

# Properties of biobased epoxy resins from epoxidized linseed oil (ELO) crosslinked with a mixture of cyclic anhydride and maleinized linseed oil

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Received 26 September 2018; accepted in revised form 4 December 2018

**Abstract.** This work aims at the development of thermosetting resins derived from epoxidized linseed oil (ELO) of high biobased content, by using a mixture of crosslinking agents, *i.e.* methyl nadic anhydride (MNA) and maleinized linseed oil (MLO). By using only MNA as crosslinking agent, the obtained resins are characterized by high stiffness and, consequently, high fragility. When MLO content increases in the crosslinking mixture, up to 25 wt%, a decrease in mechanical resistance and thermomechanical properties is detected, thus indicating that MLO can provide flexibility to ELO-based thermosetting resins which is an interesting issue to obtain tailored properties by selecting the appropriate mixture composition. In general, the thermosetting resin crosslinked with 10 wt% MLO and 40 wt% MNA gives balanced properties together with noticeable biobased content, thus broadening the potential of these materials for uses in green composites and coatings.

**Keywords:** thermosetting resins, epoxidized linseed oil, crosslinking, cyclic anhydrides, modified vegetable oils

## 1. Introduction

During the last years, a noticeable increase in the sensitiveness to environmental issues has been observed and polymeric materials of vegetable origin have attracted important attention in the last decades since they represent a feasible alternative to petroleum-derived materials. The development of biobased/biodegradable thermoplastic polymers has been widely studied in the last few decades and today and it is interesting to remark the increasing use of biopolyesters such as poly(lactic acid) – (PLA), poly( $\epsilon$ -caprolactone) – (PCL), poly(butylene succinate) – (PBS), poly(butylene adipate-*co*-terephthalate) – (PBAT), poly(butylene succinate-*co*-adipate) – (PBSA), and so on, among others [1–7]. With regard to biobased thermosetting resins, industry faces a great challenge which is total or partial substitution of petroleum-derived resins with new environmentally friendly

developments. It is possible to make polyurethane resins with vegetable oils like epoxidized rapeseed oil [8], castor oil, linseed oil [9], soybean oil [10] or cotton seed oil [11]. However, among all thermosetting resins, epoxy resins owe a privileged position as technical resins, low volatile generation, etc. Nevertheless, most industrial epoxy resins are derived from bisphenol-A which could be related to negative effects on health as well as high environmental impact [12]. For these reasons, bisphenol-A free epoxy resins are continuously being searched. It is possible to obtain biobased epoxy resins with different approaches. In the last years, many investigations have been developed and characterized in the field of epoxy resins from vegetable oils such as epoxidized linseed oil (ELO) [13–17], modified soybean oil [15, 16, 18–24] and other less known oils such as those derived from microalgal oil [25], jatropha oil [26],

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karanja oil [27], tung oil [28], cottonseed oil [29] or hemp oil [30]. However, there are other natural sources that make possibly the synthesis of epoxy resins like Vainillin [31–33], ferulic acid obtained from wheat bran and beetroot pulp [34] or abietic acid obtained from rosin [35].

Although some epoxy resins can crosslink by a homopolymerization process, the most common situation includes the use of a hardener or crosslink agent which in turn, will play a key role on final properties of the crosslinked material. It is quite usual the use of amines and anhydrides from petroleum as crosslinkers for epoxy resins [36]. Continuous exposure to these products can produce damages on health, induce rhinitis, conjunctivitis and asthma [21]. For this reason, it is important to search for new environmentally friendly hardeners to totally or partially substitute petroleum-derived hardeners. With this aim, Chen *et al.* [18] developed epoxy resins with a high bio-based content using epoxidized soybean oil (ESBO) crosslinked with modified maleopimaric acid from. Yang *et al.* [37] developed two different crosslinking agents from myrcene (a monoterpene) and castor oil to crosslink a commercial epoxy resin (E-51) with high elongation at break. Roudsari *et al.* [21] used sebacid acid as crosslinker in epoxy resins composed of a mixture of a diglycidyl ether of bisphenol-A epoxy (DGEBA) resin and ESBO. Kadam *et al.* [27] used citric acid and tartaric acid as crosslinker to obtain epoxy resin using epoxidized karanja oil and they compared these resins with petroleum epoxy resins and their thermal stability were similar. Regarding the use of amines, Darroman *et al.* [38] synthesized an amine adduct from cardanol and cysteamine that was used as crosslinker in epoxidized cardanol resins. The presence of aromatic rings allowed obtaining epoxy-amine formulations with interesting uses in the coating industry. And Stemmlen *et al.* [39] modified grapeseed oil using cysteamine chloride by thiol-ene coupling to obtain polyamine grapeseed oil that they used as crosslinked agent to obtain epoxy resin using ELO and it presented a  $T_g$  around  $-38^\circ\text{C}$ .

One of the most attracting uses of epoxy resins from vegetable oils is their use as matrices in composite materials with technical fibers such as basalt or slate fibers, and natural fibers to substitute, mainly, glass fiber reinforced composite parts with new environmentally friendly solutions. It has been reported the use of different natural fibers such as flax [40, 41],

sisal [42], hemp [43], among others as reinforcing fibers in composites with biobased epoxy matrices, due to their low weight and for being renewable. One of the main drawbacks of these green composites is their low tensile and flexural strength compared to conventional epoxy/glass fiber composites (with a tensile strength of about 250 MPa) [44]. In contrast, the use of mineral fibers is still an excellent solution since mechanical properties are remarkably improved. Samperand and coworkers [45, 46] manufactured green composites with slate and basalt fibers subjected to a previous surface treatment with different silanes. The epoxy matrix was epoxidized linseed oil (ELO) or epoxidized soybean oil (ESBO) and composite materials with a tensile strength of 350 MPa were obtained.

This research work aims at the development of high renewable content epoxy resins by using epoxidized linseed oil (ELO) and a mixture of two crosslinking agents: one conventional petroleum-derived cyclic anhydride, *i.e.* methyl nadic anhydride (MNA) and a vegetable oil derived anhydride, *i.e.* maleinized linseed oil (MLO). The optimum curing and post-curing conditions have been optimized by using differential scanning calorimetry (DSC) and oscillatory rheometry (OR) as well as a full characterization by flexural tests, mechanical-dynamical thermal analysis (DMTA), thermomechanical tests to obtain Vicat softening temperature (VST) and heat deflection temperature (HDT).

## 2. Materials and methods

### 2.1. Materials

A commercial epoxidized linseed oil (ELO) with an epoxy equivalent weight (EEW) of  $178\text{ g}\cdot\text{equiv}^{-1}$  supplied by Traquisa S.A. (Madrid, Spain), was used as base epoxy resin due to their high number of oxirane groups in the triglyceride molecule that allows to obtain a resin with higher properties than if ECSO, epoxidized cottonseed oil, or other epoxidized vegetable oil (EVO) is used, since they have fewer oxirane groups per molecule. Two different crosslinking agents were mixed to cure the ELO resin. These two crosslinkers were a petroleum-derived cyclic anhydride methyl nadic anhydride (MNA) supplied by Sigma Aldrich Química S.A. (Madrid, Spain) and a maleinized linseed oil (MLO), MLO Veomer LIN, supplied by Vandeputte (Mouscron, Belgium) with a viscosity of 1000 cP at  $20^\circ\text{C}$  and an acid value between 105 and 130  $\text{mg KOH}\cdot\text{g}^{-1}$ . MNA was used as

crosslinking to develop epoxy resins in previous laminates materials studies [45, 46] and it has been used in this work with the objective to reduce their content in the epoxy resins developed. As initiator, glycerol (99%) was used and the selected accelerator was 1-methyl imidazol (1MI), both supplied by Sigma Aldrich Química S.A. Figure 1 shows the chemical structure of all the above mentioned chemical compounds.

The base formulation to cure the ELO resin was composed of ELO/MNA with an EEW/AEW (Epoxy Equivalent Weight/Anhydride Equivalent Weight) ratio of 1.0. Then, up to 25 wt% MNA was substituted by MLO as indicated in Table 1. Additional 1 wt% glycerol and 2 wt% 1MI (with regard to the mixture of ELO and mixture hardener) were used. All the components were mechanically mixed until homogenization and subsequently poured into a poly(tetrafluorethylene) – (PTFE) mold to obtain samples sizing  $80 \times 10 \times 4 \text{ mm}^3$ . The liquid mixtures were subjected to a curing cycle of 2 h at  $110^\circ\text{C}$  followed by a post-cure stage at  $160^\circ\text{C}$  for 2 additional h. The curing conditions used in this work for ELO-based thermosetting resins will hardly be used at the industrial level due to high temperature is needed and long curing times as well. Nevertheless, by using these

**Table 1.** Formulations of thermosetting resins based on epoxidized linseed oil (ELO) crosslinked with a mixture of anhydrides, *i.e.* methyl nadic anhydride (MNA) and maleinized linseed oil (MLO).

Sample code	ELO [wt%]	MNA [wt%]	MLO [wt%]
50/0	50	50	0
45/5	50	45	5
40/10	50	40	10
35/15	50	35	15
30/20	50	30	20
25/25	50	25	25

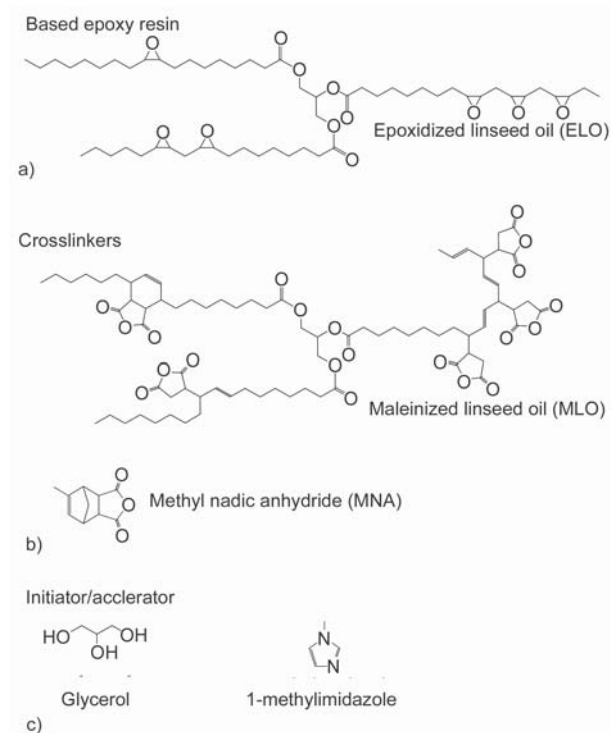
conditions it is possible to reach the best mechanical performance on cured materials. In general, the use of amine-based hardeners allows curing at lower temperatures but anhydrides require higher curing temperatures to trig the reaction. Industrially, anhydrides are the selection for high performance cured epoxies [36].

## 2.2. Study of the curing process of ELO-based thermosetting resins

The curing study was followed by differential scanning calorimetry (DSC) and parallel plate oscillatory rheometry (OR). The DSC analysis was conducted in a DSC calorimeter 821 from Mettler-Toledo (Schwerzenbach, Switzerland). All the liquid mixtures were subjected to a dynamic curing cycle from 30 up to  $300^\circ\text{C}$  at a heating rate of  $5^\circ\text{C} \cdot \text{min}^{-1}$ . Isothermal curing process at  $110^\circ\text{C}$  was followed by oscillatory rheometry in a AR-G2 rheometer from TA instruments (New Castle, USA). The procedure was configured with parallel plates with a diameter of 25 mm. The maximum deformation was set to 0.1% ( $\gamma$ ) and the selected frequency was 1 Hz. The gel time was obtained as the crossover point between the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ).

## 2.3. Study of post-curing process

The optimum post-curing conditions were studied by dynamic-mechanical thermal analysis (DMTA) using as reference the crosslinked resin 0MLO (50 wt% ELO/50 wt% MNA) after a post-curing process of 2 h at  $110^\circ\text{C}$ . Different post-curing temperatures in the  $140\text{--}180^\circ\text{C}$  and different times (1–2 h) were used. The dynamic-mechanical properties (storage modulus,  $G'$  and damping factor,  $\tan \delta$ ) were obtained in an oscillatory rheometer AR G2 from TA Instruments (New Castle, USA) equipped with an accessory for solid samples working in torsion/shear



**Figure 1.** Schematic plot of the chemical structures of a) biobased epoxy resin from epoxidized linseed oil (ELO), b) anhydride-type crosslinkers and c) initiator and accelerator.

conditions. Samples sizing  $40 \times 10 \times 4 \text{ mm}^3$  were subjected to a temperature sweep from 30 up to  $200^\circ\text{C}$  at a constant heating rate of  $2^\circ\text{C} \cdot \text{min}^{-1}$ . The selected frequency was 1 Hz and the maximum allowed deformation ( $\gamma$ ) was 0.1%.

## 2.4. Mechanical and morphological characterization

Standard flexural tests were carried out in a universal test machine ELIB 30 from S.A.E. Ibertest (Madrid, Spain). All tests were run at room temperature and using a crosshead speed of  $5 \text{ mm} \cdot \text{min}^{-1}$  using a load cell of 5 kN. At least five different samples were tested and averaged following the guidelines of ISO 178. The Shore D hardness was obtained using a Shore D 673-D durometer from Instrumentos J. Bot S.A. (Barcelona, Spain) using samples with a thickness of 4 mm. Five different measurements were carried out and average values were calculated.

To observe the fracture surface, samples were cryofractured using liquid nitrogen and then it was observed by field emission scanning electron microscopy (FESEM) in a ZEISS ULTRA microscope from Oxford Instruments (Oxfordshire, United Kingdom) using an acceleration voltage of 2 kV. Prior to sample observation by FESEM, an ultrathin platinum layer was sputtered using a high vacuum sputtering coater EM MED020 from Leica Microsystems (Buffalo Grove, Illinois, USA).

## 2.5. Thermo-mechanical characterization

A thermomechanical analysis was carried out on cured and post-cured materials in a Q400 thermomechanical analyser from TA Instruments (New Castle, Delaware, USA). Squared samples ( $10 \times 10 \text{ mm}^2$ ) and an average thickness of 4 mm were subjected to a TMA analysis in expansion from 20 up to  $15^\circ\text{C}$  at a heating rate of  $2^\circ\text{C} \cdot \text{min}^{-1}$  with a normal force of 20 mN. All the tests were run under nitrogen atmosphere with a flowrate of  $250 \text{ ml} \cdot \text{min}^{-1}$ . The heat deflection temperature (HDT) was measured following ISO 75-1. The selected method was 'A' which recommends a load of 1.8 MPa and a heating rate of  $120^\circ\text{C} \cdot \text{h}^{-1}$ . Regarding the Vicat softening temperature (VST), ISO 306 was used as the standard. VST values were obtained using the 'B' method which recommends a load of 50 N and a heating rate of  $50^\circ\text{C} \cdot \text{h}^{-1}$ . Both VST and HDT tests were carried out in a standard VICAT/HDT DEFLEX 684-As from Metrotec S.A. (San Sebastián, Spain).

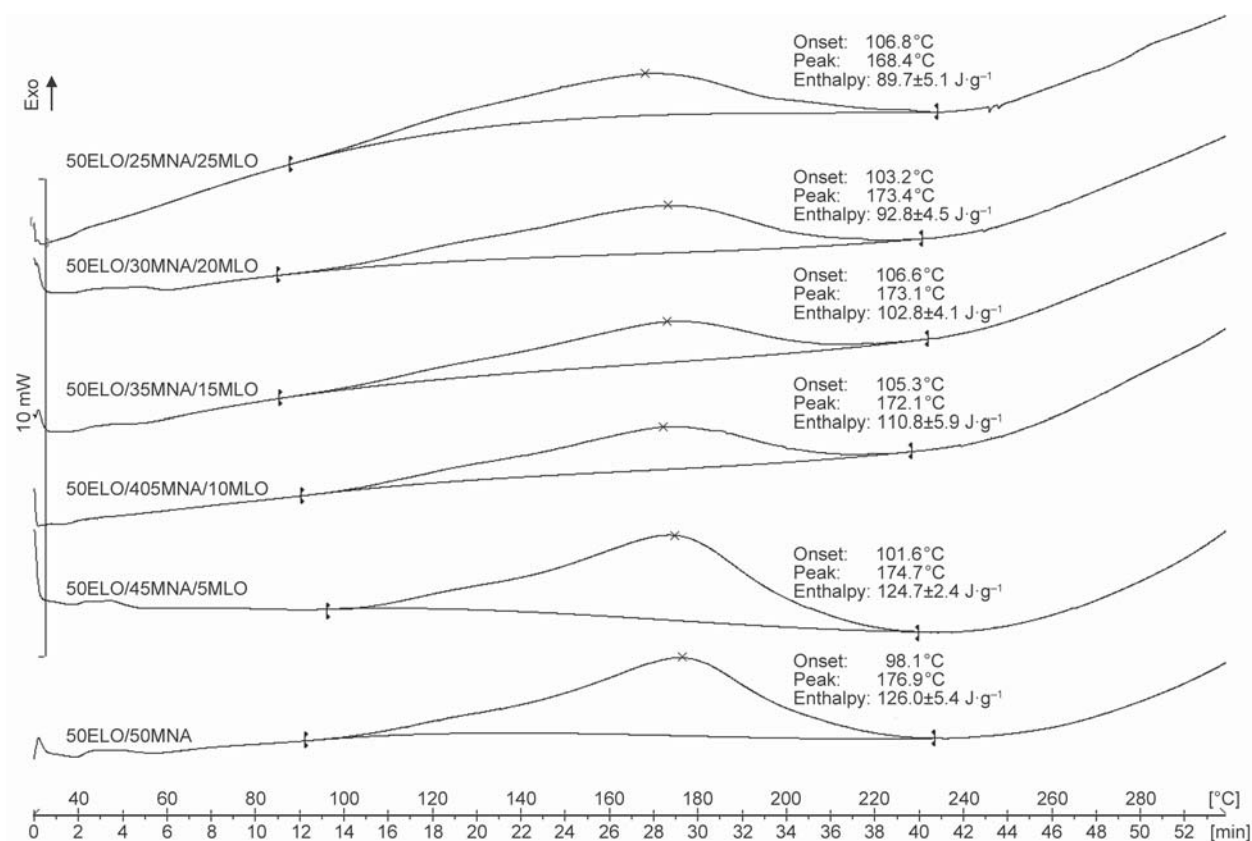
## 3. Results and discussion

### 3.1. Characterization of the curing and post-curing process of ELO-based thermosetting resins crosslinked with MNA/MLO mixtures

The curing cycle in a thermosetting resin is a key issue to obtain good properties. To evaluate this, dynamic differential scanning calorimetry (DSC) was used. Figure 2 shows a plot comparison of the exothermic peak attributable to the crosslinking process. As it can be seen, the crosslinking process starts at about  $98\text{--}107^\circ\text{C}$  and ends between  $225\text{--}235^\circ\text{C}$ , depending on the composition of the mixture hardener. It is worthy to note that the peak temperature, which represents the maximum reaction rate, shows a decreasing tendency as the MLO increases. In fact, it changes from  $176.9^\circ\text{C}$  for ELO system crosslinked with the MNA/MLO (50/0) mixture down to values of  $168.4^\circ\text{C}$  for the crosslinked system with a MNA/MLO (25/25) mixture. In addition, the enthalpy also shows the same tendency. The maximum reaction enthalpy is obtained with the MNA/MLO (50/0) mixture with a value of  $126.0 \pm 5.4 \text{ J} \cdot \text{g}^{-1}$ . As the MLO content increases, the peak enthalpy decreases thus indicating that MLO leads to less exothermicity. Thus, the ELO resin cured with the MNA/MLO (45/5) mixture shows a slight decrease in the enthalpy value ( $124.7 \pm 2.4 \text{ J} \cdot \text{g}^{-1}$ ) while the crosslinked system the MNA/MLO (25/25) mixture reaches lowest values of  $89.7 \pm 5.1 \text{ J} \cdot \text{g}^{-1}$ . This less exothermic values are directly related to the MLO chemical structure with a molecular weight over  $900 \text{ g} \cdot \text{mol}^{-1}$ . These macromolecules increase the weight but the number of epoxide groups per gram are lower than in MNA. For this reason, as the MLO content increases, the peak enthalpy also decreases.

The gel time was measured through oscillatory rheometry at isothermal conditions ( $110^\circ\text{C}$ ). This particular isothermal temperature was selected considering that the onset of the crosslinking process is located between  $80\text{--}100^\circ\text{C}$  as observed previously by DSC analysis. At the initial stage, the liquid mixture shows a phase angle of  $90^\circ$ , typical of liquids which indicates that the deformation phasor is delayed with regard to the applied stress phasor by  $90^\circ$ . When the resin is fully cured, it behaves as a typical elastic solid in which, the deformation phasor is in phase with the applied stress phasor. For this reason, it is possible to follow the crosslinking process by following the evolution of the phase angle ( $\delta$ ) with

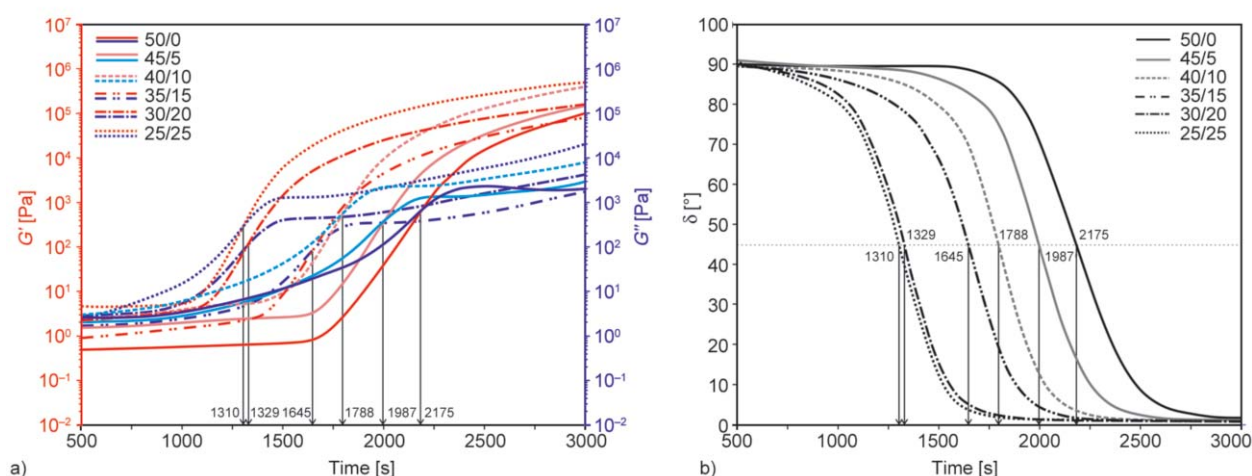




**Figure 2.** Plot comparison of the dynamic DSC thermograms of the curing process epoxidized linseed oil (ELO) crosslinked with a mixture of methyl nadic anhydride (MNA) and maleinized linseed oil (MLO).

time. The gel time can be defined as the mid-point between a fully liquid behaviour and a fully elastic solid behaviour. This implies a phase angle of 45° and the values of both the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) are equal (crossover point) [45]. To evaluate the curing conditions, the evolution of the storage modulus ( $G'$ ), loss modulus ( $G''$ ) and the phase angle ( $\delta$ ) were collected on liquid resins

cured at 110°C by OR as represented in Figure 3, and Table 2 shows a summary of the main parameters obtained. In particular, the onset ( $\delta \approx 90^\circ$ ), the end-set ( $\delta \approx 0^\circ$ ) and the crossover point ( $G' = G''$  or  $\delta = 45^\circ$ ). It can be concluded that the reaction (crosslinking) rate is higher as the MLO content in the crosslinking mixture increases. These results are in total agreement with the previous DSC results which indicated



**Figure 3.** Variation of a) the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) and b) the phase angle ( $\delta$ ) of curing process of epoxidized linseed oil (ELO) crosslinked with a mixture of methyl nadic anhydride (MNA) and maleinized linseed oil (MLO), obtained by oscillatory rheometry (OR).

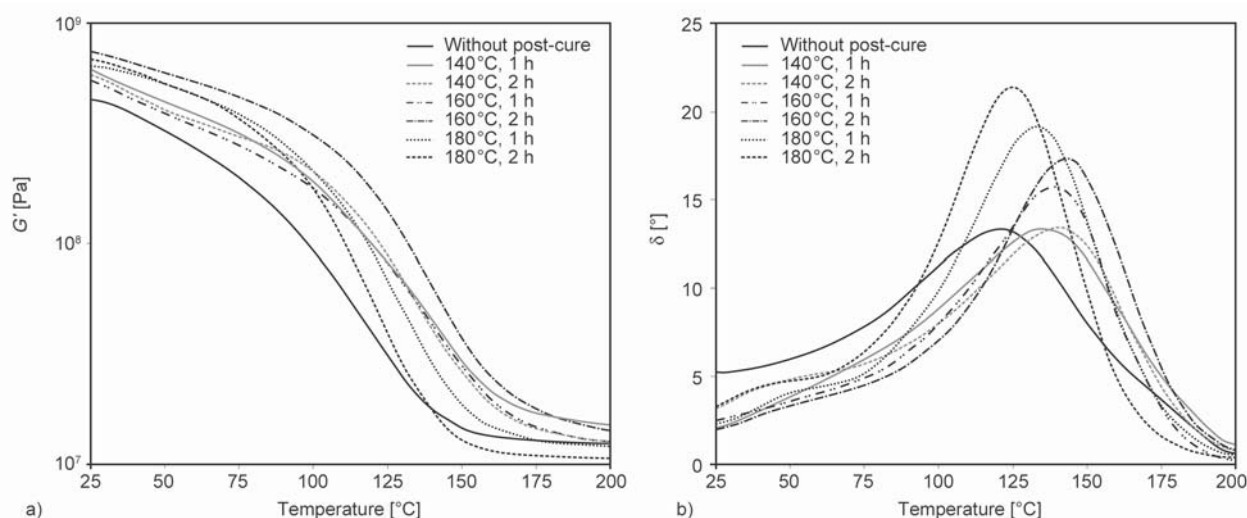
**Table 2.** Main parameters of the curing process of epoxidized linseed oil (ELO) crosslinked with a mixture of methyl nadic anhydride (MNA) and maleinized linseed oil (MLO), obtained by oscillatory rheometry (OR).

MNA/MLO [wt/wt]	Crosslinking onset ( $\delta \approx 90^\circ$ ) [s]	$G' = G''$ [Pa]	Gel time ( $\delta = 45^\circ$ ; $G' = G''$ ) [s]	Crosslinking endset ( $\delta \approx 0^\circ$ ) [s]
50/0	1678	545	2175	2939
45/5	1658	307	1987	2605
40/10	1497	514	1788	2457
35/15	1439	79	1645	2185
30/20	1186	111	1329	1849
25/25	1149	318	1310	1830

a decrease in the peak temperature which is representative of the maximum reaction rate. So that, presence of MLO, accelerates the crosslinking process. For example, the ELO-system cured with the MNA/MLO (50/0) mixture shows an onset, gel and endset times of 1678, 2175 and 2939 s respectively. These characteristic times are remarkably reduced by increasing the MLO content, so, the ELO-system cured with a mixture MNA/MLO (25/25), shows reduced time values of 1145, 1310 and 1830 s for the onset, gel and endset times, respectively. This represents a percentage decrease of about 30% with regard to the onset and a percentage decrease of almost 40% in the gel time and the endset time. This is an important feature from an industrial point of view as fully cured materials can be obtained with lower curing times. With these results, it was concluded that the use of isothermal conditions at 110 °C for 2 h is enough to obtain fully cured materials with an average thickness of 4 mm.

In addition to the cure cycle, a post-curing stage is useful to obtain the best mechanical properties in a

crosslinked polymer. The post-curing process can increase the crosslinking density thus leading to an increase in mechanical performance and in the glass transition temperature ( $T_g$ ) [47]. To evaluate the optimum post-curing conditions, the evolution of the storage modulus ( $G'$ ) and the phase angle ( $\delta$ ) were collected on cured resin of the sample 0MLO (50 wt% ELO/50 wt% MNA) subjected to several post-curing conditions as represented in Figure 4 and Table 3. It can be clearly seen that the glass transition temperature ( $T_g$ ) increase after all the post-curing cycles. Thus, the  $T_g$  of the simply cured ELO resins is close to 126.4 °C. Post-curing at 140 °C for 1 additional hour leads to a remarkable increase in  $T_g$  up to 141.2 °C and a slight increase up to 144.0 °C is obtained after 2 h at 140 °C post-curing. The most important changes are obtained after 1 h post-curing. The same situation can be observed for a post-curing cycle at 160 °C. The  $T_g$  is increased up to 147.7 °C (1 h) and 147.4 °C (2 h). Nevertheless, although increased  $T_g$  values are obtained, these are lower than those observed at 160 °C thus indicating somewhat

**Figure 4.** Variation of a) the storage modulus ( $G'$ ) and b) the phase angle ( $\delta$ ) of crosslinked 0MLO (50 wt% ELO/50 wt% MNA) with different post-curing conditions obtained by dynamic-mechanical thermal analysis (DMTA).

**Table 3.** Variation of storage modulus at different temperatures and the phase angle ( $\delta$ ) of crosslinked 0MLO (50 wt% ELO/50 wt% MNA) with different post-curing conditions obtained by dynamic-mechanical thermal analysis (DMTA).

Postcure conditions	$G'$ [MPa]					$T_g$ [°C]
	30°C	75°C	100°C	150°C	200°C	
Without postcure	495.6	238.4	119.6	15.6	13.7	126.4
140°C, 1 h	620.5	351.8	224.3	32.6	14.8	141.2
140°C, 2 h	615.2	309.3	203.0	33.2	12.2	144.0
160°C, 1 h	581.5	335.5	242.1	31.5	12.3	147.7
160°C, 2 h	809.3	504.3	356.0	46.3	14.2	147.4
180°C, 1 h	640.5	420.8	259.0	21.6	12.5	138.4
180°C, 2 h	648.2	309.3	203.0	33.2	12.2	144.0

thermal degradation. With regard to the storage modulus ( $G'$ ), all post-cured samples show increased  $G'$  values thus indicating the usefulness of the post-curing in enhancing mechanical performance. The highest  $G'$  values are obtained for a post-curing process at 160°C for 2 h which, finally, are the best post-curing conditions as both  $T_g$  and  $G'$  are remarkably increased in comparison to the other temperature-time conditions.

### 3.2. Mechanical properties of ELO-based thermosetting resins crosslinked with MNA/MLO mixtures

Table 4 shows a summary of the mechanical characterization (flexural properties and hardness) in terms of the MLO content in the crosslinking mixture. As it can be clearly seen, as the MLO content increases, both the flexural strength and modulus decrease thus indicating the flexibilization effect MLO can provide to these crosslinked resins. The ELO system cured with a MNA/MLO (50/0) mixture shows a flexural

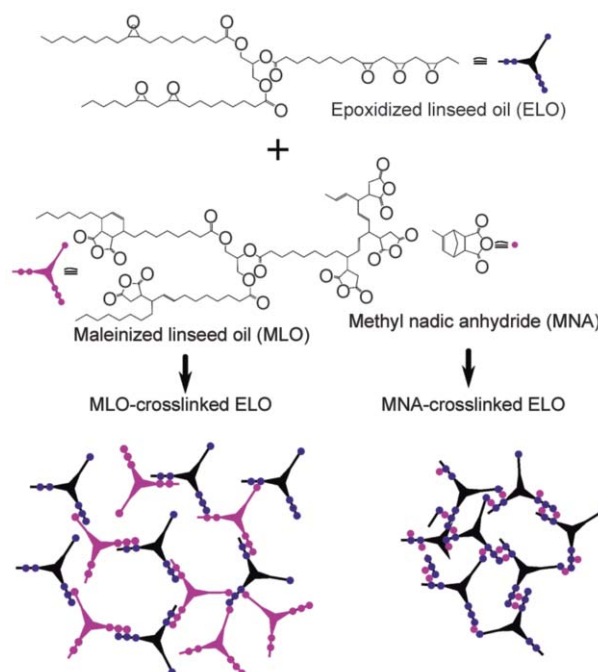
**Table 4.** Summary of mechanical properties of epoxidized linseed oil (ELO) crosslinked with a mixture of methyl nadic anhydride (MNA) and maleinized linseed oil (MLO).

MNA/MLO [wt/wt]	Flexural strength [MPa]	Flexural modulus [MPa]	Shore D
50/0	60.8 (5.8)*	1772.0 (132.0)	82.2 (2.5)
45/5	54.9 (5.4)	1460.0 (73.5)	81.9 (1.3)
40/10	47.2 (3.1)	1027.0 (46.5)	78.2 (1.9)
35/15	31.9 (4.8)	718.2 (45.2)	76.1 (1.5)
30/20	23.8 (0.5)	485.8 (33.0)	71.4 (1.8)
25/25	14.5 (0.6)	272.3 (20.9)	64.1 (1.5)

\*The numbers in parentheses stand for the standard deviation.

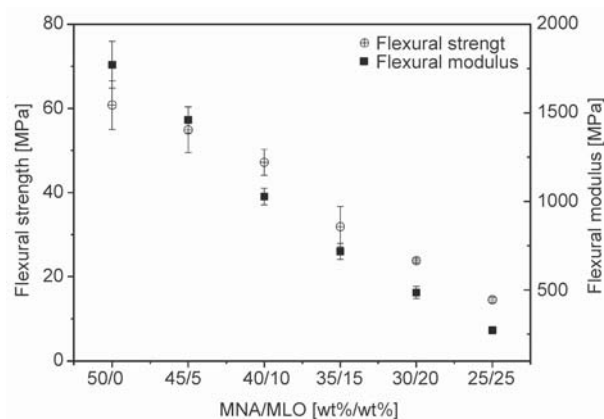
strength of 60.8 MPa and a flexural modulus of about 1.7 GPa. As it can be seen when 5 wt% MNA is replaced by MLO, MNA/MLO (45/5), the tensile strength decreases down to 54.9 MPa while the flexural modulus goes down to 1.46 GPa. The decrease in both flexural strength and modulus follows a linear tendency, as it can be seen in Figure 5. The ELO system crosslinked with a MNA/MLO (25/25) mixture shows remarkably reduced flexural properties: the flexural strength is 14.5 MPa and the flexural modulus is close to 0.27 GPa. This decrease in mechanical resistant properties is directly related to the chemical structure of the crosslinkers. On one hand, MNA is a cyclic anhydride which gives high rigidity. On the other hand, the triglyceride structure, shows linear chains corresponding to the different functionalized fatty acids and these linear chains can positively contribute to increase flexibility, thus reducing the stiffness. The effect of MNA and MLO on flexibility can be seen in Figure 6.

The Shore D hardness follows the same tendency as flexural resistant properties. The system cured with MNA/MLO (50/0) mixture, shows the highest Shore D value of about 82.2 which is reduced down to values around 64.1 by replacing 25 wt% MNA by MLO, MNA/MLO (25/25) mixture. All these results are in total agreement with the previous DSC results since



**Figure 5.** Schematic plot of the effect of methyl nadic anhydride (MNA) and maleinized linseed oil (MLO) on crosslinked epoxidized linseed oil (ELO) structures.





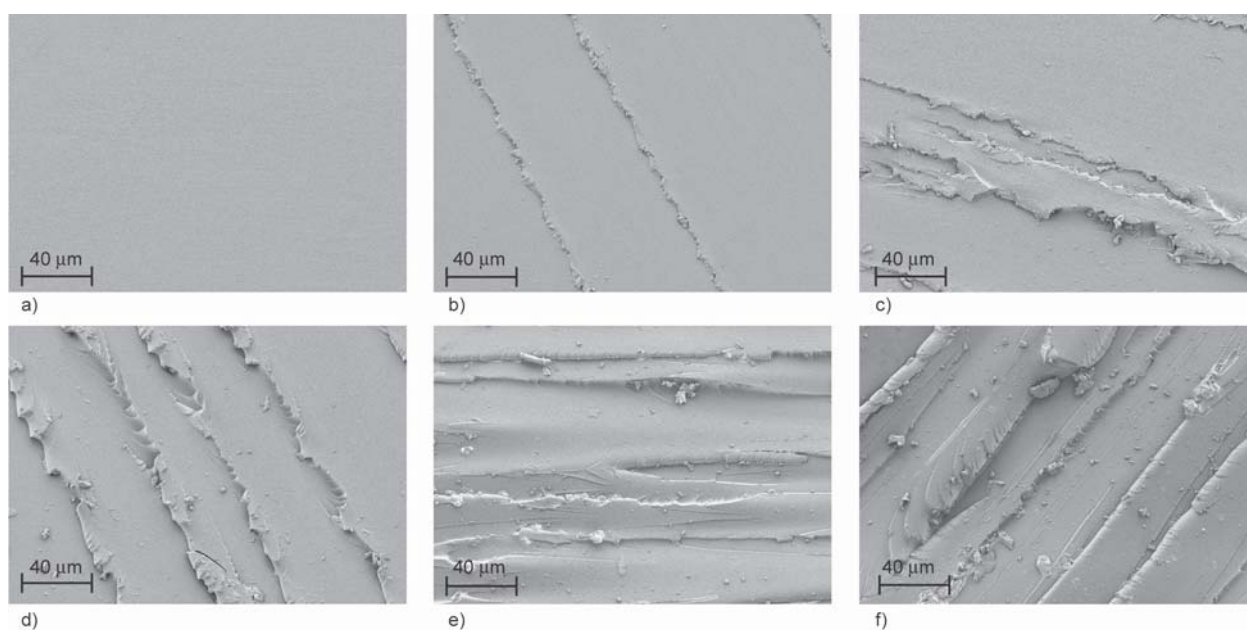
**Figure 6.** Flexural properties of epoxidized linseed oil (ELO) crosslinked with a mixture of methyl nadic anhydride (MNA) and maleinized linseed oil (MLO).

the peak enthalpy decreased as the MLO content increased, thus indicating less intensity of the crosslinking reactions with the subsequent effect on mechanical properties as corroborated by flexural tests and harness measurements. As one can see, the use of MLO as co-hardener leads to a remarkable change on overall properties. By selecting a proper MNA/MLO ratio, it is possible to obtain a wide range of mechanical properties from high stiffness materials (high MNA content) to flexible thermosetting ELO-based materials for MNA/MLO ratios of 50:50. It seems that the 40:10 for MNA/MLO ratio gives good balanced properties in terms of resistance and deformation but if we are looking for flexible thermosetting materials, higher amounts of MLO co-hardener can be employed.

To support the results obtained by flexural tests, cryo-fractured surfaces were observed by field emission scanning electron microscopy (FESEM) (Figure 7). The ELO system crosslinked with a MNA/MLO (50/0) mixture shows a smooth and homogeneous surface, typical of brittle polymers (Figure 7a). The effects of MLO on fractured surfaces is detectable even for low MLO content mixtures, MNA/MLO (45/5) as it can be seen in Figure 7b in which presence of several crack fronts can be observed which are directly related to increased flexibility. As the MLO ratio in MNA/MLO crosslinking mixtures increases (Figure 7c–7f), the number of crack fronts increase in both size and number, thus indicating increased ductility. These findings are in agreement with the flexural results that indicated the role of MLO in increasing ductility.

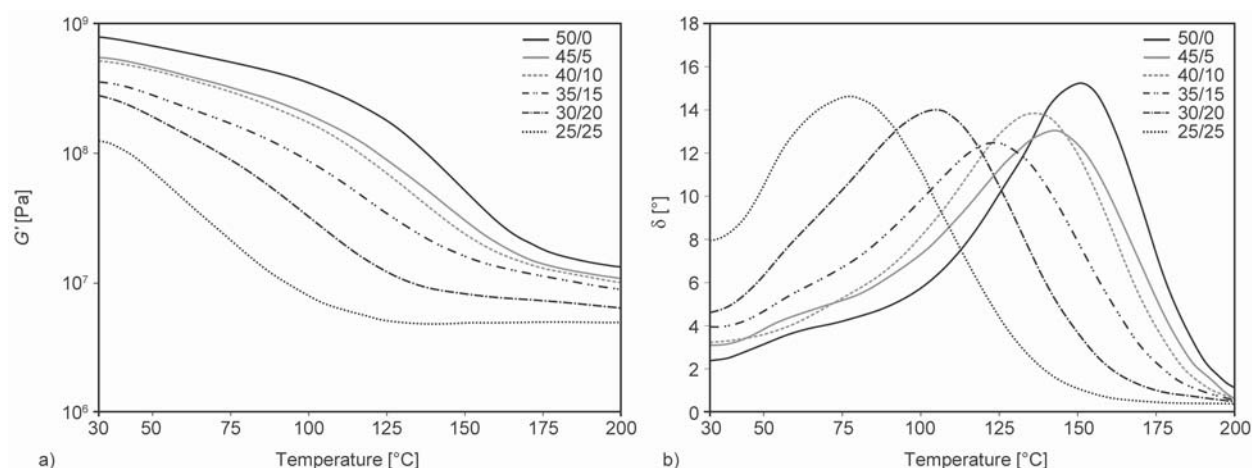
### 3.3. Thermo-mechanical properties of ELO-based thermosetting resins crosslinked with MNA/MLO mixtures

Once the post-curing cycle was defined, all cured and post-cured ELO materials crosslinked with MNA/MLO mixtures were characterized by DMTA and the main parameters (storage modulus –  $G'$  and phase angle –  $\delta$ ) were evaluated. The main results can be observed in Figure 8. As can be seen, the glass transition temperature ( $T_g$ ) decreases as the MLO content in MNA/MLO mixtures increases. The  $T_g$  of the ELO-system crosslinked with a MNA/MLO (50/0) mixture reaches high values of 150.5 °C. The flexibilization



**Figure 7.** Field emission scanning electron microscopy (FESEM) images Corresponding to fractured samples of crosslinked ELO with a mixture of MNA/MLO [wt/wt], a) (50/0), b) (45/5), c) (40/10), d) (35/15), e) (30/20) and f) (25/25).





**Figure 8.** Variation of a) the storage modulus ( $G'$ ) and b) the phase angle ( $\delta$ ) of ELO-based resins crosslinked with a mixture of methyl nadic anhydride (MNA) and maleinized linseed oil (MLO), obtained by dynamic-mechanical thermal analysis (DMTA).

effect of MLO can be seen in ELO-system crosslinked with a MNA/MLO (45/5) mixture as the  $T_g$  goes down to values of 141.0 °C. This decreasing tendency is maintained and the crosslinked ELO-system with a MNA/MLO (25/25) mixture shows remarkably low  $T_g$  values of 75.8 °C, as seen in Figure 8b. Furthermore, the effects of MLO are also detectable by following the evolution of  $G'$ . The highest  $G'$  values are obtained for the ELO-system crosslinked with MNA/MLO (50/0) due to the high rigidity of the MNA molecule compared to MLO structure. As the MLO content in MNA/MLO mixtures increases,  $G'$  also moves to lower values as seen in Figure 8a. MLO contributes to more flexible materials thus giving the possibility of tailoring the desired mechanical properties by selecting the appropriate MNA/MLO crosslinking mixture.

The thermomechanical properties of the ELO-system crosslinked with different MNA/MLO mixtures are summarized in Table 5. With regard to thermomechanical analysis (TMA), the  $T_g$  was obtained through the change in the slope of the linear expansion versus

temperature. These  $T_g$  values follow the same tendency as those obtained by DMTA analysis. With regard to the heat deflection tendency (HDT) and Vicat softening temperature (VST) it is worthy to note the same decreasing tendency as the MLO content in MNA/MLO mixtures increases. These results are in total accordance with previous flexural properties as well as dynamic-mechanical thermal analysis, showing the potential of MLO to give flexibility to crosslinked ELO resins. In particular, by replacing up to 25 wt% MNA by MLO, it is possible to obtain a HDT range from 78.2 °C (using only MNA as crosslinker) to 40.6 °C using a MNA/MLO (25/25) mixture. With regard to VST, by selecting the appropriate MLO content, it is possible to obtain flexible (low thermal stability) materials with a VST of 42.4 °C using a MNA/MLO (25/25) and also high thermally stable materials with VST values of 133.4 °C using a MNA/MLO (50/0) mixture as crosslinking agent.

If we compare the results obtained in this work with other epoxidized vegetable oil cured with different crosslinking agents made in previous works (Table 6) [15, 22], it showed that some epoxy resins developed in this work present better mechanical and thermomechanical properties than epoxy resins cured with maleic anhydride and a mix of maleic anhydride (MA) and phthalic anhydride (PA). The most important difference is found in the reduction of the crosslinking agent of petro origin maintaining a good balance in the mechanical and thermomechanical properties. With the obtained result the resin 50ELO: 40MNA:10MLO might be a good candidate to use as a matrix in green composite materials.

**Table 5.** Thermomechanical properties of ELO-based resins crosslinked with a mixture of methyl nadic anhydride (MNA) and maleinized linseed oil (MLO).

MNA/MLO [wt/wt]	TMA ( $T_g$ ) [°C]	VST [°C]	HDT [°C]
50/0	138.8	133.4	78.2
45/5	131.1	123.8	69.8
40/10	125.2	113.0	64.8
35/15	120.7	96.0	57.4
30/20	99.9	63.4	50.6
25/25	68.7	42.4	40.6

**Table 6.** A comparison of mechanical and thermomechanical properties of EVO based epoxy resins crosslinked with different agents.

Epoxy resin		Flexural modulus [MPa]	Flexural strength [MPa]	Shore D	VST [°C]	HDT [°C]	TMA ( $T_g$ ) [°C]	Ref.
EVO	Crosslinking							
ELO	MNA	1772.0	60.8	82.2	133.4	78.2	138.8	t.w.*
ELO	40MNA/10MLO	1027.0	47.2	78.2	113.0	64.8	125.2	t.w.*
ELO	60MNA/40MLO	485.8	23.8	71.4	99.9	63.4	50.6	t.w.*
ESBO	MNA (1:0.9)	334.1	–	69.0	45.9	28.0	42.6	[22]
ESBO	MNA (1:1)	432.0	–	70.0	46.0	31.2	36.3	[22]
ESBO	MNA (1:1.1)	420.9	–	66.3	45.1	29.8	34.7	[22]
ELO	PA/MA	622.8	35.8	66.5	88.8	65.0	37.2	[15]
80ELO/20ESBO	PA/MA	676.4	33.4	63.3	73.2	53.8	33.2	[15]
ESBO	PA/MA	11.1	1.3	21.9	–	–	27.0	[15]

\*t.w.: it means this work

#### 4. Conclusions

The herein obtained results suggest the usefulness of maleinized linseed oil (MLO) as renewable co-crosslinker for epoxidized linseed oil (ELO) together with a petroleum-based crosslinker such as methyl nadic anhydride (MNA), thus leading to high renewable content crosslinked epoxies. The calorimetric study revealed that MLO accelerates the crosslinking reaction as the peak temperature is moved towards lower temperatures while the peak enthalpy decreases with increasing MLO content. During a dynamic curing cycle, the crosslinking process starts at about 80–100 °C and finishes at 225–235 °C. Isothermal cure at 110 °C/2 h gives the best balanced properties in terms of mechanical and thermal properties. As the MLO content increases, the gel time decreases thus showing a faster crosslinking process. Post-curing cycle is necessary to reach the best mechanical and thermal performance. The obtained results suggest that a post-curing cycle at 160 °C and 2 addition hours gives the best mechanical properties together with the highest  $T_g$  values. MLO molecules are more flexible than MNA and this fact is responsible for a decrease in stiffness in ELO-cured resins as the MLO content increases thus giving the possibility of tailoring the desired mechanical and thermal properties on ELO-based resins by selecting the appropriate amount of MLO. In addition, as the MLO content increases, the renewable content also increases which is an important feature from an environmental point of view.

#### Acknowledgements

This work has been supported by the Spanish Ministry of Economy and Competitiveness, PROMADEPCOL (MAT2017-84909-C2-2-R). MDS is recipient of a APOSTD2018 contract (APOSTD/2018/209) from Conselleria d'Educació, Investigació, Cultura y Esport de la Generalitat Valenciana.

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