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Development of environmentally friendly composite matrices from epoxidized cottonseed oil

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“Development of environmentally friendly composite matrices from epoxidized cottonseed oil”

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Abstract

The continuous rise in oil prices has led to the use of other ways to obtain polymer materials. This paper proposes a methodology to obtain a thermosetting resin from cottonseed oil by epoxidation process. The cottonseed oil contains as most representative fatty acids: 52.5% of linoleic acid (C18: 2), 23.9% of palmitic acid (C16: 0) and 17.6% of oleic acid (C18: 1); the real iodine index, which is indicative of the number of double bonds, has a value of 107. Epoxidized cottonseed oil (ECSO) has been successfully obtained using conventional epoxidation process with hydrogen peroxide, acetic acid and sulfuric acid, maintaining a constant temperature of 70 °C with homogeneous magnetic stirring. Average oxirane oxygen content (OOC) of 5.32% can be obtained by conventional epoxidation process which represents a yield over 83%. The epoxidized oil has been crosslinked with mixtures of two cyclic anhydrides to tailor different properties on final crosslinked thermosetting resins: on the one hand, methyl nadic anhydride (MNA) which is characterized by a rigid molecular structure and on the other hand, dodecenylsuccinic anhydride (DDSA) with a long side chain that can confer flexibility. The crosslinking process has been followed by dynamic differential scanning calorimetry (DSC), ionic mobility and oscillatory rheometry (OR) as well as gel time determination. The effect of the hardener mixture (wt. % DDSA:MNA) on mechanical performance of cured materials has been followed by flexural and impact tests as well as the evolution of the storage modulus (G') by dynamic mechanical analysis (DMA) in torsion mode. By selecting the appropriate hardener mixture, it is possible to obtain crosslinked materials with different properties ranging from

stiff matrices for ECSO crosslinked with MNA to flexible matrices for ECSO cured with DDSA. This has occurred with other thermosetting resins like epoxidized soy bean oil (ESBO) or epoxidized linseed oil (ELO).

Keywords: Cottonseed oil; epoxidation; dodecenylsuccinic anhydride; methyl nadic anhydride; biobased epoxy resin.

1.- Introduction.

The increasing concern about the environmental impact of polymer materials together with the problems related to petroleum depletion act as driving forces to replace petroleum-based polymer materials by others from renewable resources with a marked environmental efficiency and, in many cases, giving solution to industrial wastes. In the field of thermosetting resins, important advances have been obtained by using vegetable oils which can be converted into epoxy resins by different epoxidation methods. [1, 2] Currently some epoxidized oils are marketed industrially in large quantities such as soybean with a production of 200,000 t/year [3]. Vegetable oils with high content of unsaturated fatty acids such as oleic acid, linoleic acid and linolenic acid may be used to obtain epoxy groups [4] by using several epoxidation processes. [5-7] A schematic representation of the epoxidation process from cottonseed oil (CSO) is shown in Fig. 1.

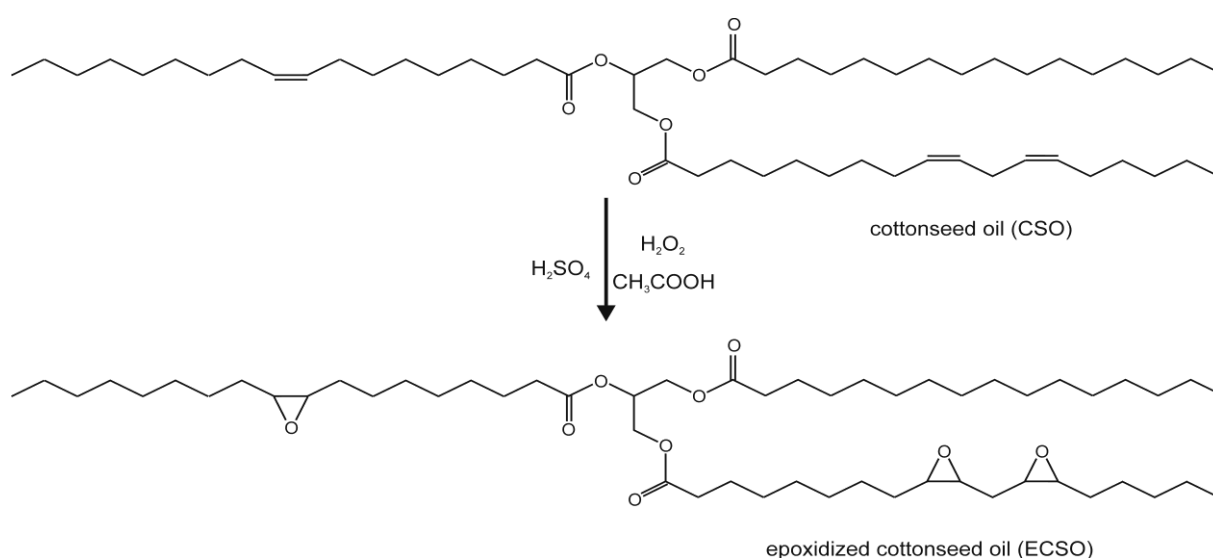


Figure 1 .- Schematic representation of the epoxidation process from cottonseed oil (CSO).

In the last decade, different epoxidation processes have been successfully used to obtain epoxidized vegetable oils (EVOs) being soybean oil (SBO) and linseed oil (LO) the most used with difference but it has been reported the use of sunflower oil [8, 9] wheat oil [10] castor oil [11] or fish oil [12] with attracting uses as industrial plasticizers. The suitability of a vegetable oil to be subjected to an epoxidation process is directly related to the total content on unsaturated fatty acids being the iodine index a high representative value for the presence of unstaurations which can be converted into oxirane rings. The epoxidation of a fatty acid is a carbon-carbon double bond reaction with active oxygen, which results in the addition of an oxygen atom, which converts the original double bond into a three member ring (oxirane) [13]. The obtained epoxides may have several applications: they can be used as plasticizers for PVC [14], also as thermosetting resins for composites or as stabilizers for plastics and coatings [2].

Cottonseed oil can be considered as a co-product or by-product of the cotton industry and it finds some uses as edible oils [15] although there is some controversy on the potential health effects due to presence of some components such as gossypol [16, 17] and less strict control than all other plants whose main product is vegetable oil; cottonseed oil is also used for soap making, cosmetics and pharmaceuticals as well as a raw material in the manufacture of plastics, fungicides, paper, textiles, fuel, etc. [18, 19] Epoxidation is another way of using this oil since the global production was 5 million tons in 2011 [20] and its potential in the composites' industry is really promising.

Epoxidized vegetable oils can be crosslinked with different compounds. In contrast to terminal epoxides (typical of petroleum-based epoxies) that can be easily reacted with amines (even at room temperature) to give fully cured materials, the epoxy groups in epoxidized vegetable oils are not located in terminal positions so that, reaction with amines is difficult. [21] Reaction of non-terminal groups proceeds with carboxylic acids; so that, cyclic anhydrides derived from dicarboxylic acids have been proposed as attractive curing agents for EVOs. Maleic anhydride (MA) and phthalic anhydride (PA) have been used as hardeners for epoxy resins; nevertheless, as they have a melt point of 52.8 °C and 131.6 °C respectively, the formulation needs previous heating to homogenize mixture with the liquid resin. For this reason, low melting temperature cyclic anhydrides are preferable since they can be easily mixed with the EVO. Some cyclic anhydrides such as methyl hexahydrophthalic anhydride

(MHHPA) and methyl tetrahydrophthalic anhydride (MTHPA) are liquids at room temperature and they are widely used as epoxy hardeners for high temperature thermosetting applications such as electric and electronic industry [22, 23]. In addition to these, other cyclic anhydrides such as alkenyl succinic anhydrides (ASA) have been proposed as curing agents for epoxy resins and the effect of the side chain length on thermal and mechanical properties of crosslinked materials has been studied. [24-26] In general terms, it has been reported a decrease in tensile strength as the side chain length in ASA increases. The rigidity of the curing agent plays a key role on mechanical properties of cured materials. Although MHHPA and MTHPA are quite rigid molecules, some derived structures offer more rigidity as it is the case of methyl nadic anhydride (MNA) characterized by the norbornene group which confers high rigidity [27] and this contributes to higher heat-distortion temperatures as well as higher stiffness on cured materials. [28]

The final stiffness of a cured epoxy not only depends on the rigidity of the curing agent molecule but also on the number of epoxy groups per triglyceride. The more epoxy groups, the higher number of crosslinking points can be achieved thus leading to more rigidity. The potential stiffness of a cured epoxide can be estimated by the equivalent epoxide weight (EEW) which represents the ratio between the molecular weight of the triglyceride and the average number of epoxide groups. Commercial epoxidized linseed oil (ELO) offers EEW in the 170-190 g equiv⁻¹ range while epoxidized soybean oil (ESBO) is characterized by lower EEW values in the 230-240 g equiv⁻¹ range (both values can vary depending on the purity on certain fatty acids such as linolenic and linoleic acids). In general terms, cured ELO epoxies are stiffer than ESBO cured materials. [29]

The main aim of this work is to evaluate the potential of cottonseed oil (CSO) as base material for obtaining epoxy-based thermosetting resins by epoxidation with *in-situ* generated peracetic acid obtained from hydrogen peroxide and acetic acid. The first part of the manuscript is focused on characterizing the epoxidation efficiency and the second part is focused on the study of the curing process of epoxidized cottonseed oil (ECSO) with mixtures of two cyclic anhydrides as well as the characterization of the final properties of the crosslinked materials. Anhydride mixtures were prepared with a flexible anhydride (DDSA- dodecenylsuccinic anhydride) and a highly rigid anhydride (MNA- methyl nadic anhydride) to tailor the desired properties on fully cured materials.

2.- Experimental.

2.1.- Materials.

The base vegetable oil for epoxidation was cottonseed oil (CSO) with a iodine value provided by the manufacturer between 109 and 120 with a density of 0.92 g cm^{-3} .

The epoxidation process was carried out with *in situ* generated peracetic acid from acetic acid (99.7% from Sigma Aldrich) and hydrogen peroxide (30 % v/v supplied by Panreac Química) in acid media: sulfuric acid (96%) supplied by Panreac Química.

Formulations to crosslink epoxidized cottonseed oil were based on two different hardeners: on the one hand, a flexible cyclic anhydride namely dodecenylsuccinic anhydride (DDSA) with an anhydride equivalent weight (AEW) of $268.39 \text{ g equiv}^{-1}$ and on the other hand a rigid cyclic anhydride, methyl nadic anhydride (MNA) with an AEW of $178.2 \text{ g equiv}^{-1}$. Both curing agents were supplied by Sigma Aldrich. The EEW:AEW ratio was set to 1:1 and additional 1 wt. % glycerol (Sigma Aldrich) and 2 wt. % 1-methyl imidazole, 1-MI (Sigma Aldrich) were added as initiator and accelerator components respectively. Fig. 2 shows the chemical structures of the different components used to crosslink the epoxidized cottonseed oil.

For the characterization of the crosslinked resins, liquid resins were placed on a silicon mold with rectangular shapes ($80 \times 10 \times 4 \text{ mm}^3$) for mechanical characterization. The curing cycle consisted on isothermal curing process at $110 \text{ }^\circ\text{C}$ for 3 h.

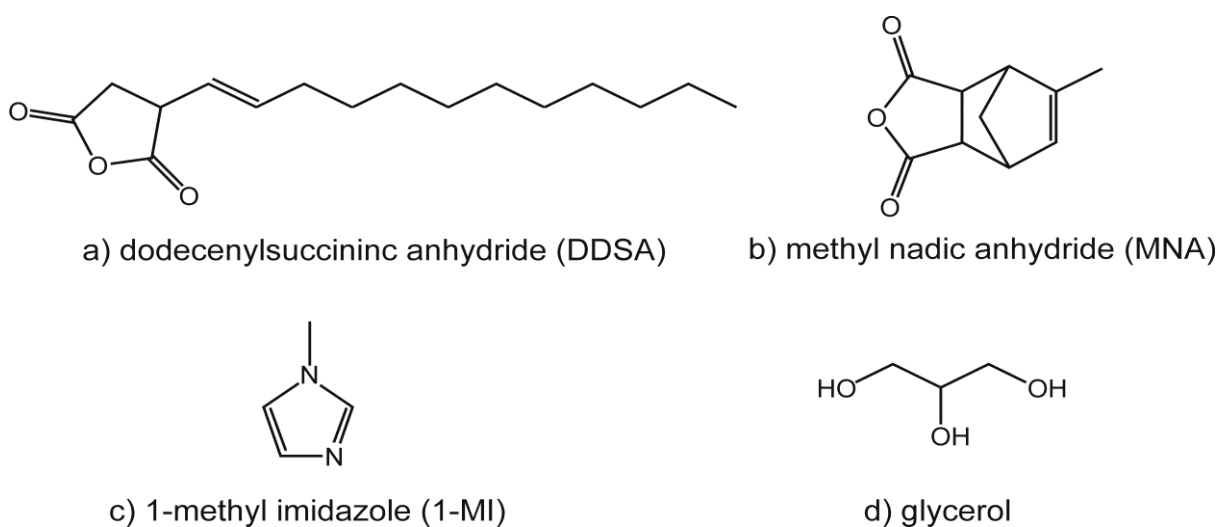


Figure 2.- Schematic representation of different components used to crosslink epoxidized cottonseed oil.

2.2.- Epoxidation process.

Epoxidation was carried out in a 500 mL three-neck round-bottom flask equipped with a heating mantle. A thermometer was connected to a neck to ensure constant temperature during reaction; the second neck was connected to a reflux condenser and the third neck was used to drop reactives and ensure inert atmosphere.

The procedure is summarized as follows: 188 g of cottonseed oil were added to the flask and magnetic stirring was maintained until a temperature of 55 °C was reached; then 19.7 mL of acetic acid was added. After 10 min at 55 °C, 192 mL (for a 3:1 ratio) hydrogen peroxide were added together with 1.52 mL of sulfuric acid. The mixture was added drop by drop in order to trigger the onset of the reaction using a dropping funnel over 30 min. The working temperature was 70 °C for 8 h; special attention was paid to reaction temperature after peroxide addition. Nitrogen atmosphere was used during peroxide addition to avoid an abrupt exothermic reaction. Samples were collected every two hours to analyze the iodine index according to Wij's method (ISO 3961:2009) [30] and oxirane oxygen (ASTM D1652-97) [31] with previous cleaning with distilled water and subsequent purification by centrifugation. Following the considerations of the ISO 3961:2009 the iodine value (W_t) has been calculated by the next formula:

$$W_t = \frac{12.69 \cdot C (V_1 - V_2)}{m} \quad (1)$$

Where C is the concentration of the sodium thiosulphate (mol/ml), V_1 is the volume of standard sample sodium thiosulphate (ml), V_2 is the volume of sodium thiosulphate used in the determination (ml), and m is the mass of the analysis (gr).

2.3.- Characterization of the curing process of ECSO by oscillatory rheometry (OR).

Evolution of the curing process was followed by plate-plate oscillatory rheometry in a AR-G2 rheometer (TA Instruments, New Castle, USA) with parallel plates ($D = 25\text{mm}$). The smallest possible amount of mixture was prepared and placed between the two plates by setting the program to an isothermal curing at 110 °C and 120 °C for 4 hours because these are the minimum temperatures required for initiation of curing process. The controlled variables were a frequency of 1 Hz and at a

constant deformation of 0.1%. Evolution of the storage modulus (G'), loss modulus (G'') and phase angle (δ) were obtained in terms of time. The last parameters have been calculated by the next formulas:

$$G' = \frac{\sigma_o \cdot \cos(\delta)}{\epsilon_o} \quad (2)$$

$$G'' = \frac{\sigma_o \cdot \sin(\delta)}{\epsilon_o} \quad (3)$$

$$\tan(\delta) = \frac{G''}{G'} \quad (4)$$

Where σ_o is the stress and ϵ_o is the strain.

In addition to this, gel time was also determined by following the guidelines of the DIN 16945 [32] in a TC-4 Gelnorm Geltimer (Gel Intrumente AG, Germany, Oberuzwill). Tests were conducted at 110 °C and 120 °C.

The evolution of the curing process was also followed by dielectric measurements with a Gelnorm DE (Gel Intrumente AG, Germany, Oberuzwill) in isothermal conditions according to DIN 16945 [32] equipped with a thermocouple sensor to ensure constant temperature. A small amount of the liquid formulation was placed on a hot plate 50 mm in diameter. The gold sensor sized 17x55x0.04 mm³ was embedded into the liquid resin to measure ionic conductivity by dielectric properties. Tests were carried out at 110 °C and 120 °C.

Additionally, the curing process was followed by dynamic differential scanning calorimetry (DSC) in a Mettler-Toledo DSC 821e (Mettler-Toledo S.A.E., Barcelona, Spain). 5-10 mg of the liquid formulations were placed inside standard 40 µL Al crucibles and subjected to a heating program from 30 °C to 350 °C at a heating rate of 10 °C min⁻¹ with a constant nitrogen flow rate of 40 mL min⁻¹.

2.4.- Mechanical characterization of the crosslinked resins.

The fracture toughness was evaluated using a Charpy pendulum from Metrotec (Metrotec SA, San Sebastian, Spain) with an energy of 6 J according to ISO 179 [33].

Flexural properties of the cured formulations were obtained in a universal test machine Ibertest 300 (Elib 30, E Ibertest S.A., Madrid, Spain) following the guidelines of the UNE-EN-ISO

178 [34]. All the tests were carried out at a speed of 5 mm min^{-1} . Each test was repeated at least five times and average values were used in data analysis.

Additionally, DMA characterization was carried out in a AR-G2 oscillatory rheometer (TA Instruments, New Castle, USA) equipped with DMA (shear-torsion mode) for solid samples. Samples $40 \times 10 \times 4 \text{ mm}^3$ were subjected to a temperature sweep program from 30 to $140 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ at a constant deformation (γ) of 0.1% and a frequency of 1 Hz.

Scanning electron microscopy (SEM) of fractured surfaces from impact tests were observed in a FEI, mod. Phenom (FEI Company, Eindhoven, The Netherlands) at a 5 kV accelerating voltage. Samples were covered with an ultrathin gold-palladium alloy with a sputter coater EMITECH mod. SC7620 (Quorum Technologies Ltd, East Sussex, UK).

3. Results and discussion.

3.1.- Optimization of the epoxidation conditions.

Initially the cottonseed oil epoxidation was carried out with different equivalent molar ratio between peroxide and cottonseed oil, 1.5 and 3 to optimize the formulation for epoxidation. Fig. 3 shows a plot representation of the effect of the excess H_2O_2 on the efficiency of the epoxidation process. It can be clearly concluded that an excess molar ratio (peroxide:oil) of 3:1 gives higher values of oxirane oxygen for an epoxidation time of 8 h than the use of an excess molar ratio of 1.5:1.

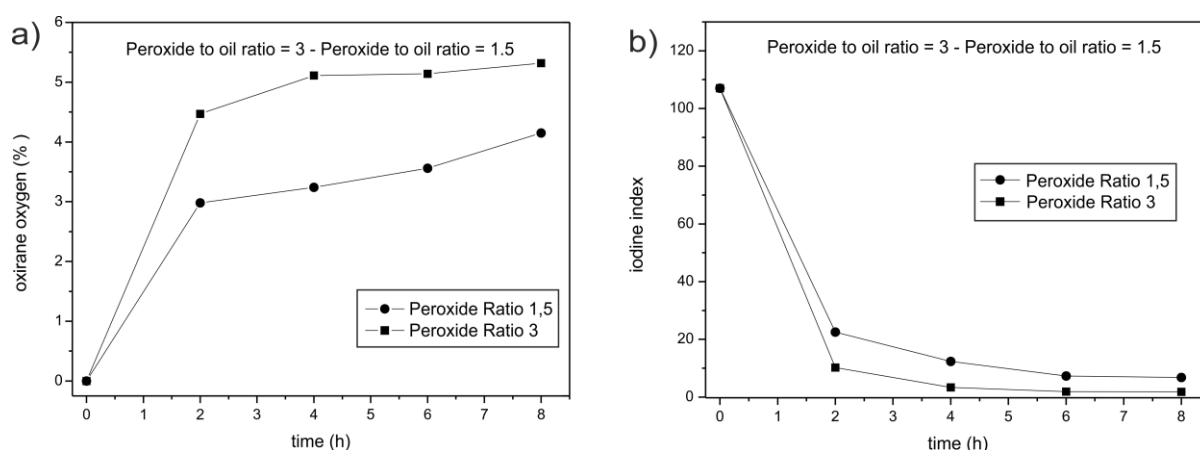


Figure 3 .- Influence of peroxide to oil ratio on a) oxirane oxygen change index during epoxidation of cottonseed oil and b) iodine index change during the epoxidation reaction.

The theoretical oxirane oxygen index calculated from the average values of fatty acid content in cottonseed oil is 6.4%. As we can see, the oxirane oxygen reaches values of about 5.32% after 8 h (for a peroxide:oil ratio of 3:1 which represents about 83% yield reaction by taking into account the oxirane oxygen criteria). Nevertheless, the initial iodine index (107) is reduced up to values of 1.79 after 8 h reaction time which indicates a 98.3% conversion of double bonds but it is important to take into account some parallel reactions which involve epoxy homopolymerization among others that do not contribute to an increase in the oxirane oxygen value but the conversion of double bonds and this fact leads to disparity in the conversion values by considering different criteria. The reaction proceeds quickly at the first two hours due to high availability of double bonds and almost no changes are observed over 8 h reaction time.

3.2. Curing of epoxidized cottonseed oil with cyclic anhydrides.

As we have described previously, dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydrides (MNA) can provide different properties to the crosslinked epoxidized cottonseed oil (ECSO) since DDSA could contribute to more flexible structures than those obtained with MNA due to differences in molecular rigidity. By combining these two cyclic anhydrides it is possible to tailor a crosslinked material to the desired properties. For this reason, DDSA:MNA mixtures have been tested as crosslinking systems for epoxidized cottonseed oil. Table 1 shows a summary of the gel time values for isothermal curing processes with different DDSA:MNA mixture hardener. The use of anhydride hardeners needs high curing temperatures in order to trigger the curing reaction and reach the gel time; so that, gel time at two different temperatures were compared. In addition, the curing rate is also related to the chemical structure of the cyclic anhydride which can contribute to accelerate or to delay the curing reaction, depending on chain length, chain mobility, etc. [35] On the other hand, it is important to take into account the anhydride equivalent weight of each cyclic anhydride which can play an important role in the viscosity increase and, subsequently, decrease in gel time values. DDSA is characterized by a AEW of 268.39 g equiv⁻¹ while MNA possesses an equivalent weight of 178.2 g equiv⁻¹. Reaction of one epoxide group in ECSO with one DDSA molecule leads to higher molecular weight crosslinked structure than in the case of MNA and this is directly related to viscosity increase

so that, viscosity increase occurs faster for the system cured with DDSA and this means lower gel time values.

DDSA (wt. %)	MNA (wt. %)	Isothermal temperature (°C)	*Gel Time (min)
100	0	110	32
		120	19
75	25	110	35
		120	19
50	50	110	40
		120	22
25	75	110	48
		120	27
0	100	110	61
		120	34

* Gel time values obtained as described in the DIN 16945 standard.

Table 1 .- Gel time values at isothermal conditions for the crosslinking of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1.

One interesting technique to follow up the curing of a thermosetting resin is by monitoring the evolution of the ionic mobility (obtained by dielectric measurements) with time. Fig. 4 shows the plot evolution of the ionic mobility versus time for different DDSA:MNA mixture hardeners. As time increases, the initial ionic mobility (expressed as percentage value, 100 %) decreases up to a constant value (asymptotic curve) which indicates fully curing of the epoxidized cottonseed oil. Initially, the liquid formulation allows the polar groups to rearrange as the electric field changes of polarity. As the

crosslinking occurs, some polar groups are attached to higher molecular weight structures and steric restrictions can occur and this can block motions of polar groups thus making difficult to rearrange with the electric field change.

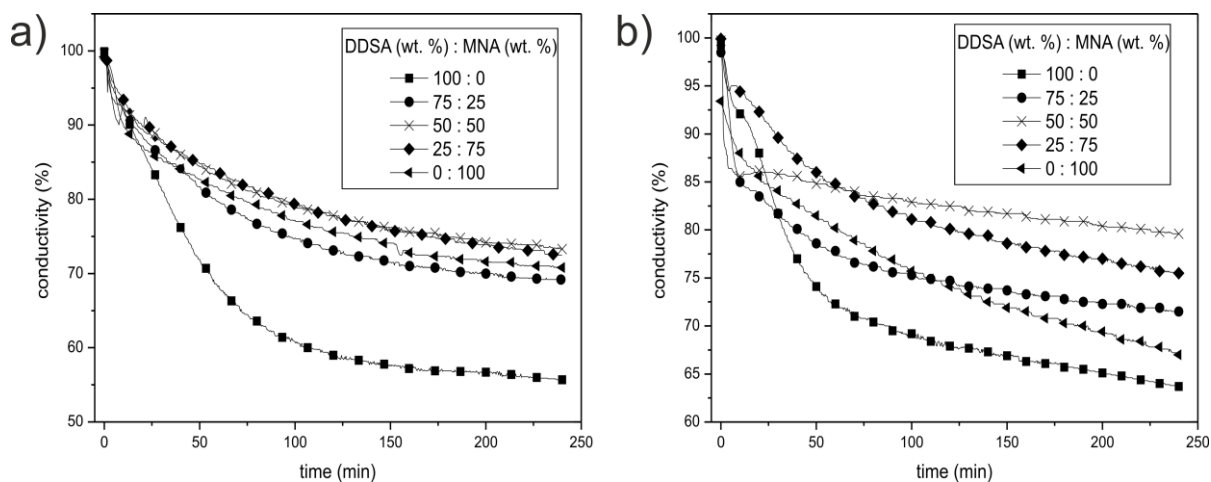


Figure 4.- Plot evolution of the crosslinking of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1 in terms of the variation of the ionic mobility with time a) 110 °C and b) 120 °C.

As expected, DDSA is a flexible molecule that enables ion mobility. As we can see in Fig. 4 a) and b), the ionic mobility of ECSO cured with DDSA decreases in a great extent if compared with the curves corresponding to ECSO cured with MNA. Presence of a flexible (high chain mobility) hardener allows the ionic mobility to change from 100% up to values of about 57% after a curing time of about 150 min. In the case of the curing with rigid (low chain mobility) molecules such as MNA, the ionic mobility is highly restricted so that, it only changes from 100% up to values of 66%. [36, 37]

The ability of each cyclic anhydride to react with epoxidized cottonseed oil can be also followed by dynamic differential scanning calorimetry (DSC). Fig. 5 shows a comparative plot of the DSC curing profiles of ECSO with different DDSA:MNA mixtures. It can be clearly observed that the peak temperature, which corresponds to the maximum reaction rate, is displaced up to higher values as the rigid anhydride content increases. The temperature peak for the system cured with DDSA is close

to 179.2 °C and this is increased up to values of 198.47 °C for the system cured with MNA. These results indicate that reaction of ECSO with DDSA occurs in a more easy way than using MNA and these results are consistent with those previously described about the gel time since we have observed that MNA leads to higher gel time values than DDSA.

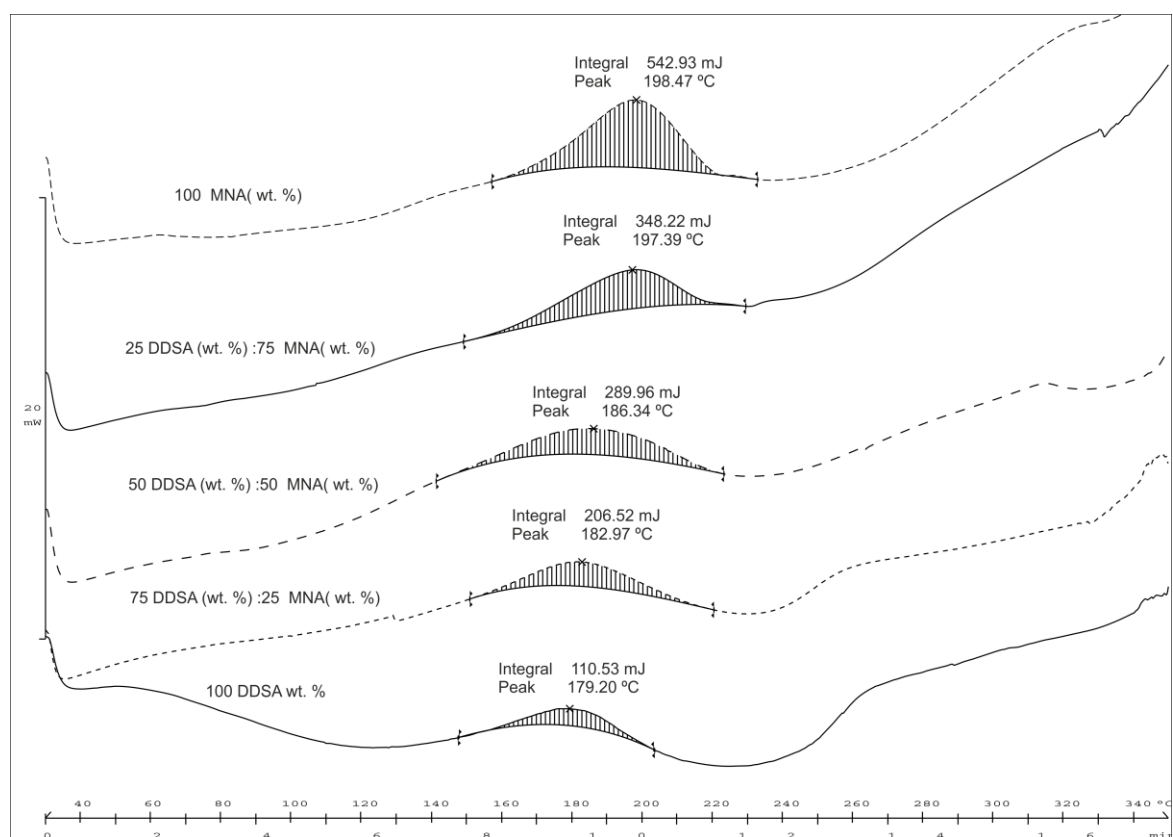


Figure 5.- Comparative plot of the dynamic DSC curing curves of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1.

Plate-plate oscillatory rheometry is highly useful to monitor the curing process by following the evolution of the storage modulus (G') or the phase angle (δ). At the early stages of the curing process, the liquid formulation is characterized by a high phase angle (close to 90 °C) and very low values of storage modulus (G'). As the crosslinking process occurs, the molecular weight of the cured material increases and, subsequently, the phase angle decreases; on the other hand, the storage

modulus increases to due to an increase in the elastic behavior of the material. This situation can be observed in Fig. 6 for the crosslinking reaction of epoxidized cottonseed oil with DDSA:MNA mixture hardeners for isothermal curing at 110 °C (Fig. 6a) and 120 °C (Fig. 6b). As it has been described previously, reaction of epoxidized cottonseed oil with dodecenylsuccinic anhydride is faster than with methyl nadic anhydride. The gel time values are lower for the system cured with DDSA in comparison to MNA-cured ECSO. On the other hand, the temperature peak by dynamic DSC is lower for DDSA cured ECSO if compared to MNA cured ECSO. This situation can also be observed by plate-plate oscillatory rheometry. The curing curve (G' vs time) for ECSO with DDSA is placed at the left while the cure curve for ECSO:MNA is remarkably displaced to longer times thus indicating that curing with DDSA occurs in a faster way. This is probably due to the fact that DDSA possesses higher anhydride equivalent weight and this leads to formation of high molecular weight crosslinked structures than in the case of MNA with a lower anhydride equivalent weight. This situation is repeated at both isothermal curing temperatures, 110 °C and 120 °C. Nevertheless, as the curing temperature increases, the curing profiles (G' vs time) move to lower times thus indicating more faster curing reactions. The use of DDSA:MNA mixture hardeners leads to intermediate curing profiles between the two extreme curves corresponding to DDSA and MNA-cured ECSO.

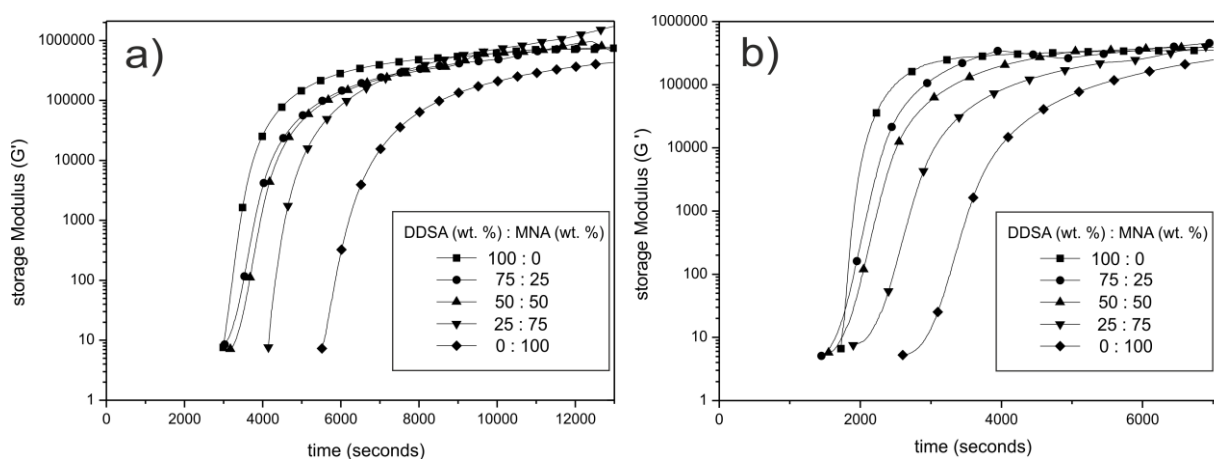


Figure 6.- Comparative plot of the evolution of the storage modulus (G') for the curing of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1, obtained by plate-plate oscillatory rheometry at a constant temperature of a) 110 °C and b) 120 °C.

The phase angle (δ) follows similar tendency. Initially, the phase angle is close to 90° corresponding to typical newtonian liquid behaviour in which the response (elongation) is 90° delayed with regard to the applied dynamic stress. As the phase angle decreases, the crosslinking reaction occurs until δ reaches values close to 0° which are representative for typical elastic behaviour of solids in which the response (elongation) is not delayed (in-phase) with regard to the applied dynamic stress (immediate response). As we can see in Fig. 7 for two different isothermal curing conditions (110°C and 120°C), curing with DDSA starts at lower times if compared to curing with MNA. This is in accordance with the gel time values shown before as well as the evolution of the storage modulus (G'). The chemical structure of MNA and DDSA plays a key role in both curing reaction rate and mechanical properties of cured materials. In a first approach, DDSA structure allows reaction at lower temperatures than MNA; this fact is directly related to the structure since anhydride group in DDSA is more accessible than anhydride group in MNA due to molecular complexity. In general terms, DDSA possesses a flexible structure while MNA is characterized by a rigid structure.

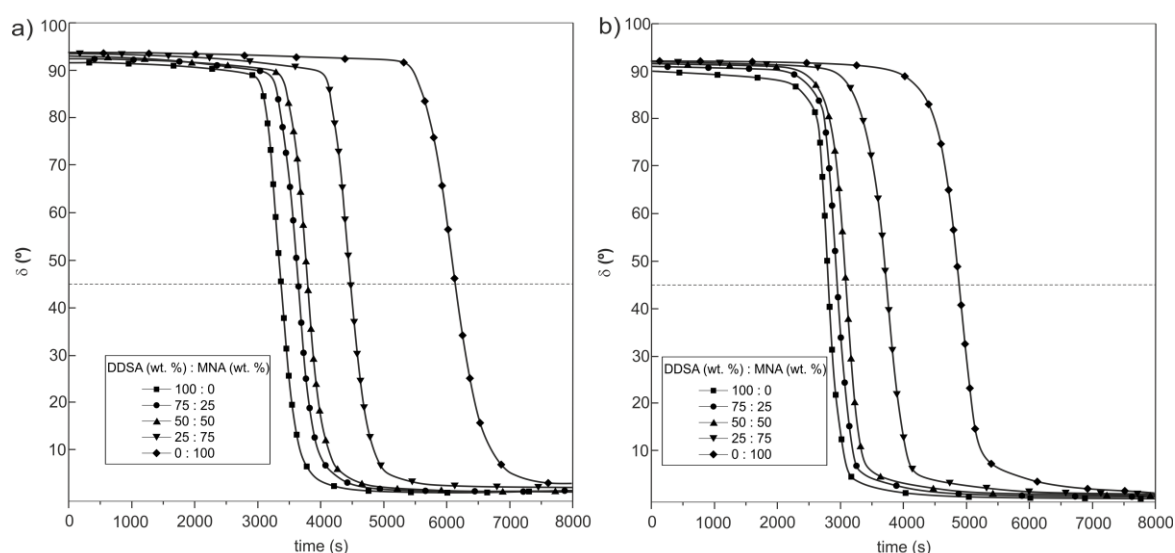


Figure 7.- Comparative plot of the evolution of the phase angle (γ) for the curing of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1, obtained by plate-plate oscillatory rheometry at a constant temperature of a) 110°C and b) 120°C .

3.3. Characterisation of the crosslinked resins

The final properties of a thermosetting resin highly depend on several issues such as resin to hardener ratio, hardener structure, curing cycle, post curing, etc. The structure of the hardener not only influences the curing behavior of ECSO-based thermosetting resins but also the final properties of the fully cured materials. Table 2 summarizes some mechanical properties of fully cured ECSO-based thermosetting resins crosslinked with different DDSA-MNA mixtures using the same resin to hardener ratio (EEW:AEW = 1:1) and same curing cycle (3 h at 110 °C). So that it is possible to evaluate the influence of the hardener mixture on final properties of crosslinked materials. In a first approach, as DDSA is characterized by a flexible structure with a long side chain it could provide flexibility to crosslinked ECSO while the highly rigid molecule of MNA could restrict chain mobility thus providing stiffness. As we can see in Table 2, the flexural modulus of ECSO crosslinked with DDSA is 38.9 MPa which is remarkably lower to the flexural modulus of ECSO cured with MNA with values of about 151.2 MPa. As expected, as the DDSA content in DDSA:MNA mixtures increases, we observe a clear increase in flexural modulus. Similar tendency can be observed in flexural strength. So that MNA contributes to an increase in mechanical resistant properties. On the other hand, DDSA contributes to good ductile properties as observed in Table 2 with impact resistance which changes from 1.92 kJ m⁻² (MNA-cured ECSO) up to twice values (DDSA-cured ECSO).

DDSA (wt. %)	MNA (wt. %)	Flexural Modulus (MPa)	Max Flexion Strength (N)	Impact Resistance (KJ/m²)
100	0	38.95 ± 1.34	11.7 ± 1.84	3.32 ± 0.31
75	25	47.42 ± 1.46	14.5 ± 0.1	2.97 ± 0.52
50	50	92.43 ± 7.96	19.05 ± 3.89	2.55 ± 0.44
25	75	110.89 ± 7.04	23.15 ± 0.35	2.35 ± 0.29
0	100	151.19 ± 4.15	29.45 ± 0.21	1.92 ± 0.32

Table 2. Results of mechanical properties of the ECSO cured resin during bending and impact tests.

Fracture surfaces of crosslinked ECSO show some differences in topographies between DDSA-cured ECSO (Fig. 8a & 8b) and MNA-cured ECSO (Fig. 8e & 8f) as it is shown in Fig. 8. Fractured surface of DDSA-cured ECSO (Fig. 8a & 8b) shows typical fracture of a rigid thermosetting material with quite smooth surface together with a fractal edge formation due to fracture mechanism with a main advancing front of a crack (longitudinal) and multiple microcracks growing perpendicular to this main axis and so on. With regard to the fractured surface of MNA-cured ECSO (Fig. 8e & 8f) we also observe a fragile fracture surface but in this case, due to fragility, we do not observe the typical fractal formation. It is only observable the main advancing front of the crack. Intermediate compositions such as 50% DDSA:50% MNA (Fig. 8c & 8d) offer a fracture surface topography intermediate between the two individual (DDSA and MNA) cured ECSO.

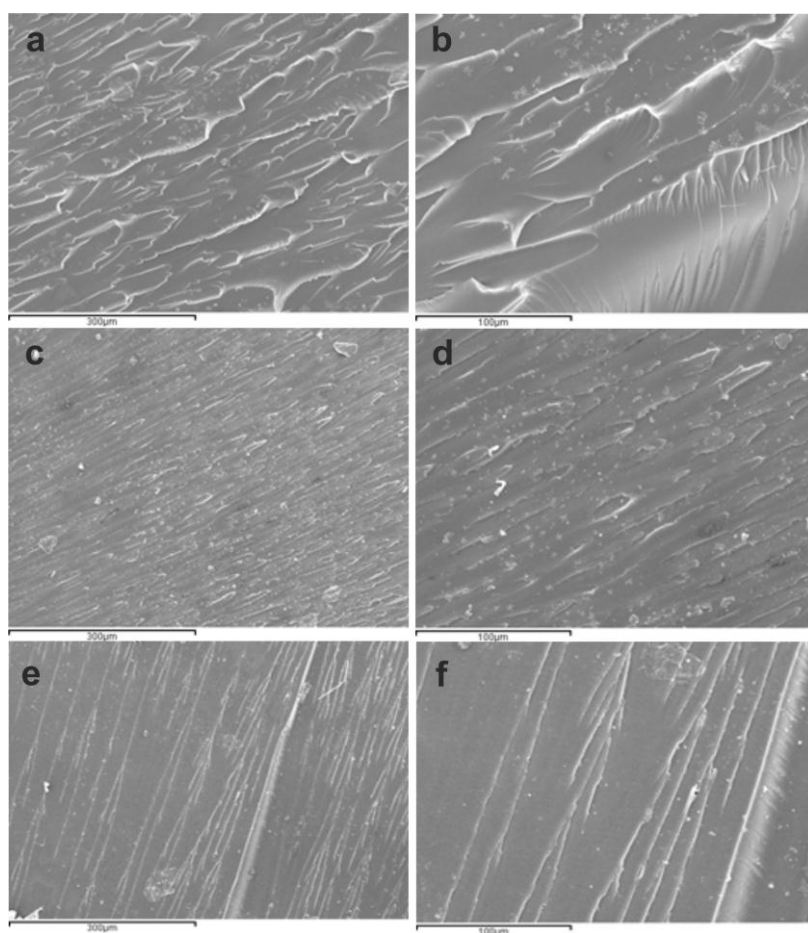


Figure 8.- SEM images of the fractured surfaces from Charpy test corresponding with different DDSA:MNA mixture impact fracture of the curing with a) 100% DDSA, x200, b) 100% DDSA, x500, c) 50% DDSA:50% MNA, x200, d) 50% DDSA:50% MNA, x500, e) 100% MNA, x200, f) 100% MNA, x500.

Fig. 9 shows the dynamic behavior of ECSO-based cured materials subjected to a temperature ramp. The evolution of the storage modulus (G') is useful to compare the effect of the hardener composition on final properties. As we can see in Fig. 9, G' shows a remarkable decrease in the 50-70 °C range which corresponds to the glass transition range. G' curve for DDSA-cured ECSO starts at values of about $3 \cdot 10^7$ Pa whilst the G' curve for MNA-cured ECSO starts at $1 \cdot 10^8$ Pa thus indicating that MNA-cured ECSO is stiffer than DDSA-cured ECSO as expected. These results are in total agreement with previous flexural properties. With regard to intermediate DDSA:MNA compositions as hardener, G' curve is placed between the two extreme curves corresponding to DDSA- and MNA-cured ECSO respectively. As we can see, all compositions overcome soft as T_g is reached but the difference in behavior after the glass transition temperature is not as remarked as prior to T_g . By taking the glass transition temperature as the $\tan \delta$ maximum, we can see the T_g value for the DDSA-cured ECSO is located at about 57 °C while the T_g value for MNA-cured ECSO is close to 65 °C which is slightly higher.

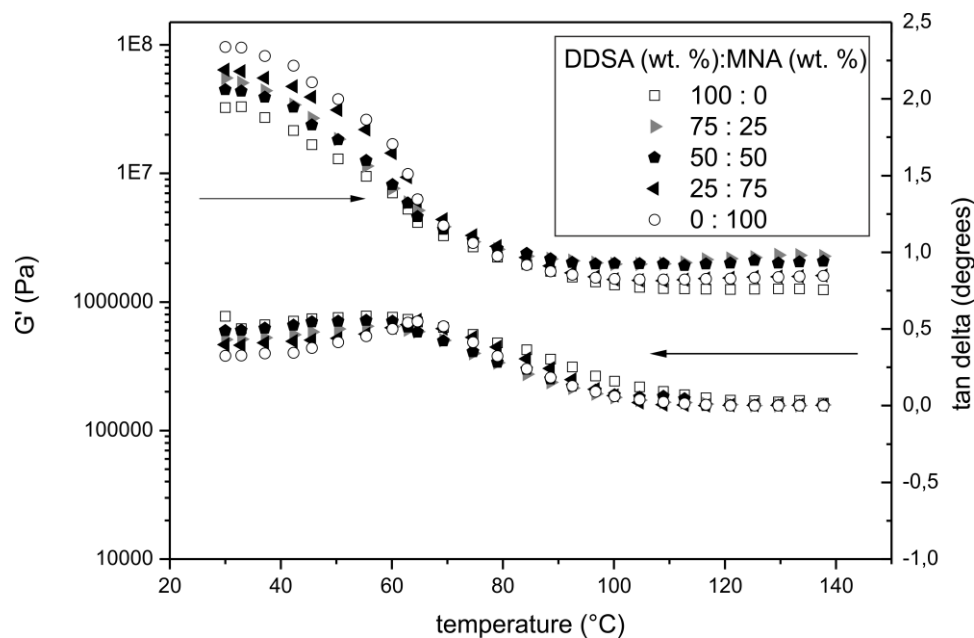


Figure 9.- Plot evolution of the storage modulus (G') and $\tan \delta$ for solid ECSO-based thermosetting resins cured with different DDSA:MNA mixture hardeners in terms of temperature.

4.- Conclusions.

As the cotton industry demands high cotton plant productions, cottonseed oil (CSO) appears as a by-product of this industry and despite some applications in the food industry are addressed for this oil (with some controversy on its healthy benefits), new additional uses must be developed to absorb the high volume of cottonseed oil. This work reports the potential use of cottonseed oil as base material for obtaining bio-based epoxy resins for the composites' industry.

The resins resulting from the cottonseed oil epoxidation can offer attracting alternatives to some petroleum-derived epoxy resins. The epoxidation of cottonseed oil with peroxide increased the final yield with a peroxide:oil ratio of 3:1 with final oxirane oxygen number of 5.32% which is a slightly lower value if compared to conventional epoxidized soybean oil (ESBO); so that, epoxidized cottonseed oil (ECSO) can compete with ESBO for similar applications (flexible thermosetting resin, plasticizer, additive for high rigidity epoxies, etc.).

Interesting thermosetting solid resins can be obtained by curing ECSO with cyclic anhydrides. In particular, by combining a flexible anhydride (dodecenylsuccinic anhydride, DDSA) and a rigid anhydride (methyl nadic anhydride, MNA) it is possible to tailor the desired properties on final cured materials as DDSA confers some flexibility whilst MNA leads to more rigid materials.

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Table Captions

Table 1.- Gel time values at isothermal conditions for the crosslinking of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1.

Table 2.- Results of mechanical properties of the ECSO cured resin during bending and impact tests

Figure Legends

Figure 1.- Schematic representation of the epoxidation process from cottonseed oil (CSO).

Figure 2.- Schematic representation of different components used to crosslink epoxidized cottonseed oil.

Figure 3.- Plot evolution of different parameters in terms of the reaction time of the epoxidation reaction, a) Evolution of oxirane oxygen index and b) evolution of the iodine index.

Figure 4.- Plot evolution of the crosslinking of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1 in terms of the variation of the ionic mobility with time a) 110 °C and b) 120 °C.

Figure 5.- Comparative plot of the dynamic DSC curing curves of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1.

Figure 6.- Comparative plot of the evolution of the storage modulus (G') for the curing of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1, obtained by plate-plate oscillatory rheometry at a constant temperature of a) 110 °C and b) 120 °C.

Figure 7.- Comparative plot of the evolution of the phase angle (γ) for the curing of epoxidized cottonseed oil (ECSO) with mixtures of dodecenylsuccinic anhydride (DDSA) and methyl nadic anhydride (MNA) at a constant EEW:AEW of 1, obtained by plate-plate oscillatory rheometry at a constant temperature of a) 110 °C and b) 120 °C.

Figure 8.- SEM images of the fractured surfaces from Charpy test corresponding with different DDSA:MNA mixture a) impact fracture of the curing with a) 100% DDSA, x200, b) 100% DDSA, x500, c) 50% DDSA:50% MNA, x200, d) 50% DDSA:50% MNA, x500, e) 100% MNA, x200, f) 100% MNA, x500.

Figure 9.- Plot evolution of the storage modulus (G') and $\tan \delta$ for solid ECSO-based thermosetting resins cured with different DDSA:MNA mixture hardeners in terms of temperature.