

Self-healable polymer networks based on the cross-linking of epoxidised soybean oil by an aqueous citric acid solution

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Epoxidised soybean oil (ESO) was cross-linked with an aqueous citric acid (CA) solution without the addition of any other catalyst or solvent. Completely bio-based polymer networks were generated. The initial system was an emulsion, but it became a homogeneous and transparent polymer network by reaction. The ability of the final materials to self-heal without adding extrinsic catalysts was assessed by stress relaxation and lap-shear tests. This was achieved by molecular rearrangements produced by thermally activated transesterification reactions of β -hydroxyester groups generated in the polymerization reaction.

Introduction

Among the different kinds of renewable raw materials, plant oils offer some advantages, such as, for instance, their worldwide availability at large scales.^{1–4} Moreover, diverse chemical reactions can be performed on vegetable oils, yielding functionalized vegetable oils (FVOs) that can be used to obtain different products. Sun and Wool⁵ gave a detailed description of possible chemical modifications that can be performed on vegetable oils to obtain different FVOs, many of which have important industrial applications. The epoxidation of double bonds present in the fatty acid chains of vegetable oils is one of the most important chemical modifications, and it can be attained by both the acid-catalyzed⁶ or the enzymatic methods.^{7,8} The main difference in the chemical structures of vegetable oils obtained from different oilseeds is the fatty acid distribution, which determines the amount of double bonds per triglyceride. Soybean oil has a large amount of linoleic (~53%) and oleic (~23%) acids, with 2 and 1 unsaturations, respectively, giving an average of about 4.6 double bonds per triglyceride,⁵ thus yielding an epoxidised oil with high functionality.

Epoxidised soybean oil (ESO) is nowadays industrially produced and commercially available, being mainly used as a plasticizer in the plastics industry. ESO can find an interesting application in the synthesis of polymer networks, giving a higher added value to a biomass-derived material. Networks can be obtained by cross-linking ESO or mixtures of ESO with

a synthetic epoxy resin, with some of the traditional curing agents used for epoxies, such as amines⁹ and anhydrides.^{10,11} Nevertheless, these traditional cross-linking agents are petroleum-derived compounds, often hazardous, and thus the search for safer biogenic substitutes becomes an attractive option, with the aim to develop a fully renewable and environmentally sound material. It is known that epoxides can react with carboxylic acids to yield β -hydroxyester linkages, and there are several polycarboxylic acids produced by sustainable biological processes that can be used as cross-linkers for ESO.¹² Citric acid (CA), a tricarboxylic acid, is a commodity produced at industrial scale by the filamentous fungus *Aspergillus niger*.¹³ However, their mutual insolubility has limited the interest in developing networks based on ESO and CA. The only reference we found in the literature was a paper by Shogren *et al.*¹⁴ dealing with the synthesis of thermosets from ESO, using several curing agents, including CA, with aluminium acetyl acetonate or tetrabutyl ammonium bromide as a catalyst.

The selection of a polycarboxylic acid like CA as a hardener of ESO provides one important property to the resulting networks. The β -hydroxyester links generated by the epoxy–acid reaction can participate in transesterification reactions in an adequate temperature range and in the presence of catalysts.^{15–17} The possibility of breaking and forming covalent bonds at different points of the network makes it possible to produce stress relaxation, self-healing and even recycling of the material by these thermally activated reactions.^{15–17}

The aim of this study was to prove that totally “green” and homogeneous ESO–CA networks can be obtained by the reaction of an initial emulsion of an aqueous solution of CA in ESO, using the protons derived by the CA dissociation in water as a catalyst of the epoxy–acid reaction. The networks exhibited

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thermally activated stress relaxation and self-healing, in the absence of specific catalysts.

Experimental

Materials

Epoxidised soybean oil (ESO; iodine value = 2.4; EEW = 241 g eq⁻¹; average molecular weight = 940 Da; average functionality = 3.9 epoxides per triglyceride) was kindly supplied by Unipox S.A. (Buenos Aires, Argentina). Citric acid (CA) monohydrate (C₆O₇H₈·H₂O; >98%; molecular weight = 210 Da) was purchased from Sigma. Both chemicals, ESO and CA, were used as received without any further purification. A representative chemical structure of ESO and the chemical structure of CA are shown in Fig. 1.

Synthesis of ESO–CA networks

A concentrated CA solution was prepared by mixing 4 parts by weight of CA·H₂O with one part of distilled water, and heating the mixture to 90 °C. After the CA was completely dissolved, the solution was poured in a glass beaker containing the appropriate amount of ESO at 90 °C, with continuous stirring to generate an emulsion of the aqueous CA solution in ESO. Different ratios of ESO to CA were used, characterized by the stoichiometric ratio $R = (\text{carboxylic acid equivalents})/(\text{epoxy equivalents})$. Table 1 summarizes the compositions of the different formulations.

The epoxy–acid reaction took place rapidly at 90 °C as revealed by the conversion of the emulsion into a homogeneous material, the continuous increase in viscosity and the

occurrence of gelation. A period of 10 min at 90 °C with continuous stirring was arbitrarily defined for the different formulations. After this time, the solution was slightly opalescent and the viscosity increased to a value that still enabled casting the solution in a glass mould covered with anti-adherent paper. The mould was placed in a convection oven (Yamato DKN400) and the polymerization was continued for 6 h at 90 °C and 12 h at 120 °C. The influence of a post-cure at 160 °C for different periods of time was investigated.

Dynamic-mechanical thermal analysis (DMTA)

Dynamic-mechanical thermal analysis (DMTA) was performed both in isothermal and dynamic modes, employing an Anton Paar Physica MCR 301 rheometer, with torsion geometry, at a frequency of 1 Hz. Specimens of rectangular cross-section (2 mm × 5 mm) were tested, with the distance between clamps equal to 17.4 mm. Isothermal tests were carried out at 160 °C for 24 h, following the evolution of the storage modulus (G') and loss modulus (G''). Dynamic tests were carried out at 2 °C min⁻¹, from -50 °C to 170 °C. Alpha relaxations (T_{α}) were defined as the maxima of tan δ peaks.

Fourier-transformed infrared spectroscopy (FTIR)

Fourier-transformed infrared (FTIR) spectra were obtained using a Nicolet 6700 FT-IR spectrometer, in the 400 to 4000 cm⁻¹ range, at a resolution of 4 cm⁻¹. The ESO spectrum was obtained in the transmission mode, using a thin coating on an NaCl crystal. For ESO–CA networks, the attenuated total reflectance (ATR) technique was used.

Stress relaxation

Shear stress relaxation was determined with an Anton Paar Physica MCR 301 device, using samples with the same dimensions as those used in DMTA. Isothermal tests were carried out in the temperature range between 120 °C and 160 °C. When the sample reached the desired temperature, a 5% torsional deformation was applied and the stress relaxation, expressed as a relaxation modulus, $G(t)$, was recorded.

Lap-shear

Modified lap shear experiments were conducted using an Instron 4467 Universal Testing Machine to evaluate the self-healing ability of the polymers. Two rectangular specimens (2 × 5 × 40 mm³) were superposed and submitted to a thermal treatment while a compressive force was applied to produce a 10% deformation. After the mending process, two sharp notches of 2 mm length and 15 mm of separation were introduced at 45° (Fig. 2). Additionally, rectangular specimens (4 × 5 × 40 mm³) subjected to the same thermal cycles and the same notched procedure as the healed specimens were prepared as control samples. Tests were carried out at 22 °C in the tension mode at a cross-head speed of 5 mm min⁻¹. Post-mortem fracture surfaces were observed by optical microscopy.

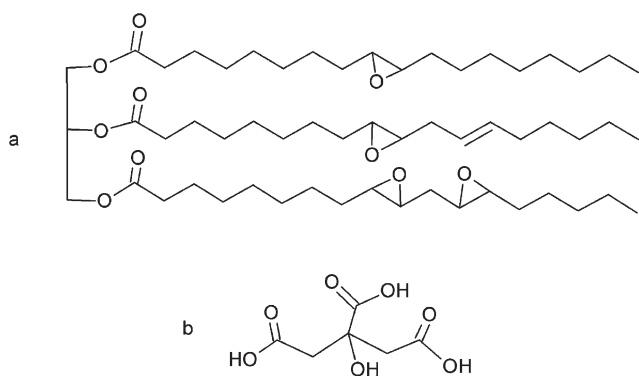


Fig. 1 Representative chemical structure of ESO (a) and chemical structure of CA (b).

Table 1 Mass (g) of each reagent used in the ESO–CA formulations

ESO	CA/H ₂ O solution		R
	CA·H ₂ O	H ₂ O	
10	2.905	0.726	1.0
10	2.324	0.581	0.8
10	1.452	0.363	0.5

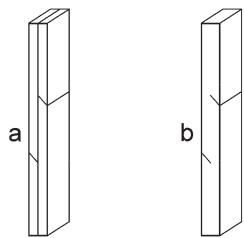


Fig. 2 Modified lap-shear tests specimen (a) and control sample (b).

Results and discussion

Cross-linking of ESO by CA

The epoxy–acid reaction is catalyzed by protons produced by the dissociation of CA in the aqueous solution, according to the scheme depicted in Fig. 3.^{18–22} The first step of this mechanism is the protonation of the epoxide (step *a*), followed by the attack of a carboxylate anion (step *b1*),^{18–20} or by a water molecule (step *b2*).^{21,22} Although the reaction with the carboxylate anion leading to a β -hydroxyester is favoured, the hydrolysis of epoxy groups does also take place. Considering the water used to dissolve CA and the water added with CA·H₂O, the initial molar ratio H₂O/COOH was equal to 1.3. In formulations with $R = 1$, there is a stoichiometric amount of carboxylic groups with respect to epoxy groups. However, water can still compete with carboxylates due to its molar excess and the smaller reactivity of the central COOH group of CA. In non-stoichiometric formulations ($R < 1$), both reactions should take place.

Apart from these two main reactions, other reactions can occur. Esterification reactions can take place between residual COOH groups and OH groups generated by the two main reactions. In particular, the vicinal diol generated by step *b2* can be esterified, leading to the same β -hydroxyester generated in step *b1*. A cationic homopolymerization of epoxy groups initiated by the protonated ring may be also proposed. However, no evidence of the occurrence of this reaction (*e.g.*, generation of ether groups) was found in the FTIR spectra.

A post-cure at 160 °C for different periods of time provided extra evidence of the cross-linking reactions taking place. Fig. 4 shows DMTA tests of ESO–CA networks synthesized with $R = 1$ and $R = 0.5$, post-cured for different periods of time at 160 °C. After the second step at 120 °C, both materials

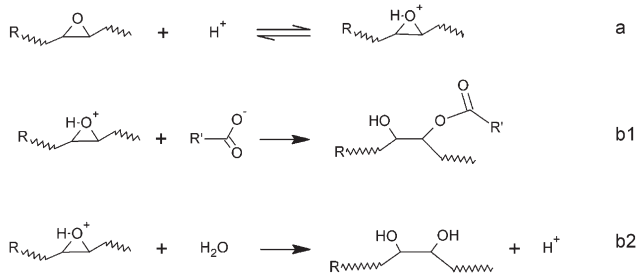


Fig. 3 Main reactions accounting for the consumption of epoxy groups of ESO.

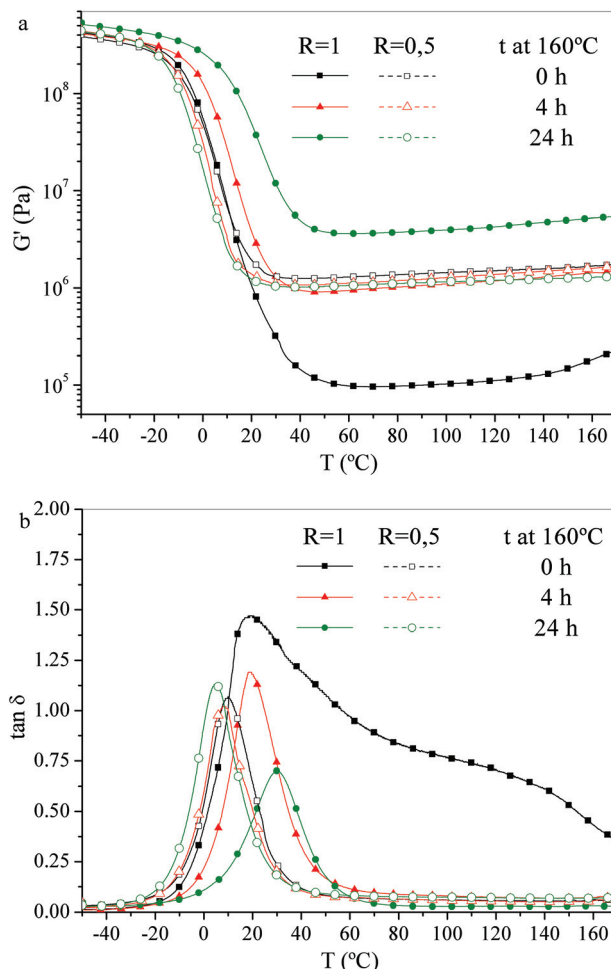


Fig. 4 Storage modulus (G') (a) and damping factor ($\tan \delta$) (b) as a function of temperature (T), for ESO–CA networks with $R = 1$ and $R = 0.5$, heated at 160 °C for different periods of time.

exhibited the typical behaviour of cross-linked polymers with alpha-relaxations located in the range of room temperature. However, the material synthesized with $R = 1$ showed a significant increase of the rubbery modulus with the post-cure at 160 °C, while the material with $R = 0.5$ showed no significant variation of the rubbery modulus by this thermal treatment (Fig. 5).

A striking feature is the fact that, after the cure step at 120 °C, the storage modulus of the material with $R = 0.5$ was significantly higher than those of materials with $R = 0.8$ and 1. As the rubbery modulus is directly proportional to the cross-link density, this means that CA acted more efficiently as a cross-linker (the three carboxylic groups reacted with epoxy groups) when added in a 0.5 stoichiometric ratio with respect to epoxy groups. The reason is that the amount of added water was also non-stoichiometric (0.65 moles per mol of epoxy group). Therefore, even in the limit of complete reaction of water by step *b2* of Fig. 3, 70% (0.35/0.5) of the carboxylic acid groups can find free epoxy groups to react with. The actual fraction of reacted carboxyls during the cure at 120 °C seems

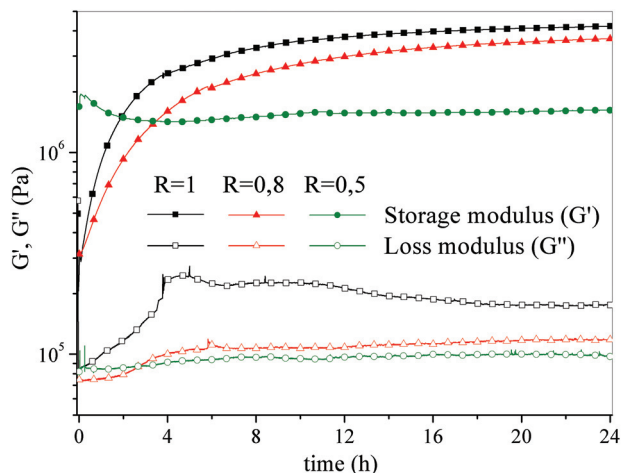


Fig. 5 Evolution of the storage modulus (G') and loss modulus (G'') during the heating at 160 °C for materials with different R values.

to be much higher than 70% as there was no significant increase of the storage modulus of this material during the post-cure step at 160 °C (Fig. 5). The small initial decrease of the storage modulus might be ascribed to the transesterification reactions (discussed in the following section) that convert effective cross-links (the three carboxylic groups of a CA unit are reacted with epoxy groups of different ESO units) into ineffective cross-links (at least two of the carboxylic groups are reacted with epoxy groups of the same ESO unit).

The situation was different for the materials synthesized with $R > 0.5$, where a significant increase in cross-link density took place during the post-cure at 160 °C. The explanation is that the fraction of tri-reacted CA units was low after the cure at 120 °C because of the strong competition from the attack on epoxy rings by water (step *b2* in Fig. 2). The residual carboxylic acid groups generated new β -hydroxyester groups during the post-cure at 160 °C, by reaction with OH groups previously generated by reactions *b1* and *b2* (Fig. 2). Most of the CA units were converted into cross-linkers producing the observed increase of the storage modulus. In the final thermosets, the storage modulus in the rubbery state increased with R as expected (Fig. 5).

FTIR spectra (Fig. 6) provided direct experimental evidence of the proposed set of reactions. The evolution of spectra in the sample with $R = 1$ is analyzed for illustration purposes. Spectra were taken after the cure at 120 °C ($t = 0$ h) and after 4 h and 24 h heating at 160 °C.

Complete consumption of epoxy groups of ESO, within the experimental error of FTIR spectra, was observed after the cure at 120 °C, as confirmed by the disappearance of the characteristic absorption bands at 823 and 843 cm^{-1} (Fig. 6c).^{23,24} The relatively intense OH absorption band (~ 3450 cm^{-1} , Fig. 6a) arises from OH groups generated by both reactions *b1* and *b2* (Fig. 3). The generation of new ester groups cannot be assessed due to the strong absorbance of ester groups of ESO. However, the broad peak in the carbonyl region has a shoulder at about 1711 cm^{-1} (Fig. 6c) assigned to free carboxylic groups.²⁵ This

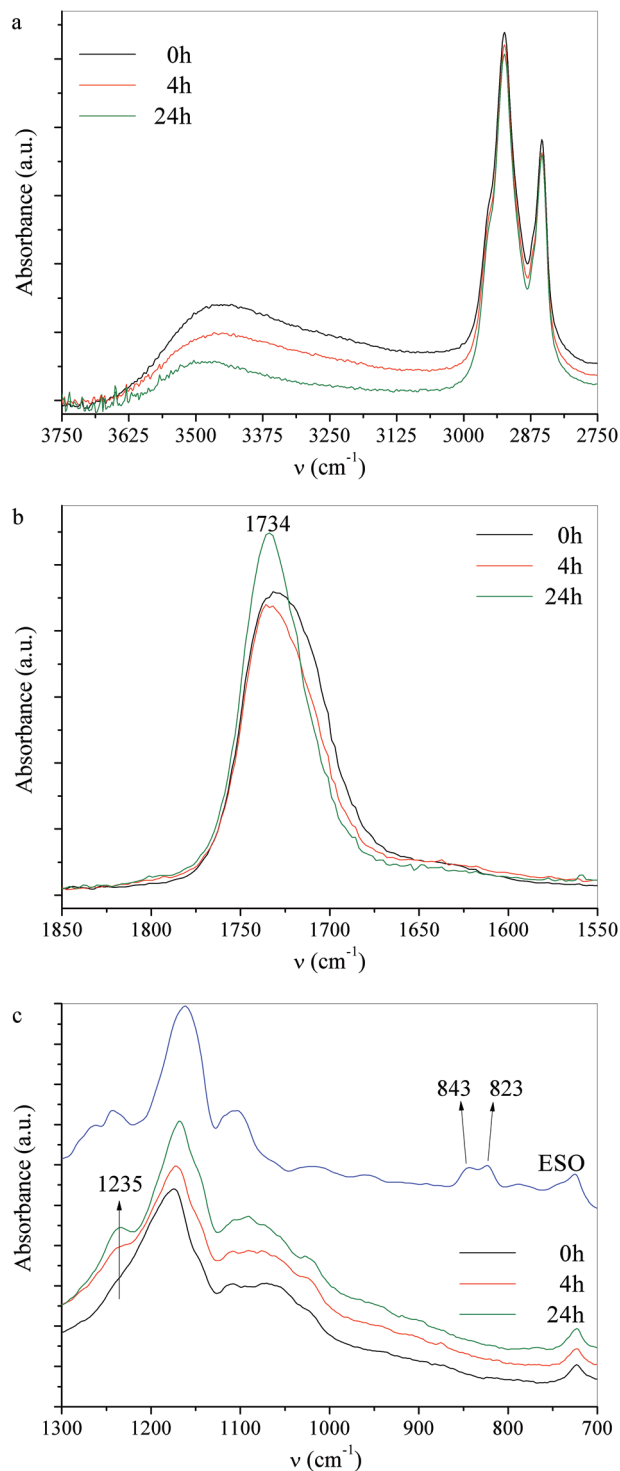


Fig. 6 FTIR spectra of ESO-CA networks with $R = 1$ heated at 160 °C for different periods of time. (a) 3750 cm^{-1} to 2750 cm^{-1} ; (b) 1850 cm^{-1} to 1550 cm^{-1} ; (c) 1300 cm^{-1} to 700 cm^{-1} .

confirms that a fraction of epoxy groups is consumed by hydrolysis with water (reaction *b2*, Fig. 3).

The esterification reaction produced during the heating at 160 °C by the reaction of residual COOH groups with OH groups is confirmed in three different regions of the FTIR

spectra. In the first place, there is a significant decrease of the OH absorption band after 4 h and 24 h heating (Fig. 6a). In the second place, the shoulder assigned to free carboxylic acid groups was no longer present after 24 h heating (Fig. 6b). Finally, a new absorption band at 1235 cm^{-1} , corresponding to the C–C₃ skeletal stretching of citric acid triesters (CA units where the three COOH groups have reacted)²⁶ was generated during the heating period at $160\text{ }^{\circ}\text{C}$ (Fig. 6c).

The material synthesized with $R = 0.5$ did not show significant variations in the FTIR spectra during the heating at $160\text{ }^{\circ}\text{C}$, in agreement with the small variation produced in the rubbery modulus during this period.

Transesterification reactions

The most interesting property of the ESO–CA thermosets derives from the presence of β -hydroxyester groups in the crosslinking units. These groups can undergo transesterification reactions at relatively high temperatures and in the presence of adequate catalysts.^{15–17} The reader is referred to a recent paper by Leibler's group where the existence of these reactions is assessed through the use of model compounds.¹⁶ These bond-exchange reactions enable healing and recycling of the materials.^{15–17}

The question we asked was if transesterification reaction could take place in ESO–CA thermosets by thermal activation in the absence of extrinsic catalysts. For this purpose, we examined the possible occurrence of thermally-activated stress relaxation in our materials.

Stress relaxation

Fig. 7 shows the evolution of the relaxation modulus at $160\text{ }^{\circ}\text{C}$ for the ESO–CA polymer networks synthesized with different stoichiometric ratios and a reaction time in the post-cure step at $160\text{ }^{\circ}\text{C}$ enough to obtain an almost constant value of the storage modulus. It is noteworthy that stress relaxation took place in the absence of any extrinsic catalyst. The relaxation rate increased when the value of R decreased, a fact that

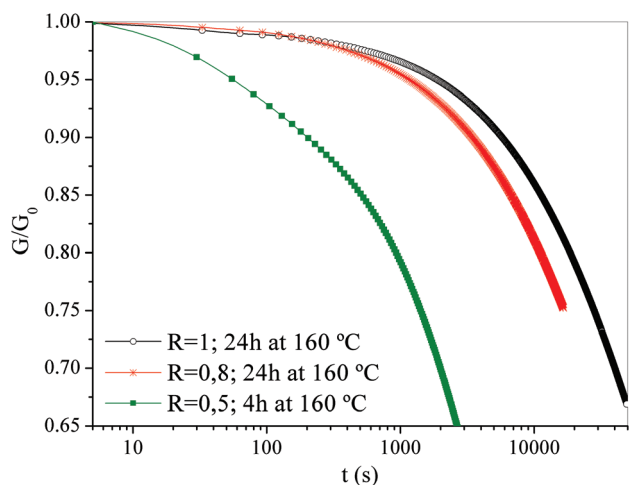


Fig. 7 Evolution of the relaxation modulus (G) at $160\text{ }^{\circ}\text{C}$, for ESO–CA networks with different R values subjected to a deformation of 5%.

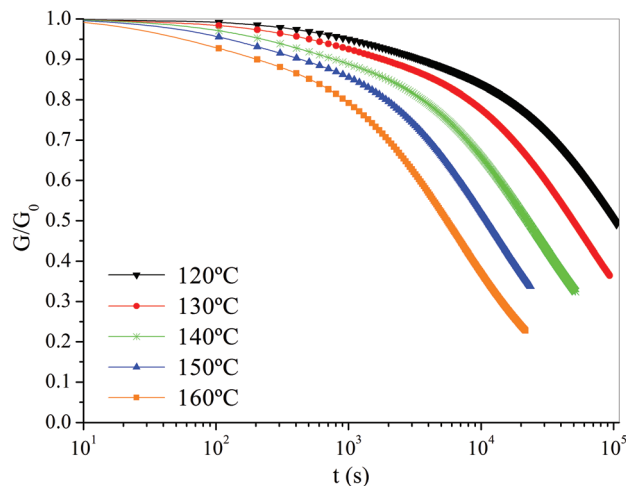


Fig. 8 Evolution of the relaxation modulus (G) at different temperatures, for an ESO–CA network with $R = 0.5$ heated 4 h at $160\text{ }^{\circ}\text{C}$ and subjected to a deformation of 5%.

can be assigned to the corresponding decrease in cross-link density and/or to the increase in the residual OH concentration. It has been reported that the transesterification reaction (and thus stress relaxation) rate increases with the concentration of OH groups.¹⁶

The influence of temperature on the stress relaxation rate was analyzed for the ESO–CA thermoset synthesized with $R = 0.5$ and post-cured at $160\text{ }^{\circ}\text{C}$ for 4 h. Fig. 8 shows the evolution of the relaxation modulus for temperatures in the $120\text{ }^{\circ}\text{C}$ – $160\text{ }^{\circ}\text{C}$ range. The relaxation rate increased with temperature in correspondence with the increase in the transesterification rate. Relaxation rates lie in the same range as those reported for Zn^{+2} catalyzed systems.¹⁷

A characteristic relaxation time can be defined as the time needed to achieve a particular G/G_0 value at a given temperature. Two characteristic relaxation times were defined, corresponding to $G/G_0 = 0.6$ and 0.37 . Fig. 9 shows the fitting of these relaxation times (τ) to an Arrhenius-type equation:

$$\ln \tau = \frac{E_a}{RT} - \ln A \quad (1)$$

where E_a represents the activation energy of the transesterification reaction. An excellent fitting for both relaxation times was obtained, with a slight difference between the activation energy values ($\sim 3\%$), and an average value of about 104 kJ mol^{-1} . This value is slightly higher than the values reported by Leibler *et al.*,¹⁷ for transesterification reactions catalyzed by Zn^{+2} salts.

The time–temperature superposition principle can be applied to generate a master curve including all the experimental data obtained at different temperatures. A shift factor $a_T(T)$ must be used:

$$a_T(T) = \exp \left[\frac{E_a}{R \left(\frac{1}{T} - \frac{1}{T_0} \right)} \right] \quad (2)$$

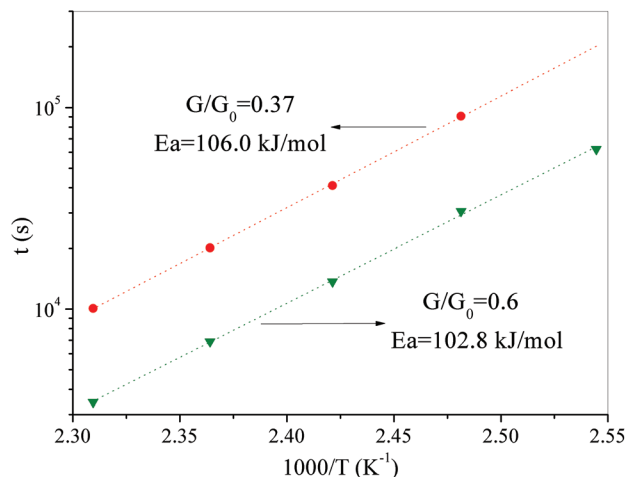


Fig. 9 Fitting of experimental values of relaxation times (τ) to an Arrhenius-type equation.

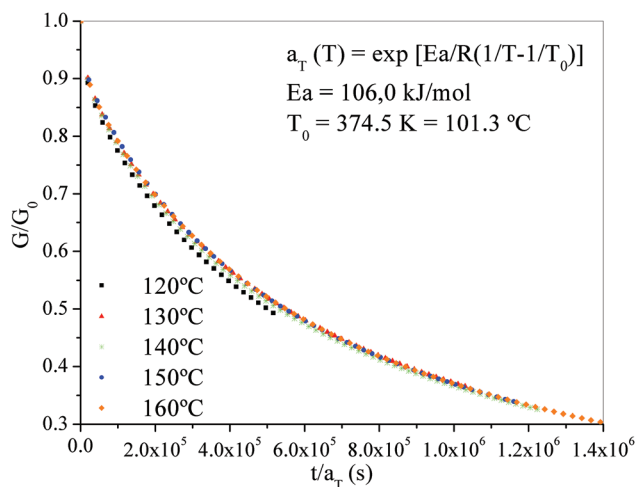


Fig. 10 Master curve of the relaxation modulus as a function of time, obtained by fitting results in the 120–160 °C range.

The resulting master curve obtained with $E_a = 106 \text{ kJ mol}^{-1}$ and $T_0 = 374.5 \text{ K}$ is shown in Fig. 10. This curve is useful to estimate relaxation times for temperatures different from those used to obtain the experimental data.

Self-healing

Stress relaxation experiments provided indirect evidence of the existence of thermally-activated transesterification reactions in the totally “green” ESO–CA thermosets. These reactions can be used for the self-healing and recycling of the material.

To prove the self-healing properties, qualitative assays were made on samples of ESO–CA network with $R = 0.5$, post-cured at 160 °C for 4 h. Mending was performed at 140 °C for 1 h and at 160 °C for 1 and 2 h. A single piece was obtained after this period through the welding of contact surfaces by transesterification reaction. A quantification of this result by

modified lap-shear tests was intended as described in the Experimental section. Fig. 11 shows stress–strain curves for these tests. The sample mended at 140 °C for 1 h underwent adhesive failure, indicating a poor bonding strength. However, there was no de-bonding of specimens mended at 160 °C through the contact surface, and cohesive failure was observed instead. It is worth noting that the material mended at 160 °C reached the same stress and strain levels (within experimental error) of the control sample before breaking. Fracture surfaces of specimens healed at 160 °C are shown in Fig. 12. In the sample mended for 1 h, the same failure mechanisms as in the virgin material are seen, even though a weld line which induced steps in the crack front is observed. In the sample mended for 2 h, the weld line has disappeared and fracture surface is undistinguishable from the one of virgin material. These results indicate that self-healing of the material was effectively achieved.

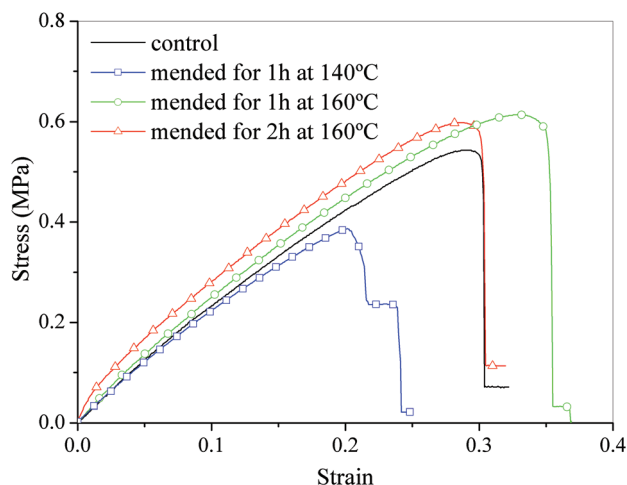


Fig. 11 Strain–stress curve for lap-shear tests of mended specimens compared with control ESO–CA sample.

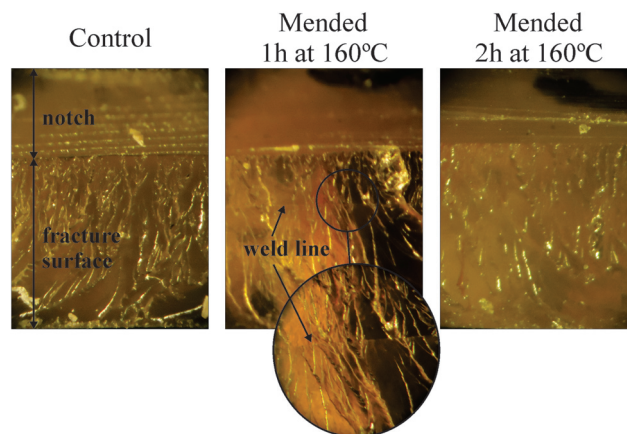


Fig. 12 Fracture surfaces of samples mended for 1 and 2 h at 160 °C, and control sample.

Conclusions

Epoxidised soybean oil (ESO) was cross-linked with an aqueous citric acid (CA) solution without the addition of any other catalyst or solvent. Completely bio-based polymer networks were generated. The initial system was an emulsion, but it became a homogeneous and transparent polymer network after the selected cure cycle. The reaction was initiated by the protonation of epoxy groups followed by the attack of carboxylate groups (epoxy-acid reaction) or water molecules (hydrolysis of epoxy groups). Residual COOH groups underwent esterification reactions with OH groups at high temperatures. The resulting polymer networks contained β -hydroxyester groups together with a fraction of vicinal diol groups. Transesterification reactions of the β -hydroxyester groups were evidenced by stress relaxation and lap-shear tests. The completely "green" ESO-CA networks are smart materials capable of stress relaxation and self-healing without the addition of any extrinsic catalyst. Transesterification reactions could enable the recycling of parts by milling followed by compression moulding at 160 °C.

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