relatively low reactivity of the aliphatic epoxy precursor.

380

381 3.3.2. Thermal properties

382 The results of the thermogravimetric analysis are shown in Figure 6 (a) and (b) and the results
383 of the initial decomposition temperature (IDT) and the temperature of maximum rate of
384 degradation (T_{\max}) as a function of EGU content is summarized in Table 3. The IDT values of
385 all resin formulations were observed in a narrow temperature range, c.a. from 190 °C to 212
386 °C, for neat EGU and neat DGEBA, respectively (Fig. 6, Table 3). The low thermal stability
387 of resin blends with high EGU content was associated with the presence of a greater amount
388 of thermally cleavable ester bonds and linear aliphatic moieties in comparison with the
389 aromatic DGEBA materials [22]. Resin blends with EGU content up to 70 wt.% decomposed
390 in one single step (Fig. 6 b), while for higher DGEBA content (including neat DGEBA), two
391 degradation stages were clearly observed (Fig. 6 b). The first process resulted from chain
392 scission in the EGU and CGTU ester groups as confirmed by the decomposition process of
393 pure components [41]. The second step, was ascribed to the thermal scission of ester groups
394 and β -esters formed by the ring opening of EGU-DGEBA. Char content decreased when EGU
395 was increased, and values were lower than 3% for all formulations (Table 3). As the char
396 yield is inversely proportional to the hydrogen content of cured resins [43], the obtained result
397 is consistent with the greater number of methylene and methyl groups in resins with high
398 EGU proportion. Our results are in line with those reported for different carboxylic acid-cured
399 epoxy resins from vegetable oils [12].

400 **Insert table 3**

401 **Insert Figures 6**

402

403 3.3.3. Tensile properties

404 Figure 7 shows the tensile properties of the produced resins. EGU-DGEBA cured with
405 flexible CGTU afforded rubber-like thermosets, exhibiting low tensile strength that increased
406 with the proportion of DGEBA, while elongation gradually decreased. The soluble fraction of
407 all resins indicated substantial curing (Table 3). Therefore, the differences in mechanical
408 behavior cannot be ascribed to this parameter but to the structural differences. The hard and
409 rigid benzene building blocks in DGEBA, increased the stiffness of the DGEBA-rich resins
410 (Fig. 7). Tensile parameters evidenced the highly flexible nature of the neat EGU/CGTU
411 network, which is consistent with the aliphatic triglyceride structure of EGU and CGTU.
412 Indeed, when resins with high EGU proportion are stretched, the long aliphatic chain in both
413 bio-derived precursors could move more freely to offset and balance with the external forces, so
414 resins are more extendable. Tensile parameters are compatible with the fact that both resins are
415 in the rubbery state at room temperature, in line with the T_g values determined from fragments
416 of oven-cured resins (Fig. 7). The values obtained were close to those reached in the second
417 dynamic DSC run (Table 3). Tensile properties of epoxy resin blends obtained herein were
418 comparable to values reported for ESO-succinic acid [14] and ESO-SA [15], but lower than
419 those obtained for ESO-carboxyl terminated polyamide [14] and ELO-dicarboxylic acids with
420 different chain length [24].

421 **Insert Fig. 7**

422

423 **3.3.4. Optical properties and color attributes**

424 DGEBA resin displayed the highest L value (95.08%, Table 4) that decreased with EGU
425 proportion, reaching 84 % for neat EGU (Table 4). The reduction in parameter L (lightness) was
426 most likely explained by the increasing coloration (see color parameters in Table 4), since
427 opacity values varied marginally with increasing DGEBA. All values of parameter a* were
428 negative, indicating that samples became slightly greenish with EGU. In turn, b* value was

429 positive for all formulations, that of neat EGU being the highest one, by the natural yellowish
430 color of EGU precursor before curing.

431 **Insert Table 4**

432 Synthetic epoxy resins are usually poor UV absorber which might induce UV-degradation with
433 the concomitant loss of structural integrity. UV-Vis spectra of the epoxy resin blends (Figure 8)
434 demonstrate that transmittance in the UV range (<400 nm) significantly drops with increasing
435 EGU proportion, evidencing that the bio-derived precursor can absorb UV radiation with no
436 addition of any UV-absorbing molecules. ESO-based thermosets cured with carboxyl-terminated
437 polyamide oligomer at different epoxy/acid ratio [14] also evidenced UV-absorption, but such
438 effect was assigned to the increased crystallization of the sample with increasing the level of the
439 polyamide. With increasing wavelength, transmittance increased indicating the reduced effect
440 toward the visual light (Fig. 8). If transmittance values at 750 nm are compared, all resins show
441 similar transparency. Accordingly, it is clear that by controlling the proportion of each epoxy
442 precursor in the formulation, it is possible to obtain resins with both good transparency and UV
443 barrier properties. This opens up new opportunities for the applicability of EGU-
444 DGEBA/CGTU resins as high biomass coating materials particularly crucial for UV-sensitive
445 surfaces or products.

446 **Insert Fig. 8**

447

448 **4. Conclusions**

449 A novel green trivalent carboxylic acid (CGTU) was obtained by thiol-ene coupling of
450 thioglycolic acid onto renewable GUD and used as cross-linking agent of epoxy resin blends
451 with biobased content higher than 50%. by blending synthetic DGEBA with renewable EGU.
452 The long aliphatic chains from EGU and CGTU impart elasticity, flexibility and low glass
453 transition temperature to the resulting resins, restricting their applications as structural

454 materials. Since the reaction of EGU-DGEBA resin blends with CGTU endows hydroxyl-
455 functionalized soft networks that can adhere onto glass substrate (as it was experimentally
456 evidenced), the potential application of these environmentally sound epoxy resins is mainly as
457 adhesives or as UV-protective coatings.

458

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464

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595 **FIGURE CAPTIONS**

596

597 **Scheme 1.** Reaction pathway for the conversion of 10-UDA into GUD, EGU and CGTU, and
598 related epoxy resins.

599 **Figure 1.** FTIR spectra of (a) 10-UDA, (b) GUD, (c) EGU and (d) CGTU.

600 **Figure 2.** HSQC spectra of (a) GUD and (b) EGU. (Signals assigned to aromatics derive from
601 traces of toluene from separation procedures).

602 **Figure 3.** ^1H NMR of CGTU.

603 **Figure 4.** Dynamic thermograms of the EGU-DGEBA/CGTU systems (10 °C/min and N_2
604 atmosphere (a) First scan, (b) Second scan.

605 **Figure 5.** Gelation time for DGEBA/CGTU and EGU/CGTU neat resins at different
606 temperatures.

607 **Figure 6.** TG/DTG curves of the produced biobased epoxy resins

608 **Figure 7.** Tensile properties of the biobased thermoset resins.

609 **Figure 8.** Overlay total transmittance curves of thin films of EGU-DGEBA/CGTU resins.

610

611

Table 1. Analytical parameters of the synthesized GUD, EGU and CGTU

Precursor acronym	Calculated biobased content (wt.%)	Acid value (AV, meq/g)		Hydroxyl value (VOH)		Iodine value (IV, g I ₂ /100g)		Epoxy value		Epoxy equivalent weight (EEW)		Yield (%)
		Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	
GUD	100	0	<0.005	-	0.02	129	126	-	-	-	-	95
EGU	100	-	-	-	-	<1	0	4.69	4.12	213	227	89
CGTU	85.7	3.44	3.36	-	-	<1	0	-	-	-	-	98

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613

614 **Table 2.** Biobased content (Wt.%), curing parameters and glass transition temperature (Tg)

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EGU (wt.%)	Biobased ^a content (wt.%)	ΔH_r (KJ/ee)	T _{p1} (°C)	T _{p2} (°C)	Tg ^b (°C)
0	52	47	124	-	-14
20	59	45	125	-	-19
50	71	41	132	163	-27
70	78	40	-	164	-35
100	92	39	-	164	-42

623 a. Calculated as the content (in weight) of bio-derived carbon according to United States Department of
624 Agriculture

625 b. From DSC

626

627 **Table 3.** Soluble fraction (W_{soluble}), glass transition temperature (T_g), and TGA parameters of
 628 the bio-based resins.

EGU (wt.%)	W_{soluble}^a (wt.%)	$T_{0,0.03}$ (°C)	T_{max}^1 (°C)	$T_{\text{max}2}$ (°C)	Char ₆₅₀ (wt.%)
0	1.2±0.2	212	290	351	2.1
20	2.1±0.1	210	289	351	1.7
50	3.4±0.0	201	287	-	2.2
70	3.4±0.3	195	285	-	1.2
100	4.3±0.5	190	282	-	1.6

a. Determined by Soxhlet

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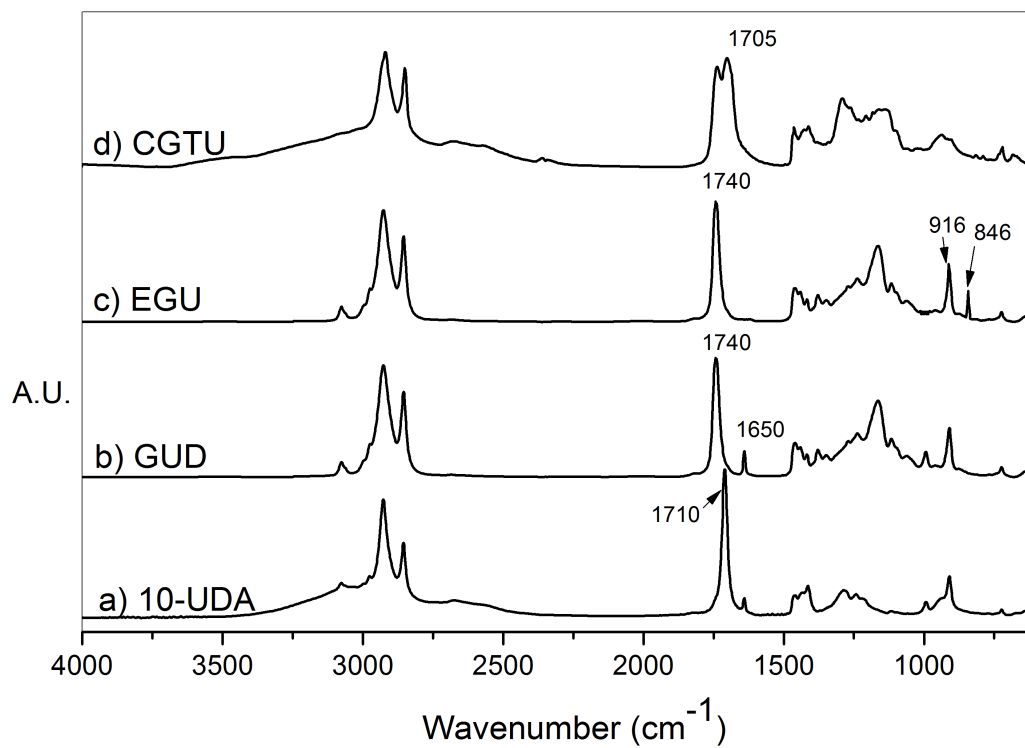
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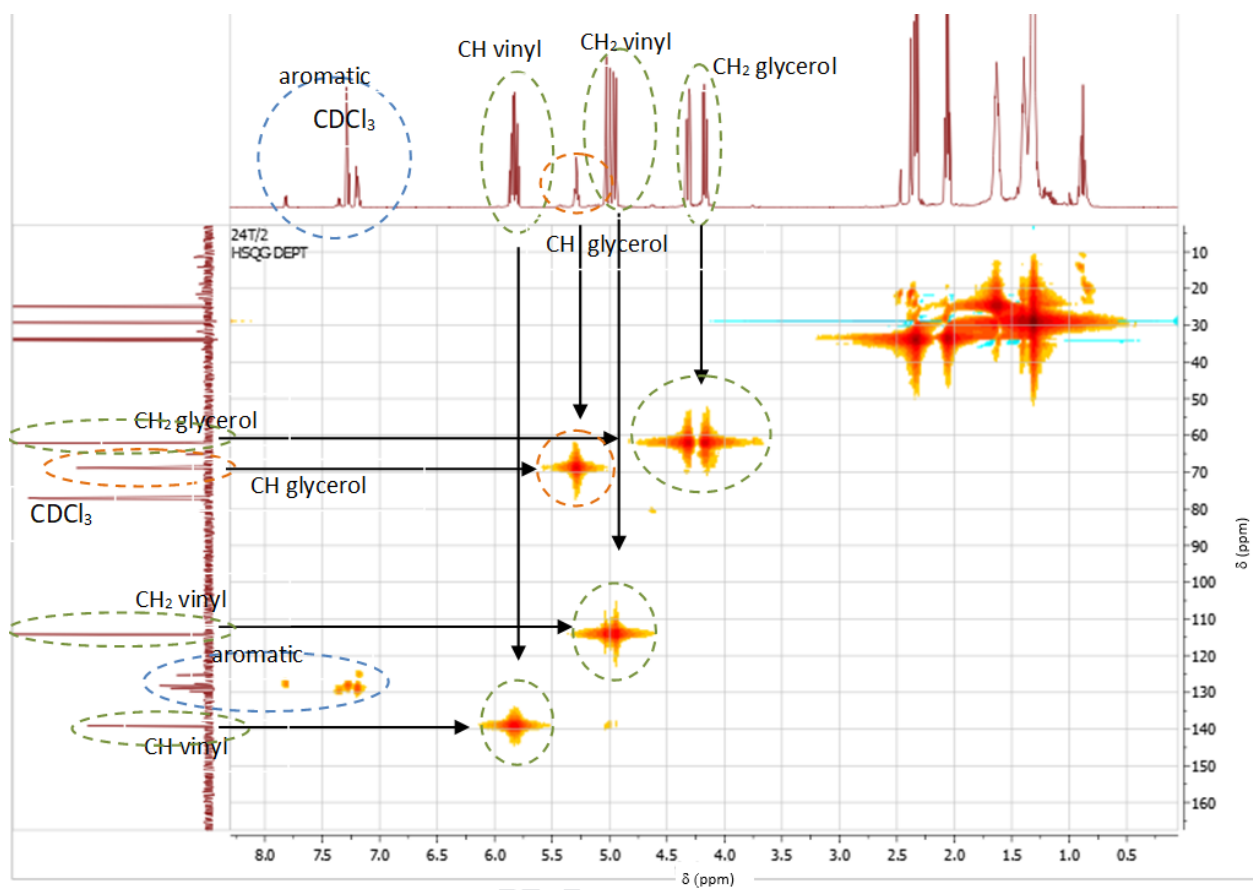
Table 4. Color attributes and opacity of the thermosetting bioresins

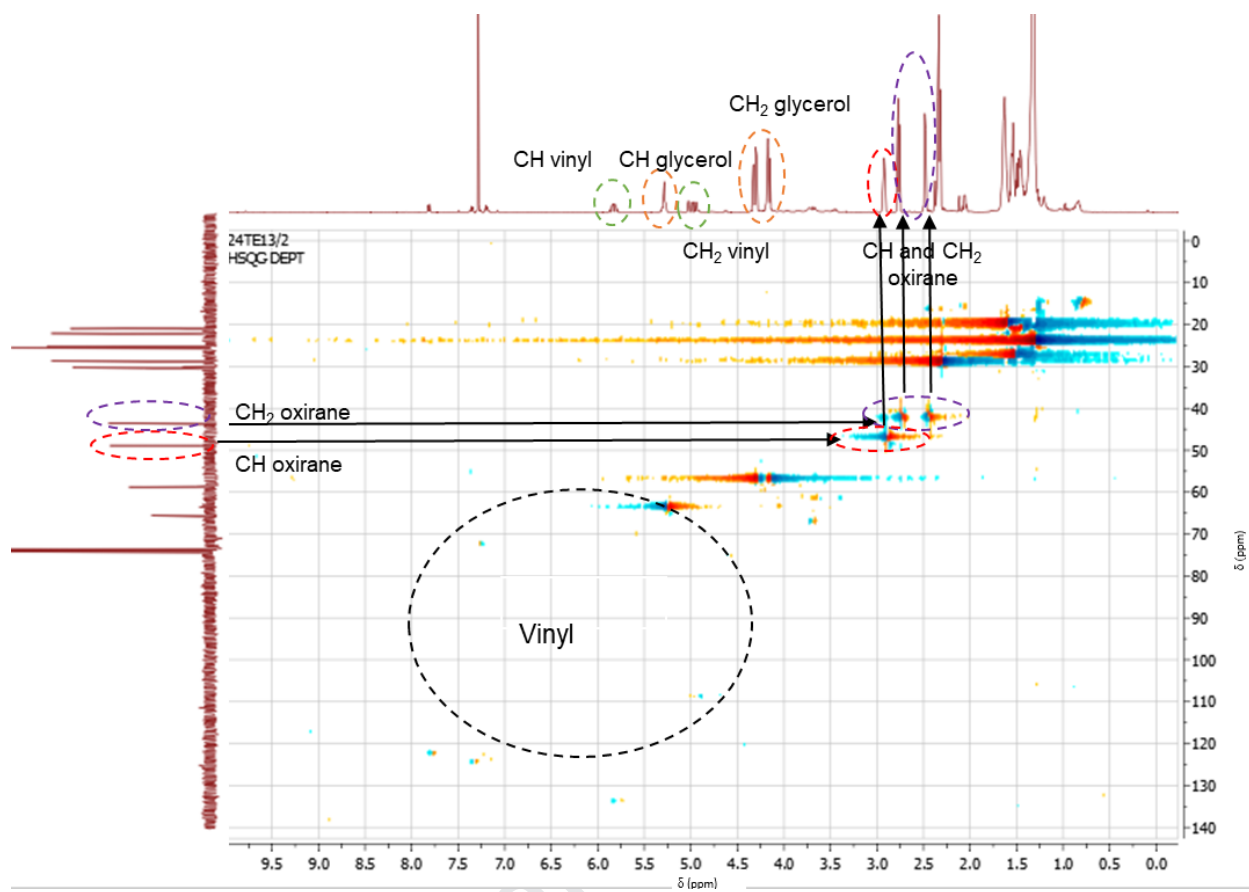
EGU (wt.%)	L	a*	b*	C*ab	h*ab	ΔE	Opacity (%)
0	95.08	-2.43	3.9	8.02	-1.15	5.22	9.81±0.2
20	91.02	-3.14	17.03	22.08	-1.33	9.70	9.95±0.2
50	87.49	-4.11	34.17	40.27	-1.48	13.26	10.21±0.2
70	86.77	-4.39	38.48	44.87	-1.49	14.55	10.33±0.2
100	84.11	-4.8	47.05	54.23	-1.71	16.68	10.59±0.2

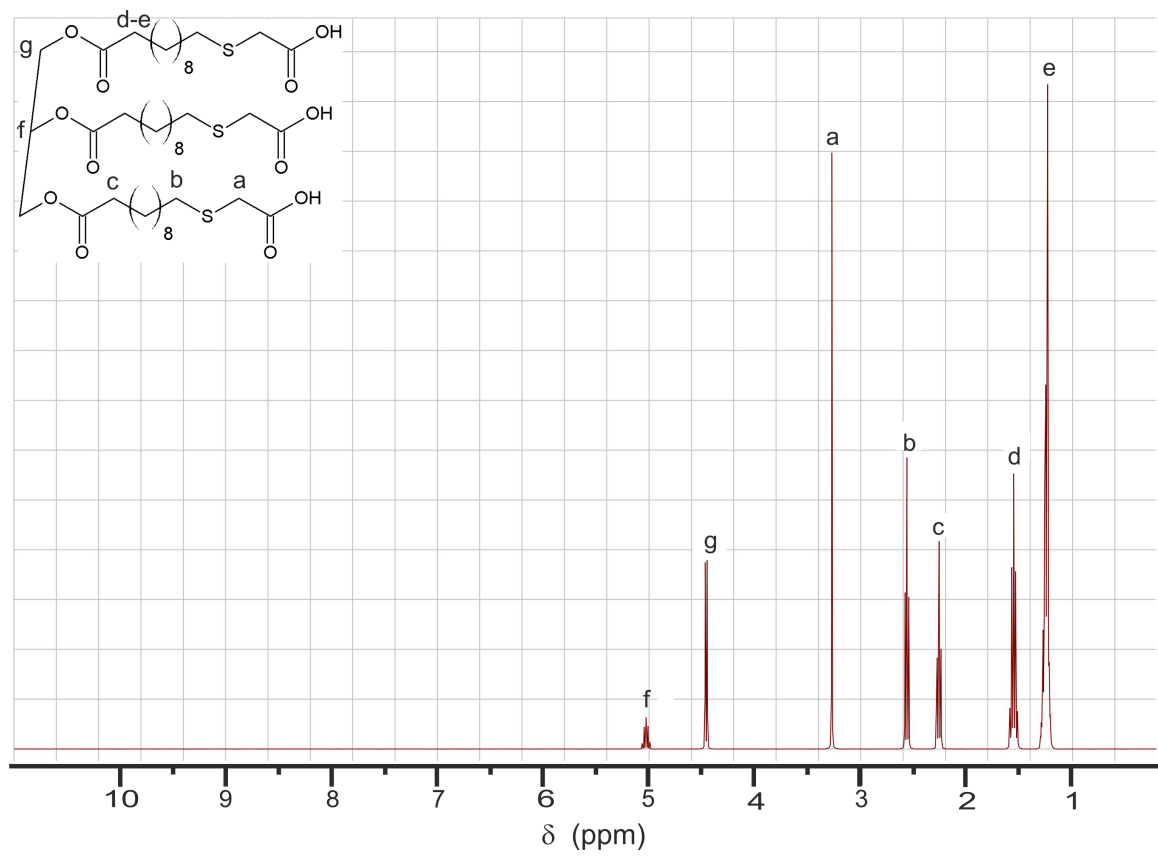
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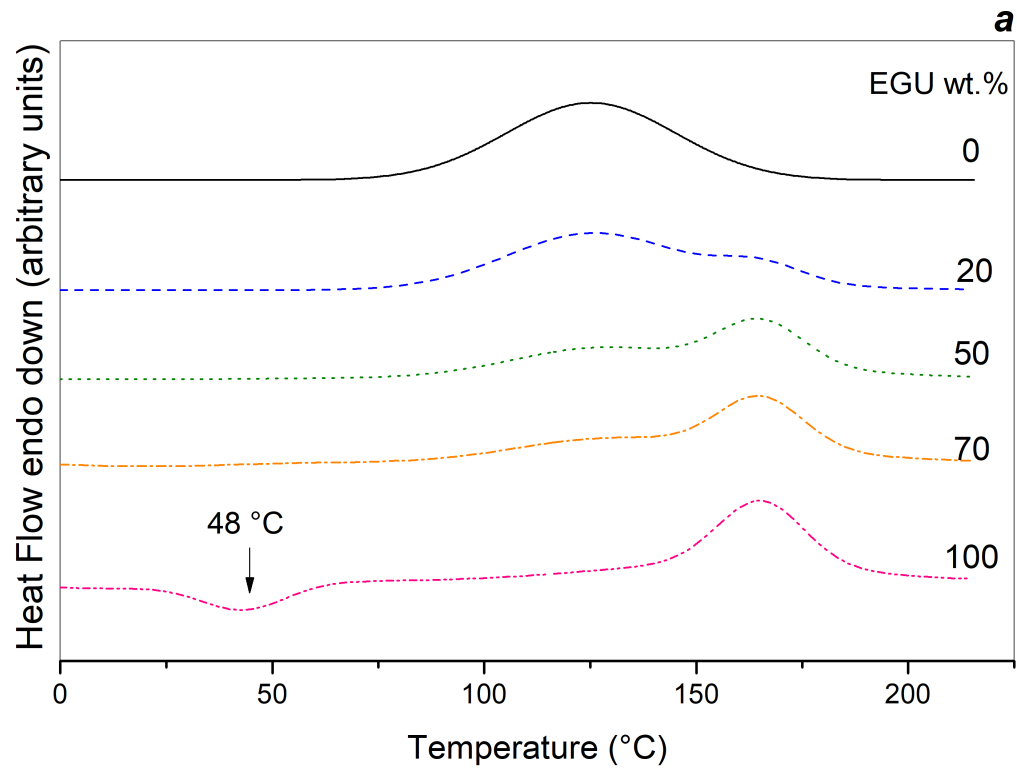
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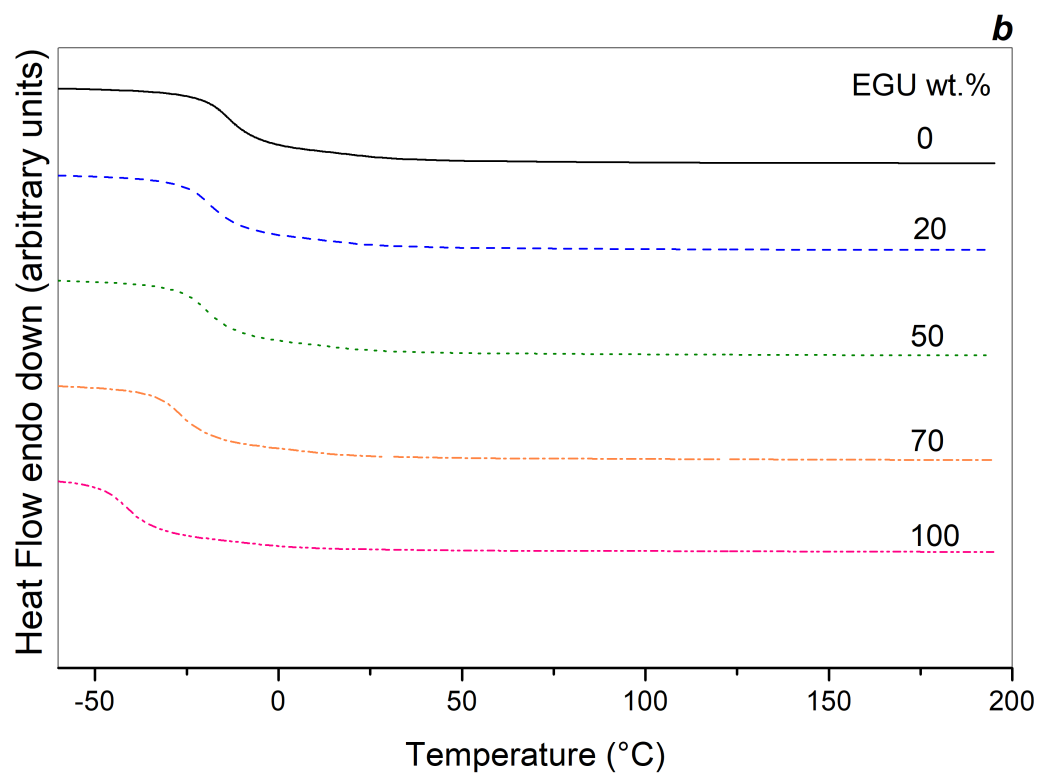


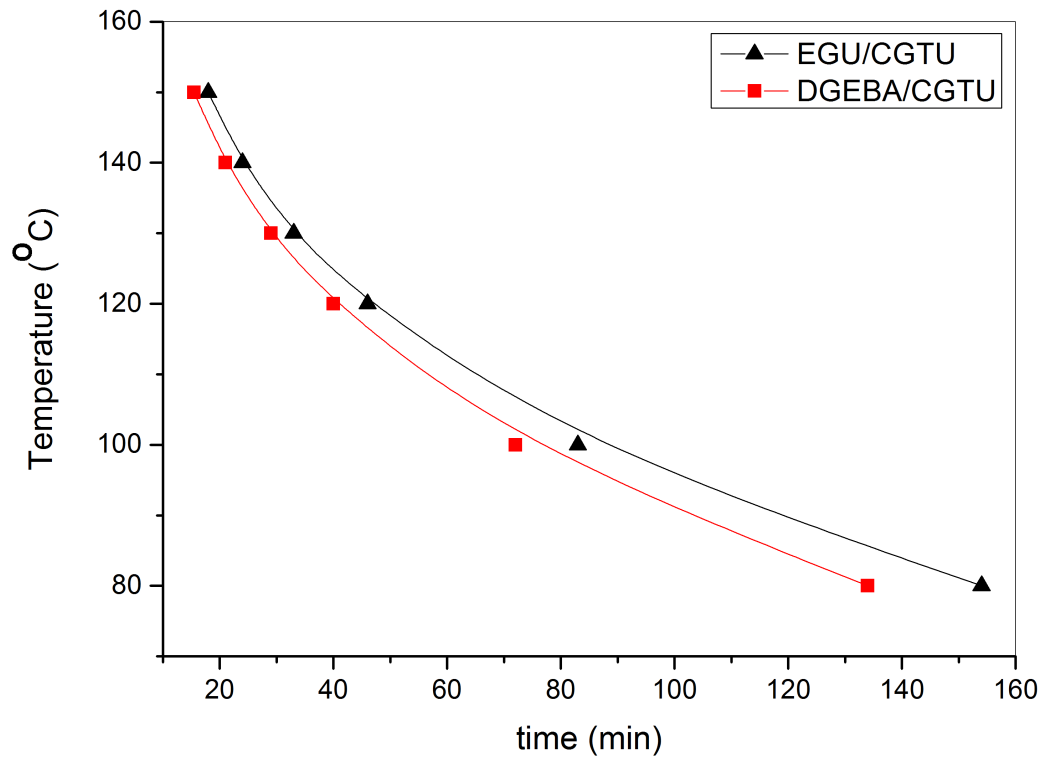


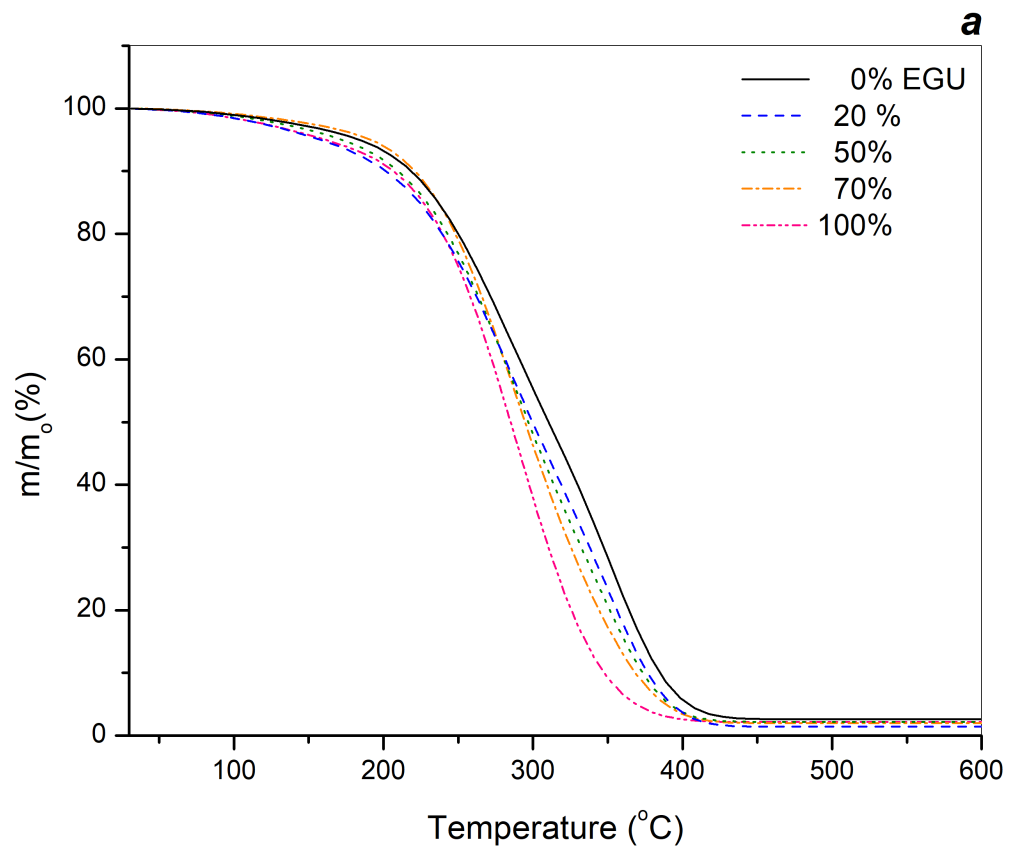


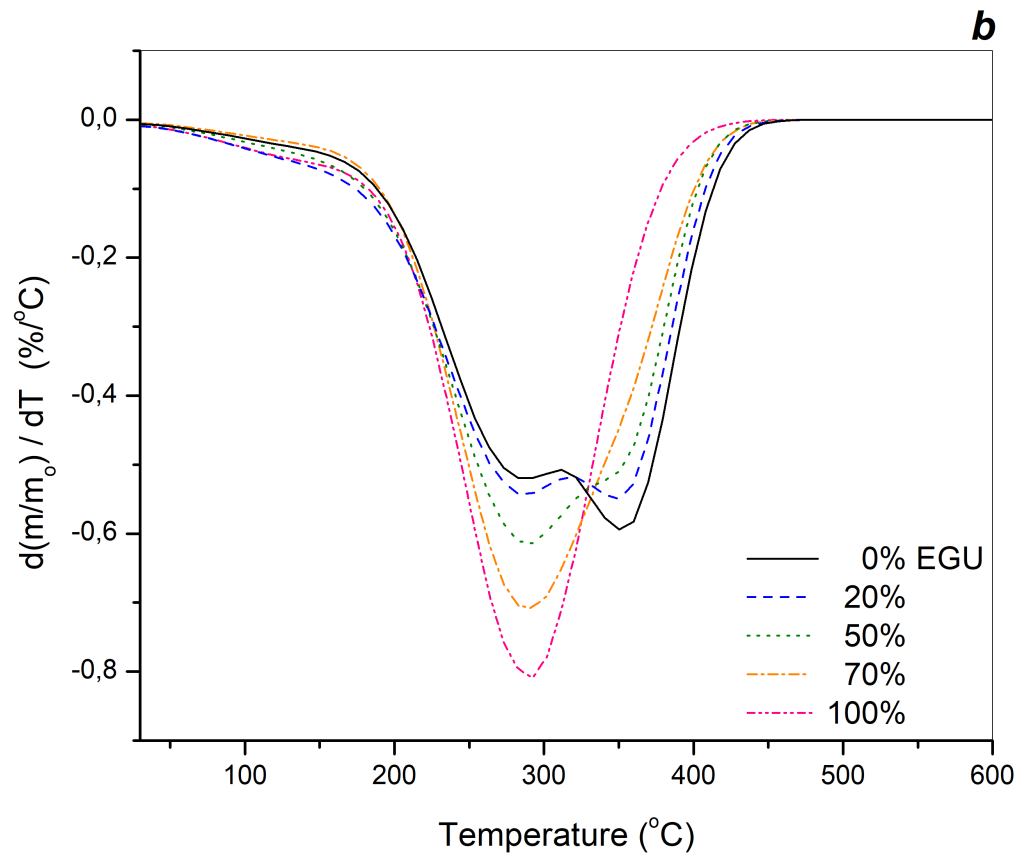


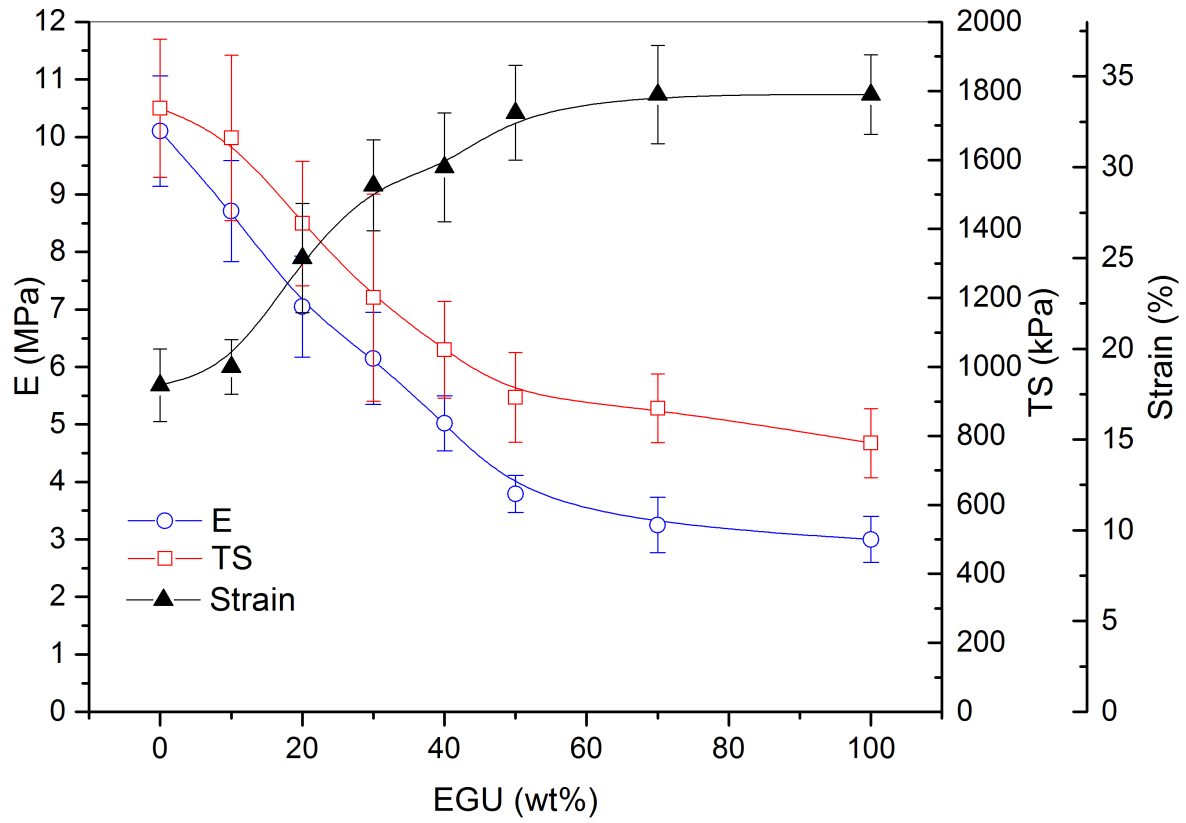


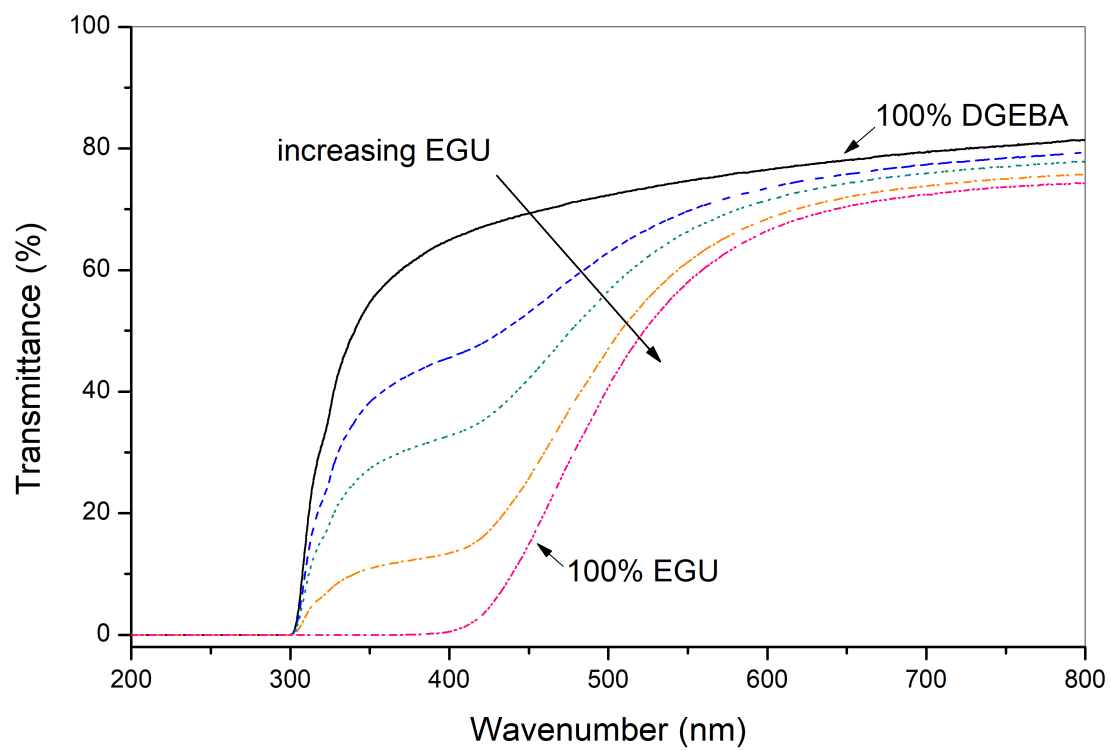


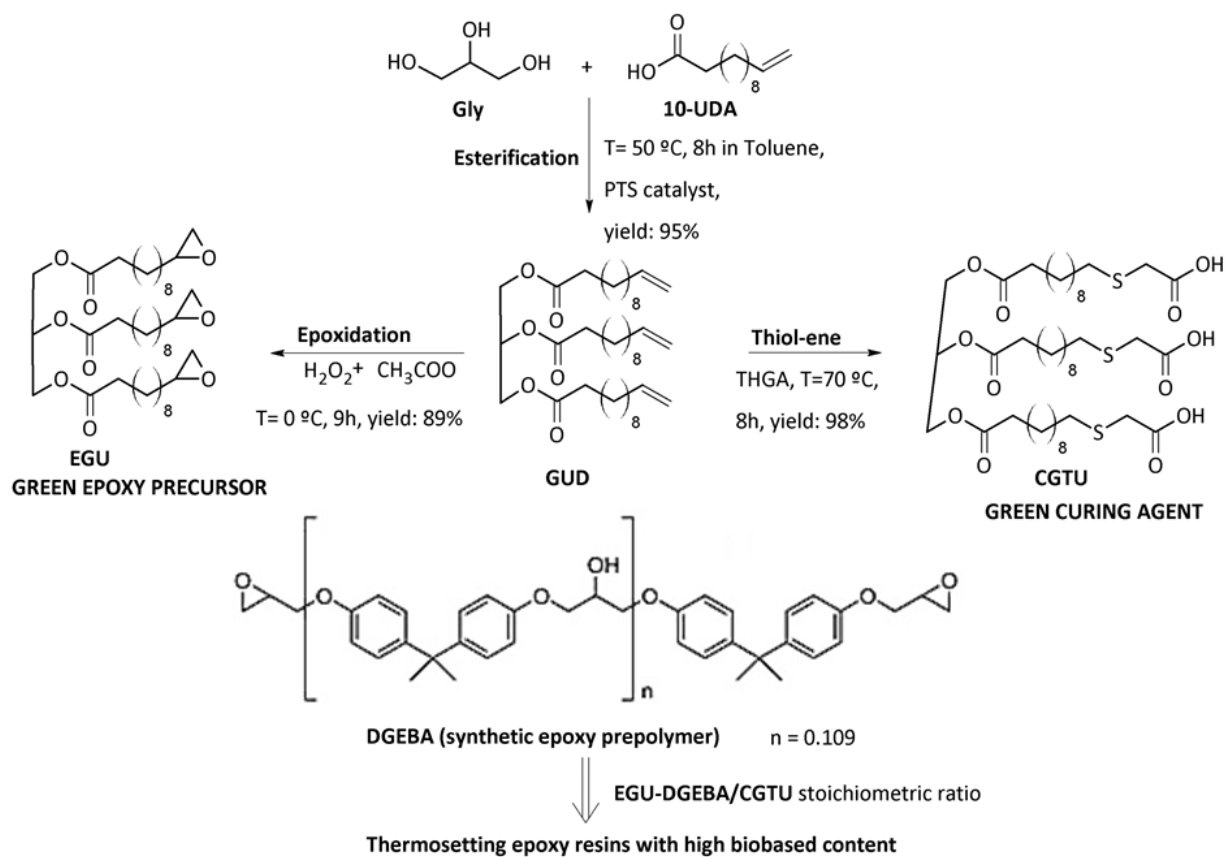












Highlights

- Biobased epoxy precursor (EGU) and tricarboxylic acid hardener were synthesized from renewable 10-undecenoic acid
- Curing behavior of EGU-DGEBA blends and stoichiometric amounts of biogenic hardener was explored
- Thermal, mechanical and optical properties of the produced resins were studied
- Resins have tunable UV and visible light protection

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I N T E R M A

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On behalf of the co-authors, I declare that we have no conflict of interest.

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