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Polymeric networks based on tung oil: Reaction and modification with green oil monomers

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ABSTRACT

A highly unsaturated vegetable oil (tung oil) was cationically copolymerized with a vegetable oil derived monomer, that replaces the more frequently used styrene. The synthesized comonomer was methyl ester of tung oil, obtained by transesterification of the plant oil with methanol. Alternatively, the incorporation of a green modifier, a commercial acrylated epoxidized soybean oil, was also considered. The use of any of these modifiers allowed preparing materials with an elevated content of bio-derived components.

All the materials obtained presented good mechanical damping capacity, as well as dynamic mechanical properties comparable to analogous materials obtained by copolymerization with styrene. Incorporation of low concentrations of divinylbenzene in the formulations allowed increasing rigidity and glass transition temperatures (Tg) of the materials. One of the formulations prepared by copolymerization with the tung oil methyl ester presented shape memory behavior.

1. Introduction

The interest in using renewable resources to develop new materials has been growing during the last years. In particular, the use of natural oils has received much attention because they offer the advantages of wide availability and a basic structure with varied chemical functionalities (depending on the plant origin) that allows synthesizing different products for a large number of applications [1–4].

Vegetable oils are considered one of the most important sources of renewable raw materials for the production of bio based polymers because of the large number of reactive sites in their structures capable of being chemically modified or, in some cases, capable of directly reacting to form polymeric materials [1,5,6]. In particular, tung oil (TO) is extracted from the tung tree seeds and is composed mainly of α-elaeostearic acid (77–82%) containing three conjugated double bounds, oleic acid (3.5–12.7%) with one double bond and linolenic acid (8–10%) with three non-conjugated double bonds [7–10]. This feature is responsible for the excellent drying properties, which are widely exploited in the industry of paints and varnishes [9,11–13], and it is also responsible for the capability of this oil to cationically polymerize with monomers such as styrene, giving rise to materials with a variety of properties from elastomers to rigid polymers, depending upon the monomer and the used stoichiometry [6,7,14]. In particular, the use of tung oil is appealing because the conjugated C=C of the α-elaeostearic acid make unnecessary any modification of the oil.

In recent years, different groups have published scientific contributions focused on resins or polymer precursors obtained from vegetable oils and fatty acids (Wool et al. [15–18]; Larock et al. [5,19–27]; Petrovic et al. [26,28,29]; Mosiewicki et al. [30]). On the other hand, other authors have devoted their efforts to find/synthesize

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environmentally friendly monomers based on vegetable oils that could replace petroleum-based monomers such as styrene and divinylbenzene (Khot et al. [31]; Hu et al. [32]; La Scala et al. [33]; Can et al. [17]; Quirino et al. [34]). For example, La Scala et al. [33] synthesized unsaturated monomers starting from fatty acid and glycidyl methacrylate, which were free radically polymerized with a vinyl ester resin.

Following the international pressure of the general public, governments and organizations for replacing petroleum based chemicals, commercial bio-based products have already been introduced in the market. According to international regulations a material that has more than 20% of bio-based content, can show a "bio" label indicating such a percentage.

Fatty esters obtained from the transesterification of tung oil with methanol, can be considered as polymeric precursors with conjugated unsaturations that are reactive in cationic polymerizations. In general, the transesterification reaction of a vegetable oil is one in which a triglyceride is reacted with an alcohol in the presence of a strong acid or a base to produce a mixture of esters of fatty acids and glycerol [35,36].

Vegetable oil have been extensively modified by reaction of the original unsaturations to produce chemicals of different functionalities from those originally present in vegetable oils, such as acrylate groups that can participate in radical polymerization reactions. The synthesis of this type of precursor is possible by the epoxidation of the unsaturations followed by reaction with acrylic acids that incorporates terminal unsaturations [37]. Although, acrylate groups do not participate in cationic reactions [38], the acrylated epoxidized soybean oil can be used as a highly compatible green modifier in oil based reactive mixtures.

Thus, in the present work, petroleum based comonomers, which were used in the past [5–7] in the cationic copolymerization of vegetable oils, were replaced by a bio-based comonomer, methyl ester of tung oil. This type of formulation allows increasing even more the percentage of bio-based content in the final materials and avoids the use of an aggressive chemical reactant such as styrene. Also a bio-based modifier, acrylated epoxidized soybean oil, was considered in the formulation of modified tung oil networks.

The properties of the obtained polymers were compared with those measured previously for tung oil/styrene copolymers.

2. Experimental

2.1. Materials

Tung oil (TO) composed of α-elaeostearic acid (main component, 84 wt.%) was supplied by Cooperativa Agrícola Limitada de Picada Libertad, Argentina. For the transesterification reaction, methanol (99.98% pure, Biopack, Argentina), sodium hydroxide (97% pure, Anedra, Argentina) and sulfuric acid (98.5% pure, Anedra, Argentina) were used. Acrylated epoxidized soybean oil (AESO) was purchased by Sigma–Aldrich. The following materials were purchased from Cicarelli Laboratory, Argentina: divinylbenzene 80% pure (DVB), styrene 99.5% pure (St) and tetrahydrofurane 99% pure, (THF). Boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) with 46–51% BF_3, obtained from Sigma–Aldrich was the initiator of the cationic reaction.

2.2. Methods and techniques

2.2.1. Methyl ester (ME) synthesis from tung oil (TO)

For the synthesis, 300 mL of TO were mixed with 90 mL of methanol and 1.8 g of sodium hydroxide in a glass reactor with mechanical stirring for 45 min at 50 °C. Two phases were obtained (ME and glycerol) which were separated in a separating funnel. The ME was purified by washing with a 0.015 N sulfuric acid solution, and subsequent washings with distilled water to neutral pH. Finally, the ME was dried using a rotary evaporator under vacuum for 2 h at 50 °C.

2.2.2. Preparation of green polymeric materials

A selected quantity of ME, AESO or St (and minimum amounts of DVB depending on the formulation) were incorporated to the tung oil (TO) and the mixture was stirred. This step was followed by the addition of the modified initiator prepared by mixing tetrahydrofuran, THF (5 wt.% with respect to the reactive mixture) with boron trifluoride diethyl etherate (3 wt.% with respect to the reactive mixture). As it was reported in previous works, due to the poor miscibility of the catalyst in the oils, it must be solvent-modified to obtain a homogeneous initial solution [12,39,40]. The mixture was vigorously stirred and finally poured into glass plates of 13 mm × 18 mm separated by a rubber cord of 1 mm of thickness and kept closed with metal clamps. The reactants were heated first at 25 °C for 12 h, then at 60 °C for 12 h and finally at 100 °C for 24 h. The weight ratio of TO/ME was selected as 70/30 and the percentage of DVB (0, 5 and 10 wt.%) was calculated relative to that of the total mix of TO/ME. The chosen nomenclature was 70TO/30ME, [70TO/30ME]/5DVB and [70TO/30ME]/10DVB. For the polymers modified with AESO, the weight ratio of TO/AESO was 90/10 with aggregates of 5 and 10 wt.% of DVB calculated relative to that of the total mix of TO/AESO. Besides, polymers TO/AESO with weight ratios of 70/30, 80/20 and 90/10 were also prepared. The chosen nomenclature is indicative of the weight ratios utilized in the synthesis as shown: 70TO/30AESO, 80TO/20AESO, 90TO/10AESO, [90TO/10AESO]/5DVB and [90TO/10AESO]/10DVB.

2.2.3. Chemical characterization of the materials (FT-IR)

FT-IR spectra of the ME, AESO and derived modified polymers were recorded by using the attenuated total reflection method (ATR) with a Thermo Scientific Nicolet 6700 FT-IR spectrometer. The spectra were obtained over the range of 500–4000 cm^{-1} with a resolution of 2 cm^{-1} and averaged over 32 scans.

2.2.4. Nuclear magnetic resonance spectroscopy (^1H NMR)

^1H NMR spectra of the samples were recorded on a Bruker AM500 spectrometer (500 MHz) using $CDCl_3$ as solvent.

2.2.5. Dynamic-mechanical tests (DMA)

A Perkin Elmer dynamic mechanical analyzer (DMA 7) was used to determine the dynamic mechanical behavior of the samples. The tests were carried out under nitrogen atmosphere, using the temperature scan mode, tensile fixtures and dynamic and static stresses of 50 and 100 Pa, respectively. The average sample dimensions were $20 \times 5 \times 0.5\ mm^3$. At least two tests for each sample were carried out in order to confirm the reproducibility of the results.

2.2.6. Mechanical tests

Microtensile testing: was performed at 18 °C on tensile specimens of 5 mm × 35 mm × 1 mm cut from the molded plaques, using an universal testing machine (INSTRON 8501), in accordance with ASTM D 1708-93 using a cross-head speed of 5 mm/min. Young's modulus (E), ultimate stress (σ_u) and elongation at break (ε_u) were determined from the average values of at least four replicates for each sample.

Thermomechanical cyclic tensile testing: was performed on microtensile specimens of 5 mm × 35 mm × 1 mm using a universal testing machine equipped with a heating chamber (INSTRON 8501) in order to quantify the shape memory behavior of the samples that exhibit this property. Samples were conditioned at 25 °C and then elongated to different percentages of the original length at a speed of 5 mm/min. Next, the samples were cooled below Tg (T = 0 °C was used) and unloaded. To measure the recovery stress, the samples were heated to 25 °C maintaining the strain constant and equal to ε_r, while the stress developed was recorded by the load cell. Finally, the samples underwent the recovery process by heating for ten minutes at 25 °C and zero stress. The strain maintained after unloading, and the residual strain of each cycle were used to calculate the fixity (R_f) and recovery (R_r) ratios from these tests, as indicated in the following equations:

$$R_f(\%) = \frac{\varepsilon_r}{\varepsilon_m} \times 100; \quad R_r(\%) = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \times 100$$

where ε_m is the maximum strain in the cycle, ε_r is the residual strain after unloading at the lower temperature and ε_p represents the residual strain after heating at 25 °C.

3. Results and discussion

3.1. Characterization of the methyl ester from tung oil (ME)

Fig. 1 shows the FT-IR spectra of ME and tung oil. In particular, the spectrum of ME shows a peak at 3010 cm^{-1} that corresponds to absorption of the carbon–carbon unsaturations. The peak at 991 cm^{-1}, is due to absorption of the conjugated unsaturation of the elaeostearic acid chains. The presence of these two peaks that were originally present in the spectrum of tung oil, indicates that the carbon–carbon double bonds were preserved during the transesterification reaction and are available for reaction in the subsequent copolymerization step. The intensity of the peaks at 1459 and 1430 cm^{-1} due to the asymmetric and symmetric vibrations of the C—H bonds

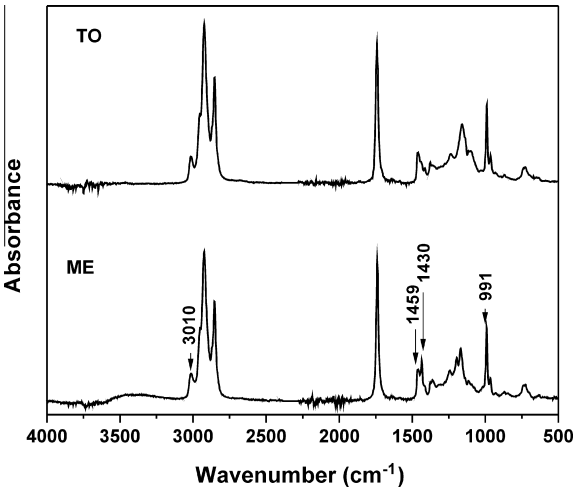


Fig. 1. FT-IR spectrum of methyl ester (ME) from tung oil (TO) and tung oil (TO).

of the methyl ester group (—$COOCH_3$) increase after transesterification confirming that the reaction took place.

Fig. 2 shows the ^1H NMR spectrum of the ME of tung oil. To simplify the analysis, it was considered that the ester was composed mainly of methyl ester of elaeostearic acid, with a minor content of ester from oleic acid. The assignment of the peaks is also shown in Fig. 2.

The main difference with respect of the spectrum of the tung oil reported in a previous work [10], is the almost negligible contribution of the peaks associated to the glycerol structure in the spectrum of the methyl ester. This result is expected if the product obtained has been properly separated from unreacted triglycerides and glycerol (product of reaction). Moreover, the peaks assigned to protons associated to double bonds remain after the reaction (multiplets marked in Fig. 2 with letters a, b, c, d and e). A new peak at 3.7 ppm was observed in the methyl ester corresponding to the protons of the methyl group. The contribution of each acid calculated from the spectrum of Fig. 2 suggests that the methyl ester of tung oil is composed of a mixture 82.2% (molar) of the ester of the eleostearic acid and 17.8% (molar) of that of the oleic acid. This result agrees very well with the composition of the TO reported in a previous work [10]. The areas marked on the spectrum of Fig. 2 as A and B are negligible compared to the other peaks considered for the calculation, however, they indicate the presence of trace amounts of fatty acids (peak at 7.25 ppm) and unreacted triglycerides (4–4.5 ppm).

3.2. Characterization of acrylated epoxidized soybean oil (AESO)

The AESO is a commercial product that was used without further purification. Fig. 3 shows the spectrum obtained by FT-IR of the acrylated epoxidized soybean oil.

The spectrum obtained is in very good agreement with the reports in the literature [41,42]. The structure of the acrylated epoxidized soybean oil has the characteristic peak corresponding to the hydroxyl group derived from

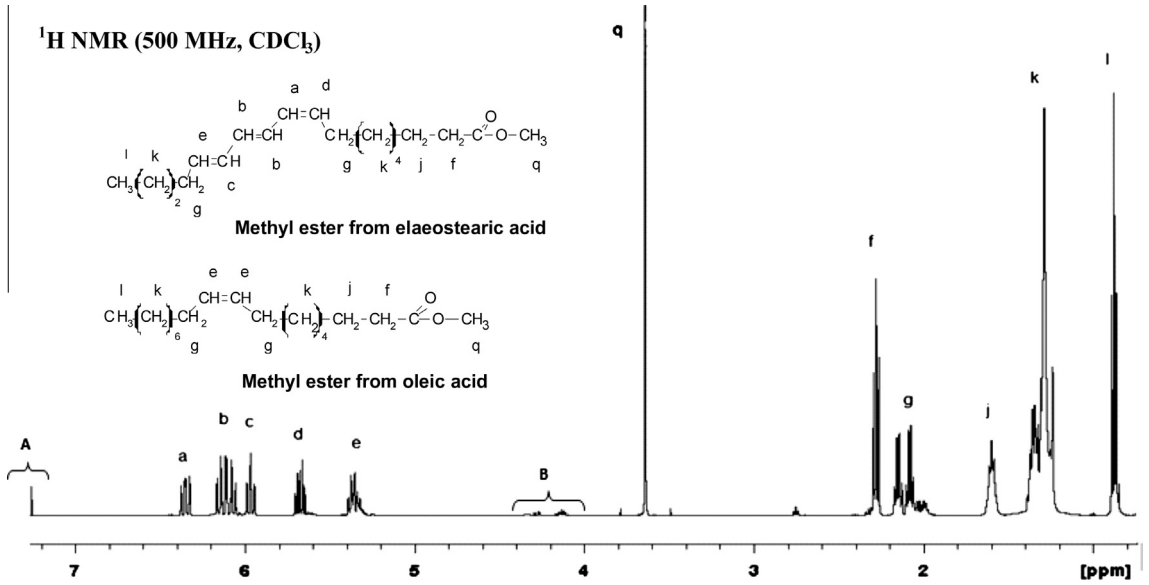


Fig. 2. ^{1}H NMR spectrum of methyl ester (ME) from tung oil.

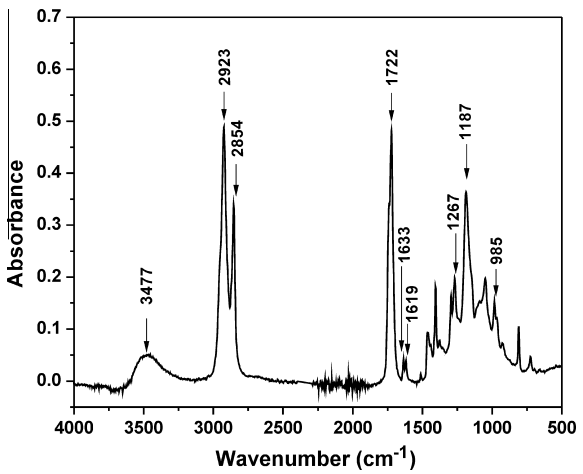


Fig. 3. FT-IR spectrum of acrylated epoxidized soybean oil (AESO).

the epoxy ring opening at 3477 cm^{-1}. The methyl and methylene groups of the glycerides of the acrylated epoxidized soybean oil are observed in the peaks at 2925 and 2854 cm^{-1}. The peak at 1722 cm^{-1} corresponds to the absorption of the carbonyl group of the esters in the acrylate and the glyceride groups (C═O) and the peak at 1619 cm^{-1} is related to the double bond (C═C) in the acrylate group. The presence of vinyl functionalities (—CH═CH_2—, —CH_2═CH(CO)—O—) is reflected in the 1633 cm^{-1} and 985 cm^{-1} peaks. The spectrum peaks at 1187 and 1268 cm^{-1} are attributed to stretching of the bonds (C—O—C) and (C—O) of the ester group. The peaks between 824 and 843 cm^{-1} related to the epoxy groups are not observed in the FT-IR spectrum as a result of the effective acrylatation reaction.

The ^{1}H NMR spectrum of the acrylated epoxidized soybean oil (AESO) can be seen in Fig. 4.

The signal corresponding to the hydrogens associated with epoxy group carbons (which should appear at approximately 3 ppm) is not present, which confirms an effective acrylatation of the epoxidized soybean oil (ESO) as mentioned in the analysis of the FT-IR results and in agreement with previous reports [41]. The AESO presents a specific peak at 3.8 ppm attributable to the **"u"** proton generated at the epoxy ring opening [43]. In addition, the three peaks in the range of 5.8–6.5 ppm correspond to the three acrylate group protons [31]. The peak appearing at 2.3 ppm (f) is assigned to the resonance of the protons associated to the methylene groups in the alpha position to the carbonyl group. The two multiplets at 4.4 and 4.1 ppm (n and p) correspond to the four methylene protons of glycerol in the triglyceride molecule. The multiplet at 5.3 ppm (m) corresponds to the central proton in the glycerol structure [31,43,44]. The peak at 0.9 ppm is assigned to the protons of terminal methyl groups (l). The latter peak area was taken as the basis for calculating the average acrylate groups of AESO structure. The calculated value is 2.8 acrylate groups per molecule of AESO, in agreement to the approximate value of 3.0 reported in literature for other synthesized AESO's [31,41].

3.3. Polymers of tung oil and its derived methyl ester

Scheme 1 shows a graphic representation of the reaction between tung oil and ME by cationic polymerization. As already indicated in the introduction, this formulation allows to obtain materials with a bio content as high as 92% (for the methyl ester copolymer) instead of the 62% reached before for the styrene copolymer. Some of the new materials were modified to obtain more competitive properties and thus, a low percentage of divinylbenzene was incorporated to the formulation. In these materials the biobased percentages are above 80%.

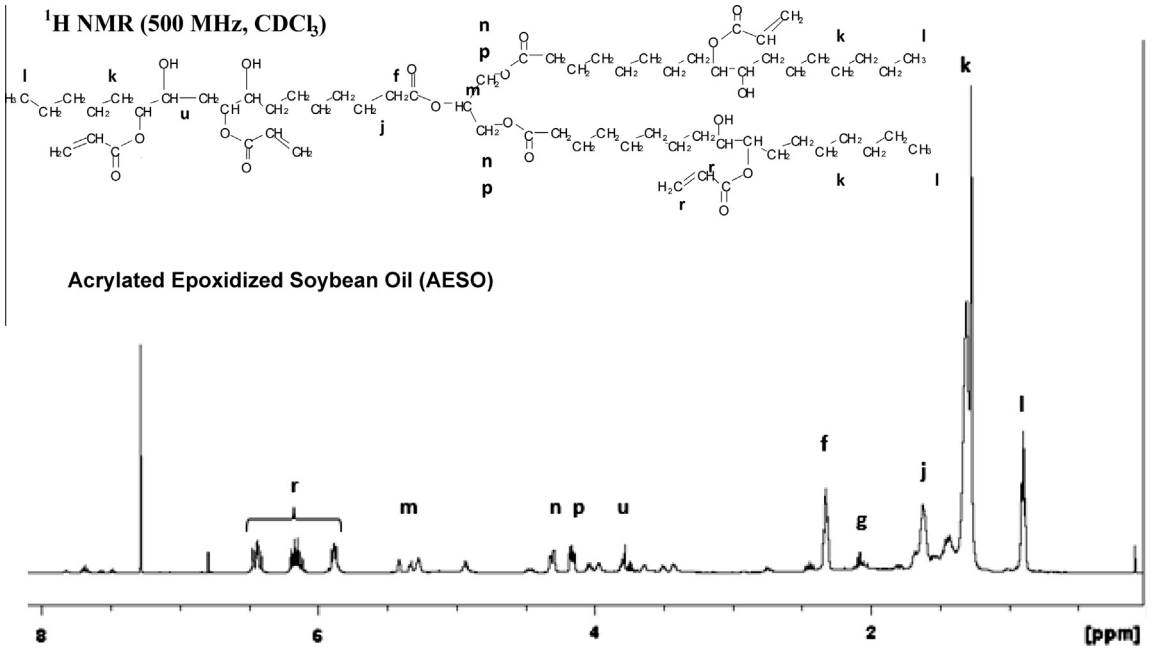


Fig. 4. ^{1}H NMR spectrum of acrylated epoxidized soybean oil (AESO).

Fig. 5 shows the FT-IR spectra of the samples 70TO/30St and 70TO/30ME. The peak at 3010 cm^{-1}, corresponding to the carbon–carbon unsaturations of TO is barely noticeable in the spectra of cured materials, which is an indication of the success of the copolymerization with any of those two monomers.

Comparison of the spectra of samples 70TO/30St and 70TO/30ME shows that there are absorption bands that are common to both spectra. For example, the peaks present at 2921 and 2852 cm^{-1} are assigned to the C—H bonds in the structure of the TO.

The major difference between the spectra is the relative intensity of the two absorption peaks at 1710–1740 cm^{-1}. The peak at 1740 cm^{-1}, corresponding to the ester groups of the triglyceride molecules, is more intense in the 70TO/30ME copolymer due to the contribution of ester groups which are incorporated when using ME. Additionally, small peaks at 3025–3080 cm^{-1} appear in the spectra of the sample 70TO/30St due to the =C—H stretching vibrations of the aromatic ring of the St.

3.3.1. Dynamic-mechanical tests (DMA)

Fig. 6 shows tan δ as a function of temperature for 70TO/30ME, 70TO/30St and TO/ME copolymers with the addition of 5 and 10 wt.% of DVB (relative to the 70TO/30ME reactive mixture).

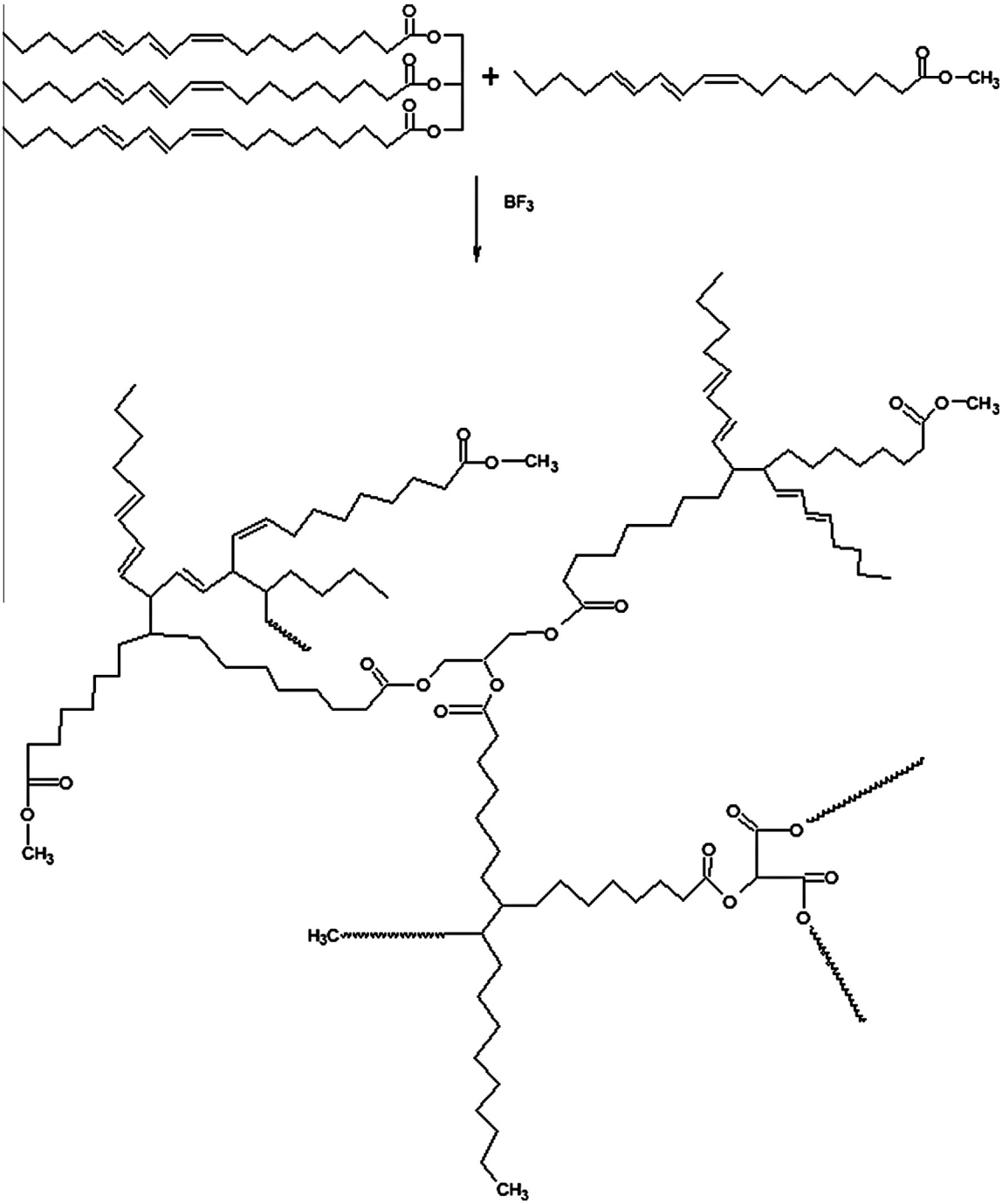
The maximum in the curve of tan δ (taken as the glass transition temperature, Tg, of a sample) occurs at a similar temperature for the samples 70TO/30ME and 70TO/30St. On the other hand, the peak is lower and wider for the copolymer with ME, which is probably related to a more heterogeneous network. This new monomer is more flexible than styrene and it also contributes with pendant chains to the crosslinked structure.

As it could be expected, the addition of a small percentage of DVB leads to the increase of the rigidity of the copolymer and the glass transition temperature (Tg) is shifted to a higher value. Depending on the DVB concentration, the Tg values ranged between 10 °C and 45 °C (Table 1), the latter being the value corresponding to the sample with the highest DVB content.

Fig. 7 shows the storage modulus as a function of temperature for the same copolymers. It can be seen that above room temperature, the storage modulus of the material formulated with ME is higher than the value corresponding to the sample prepared with 30 wt.% of St. This fact is related to the higher crosslinked density resulting from the use of the molecule of ME that has a higher functionality than styrene (Styrene: 1 mol C=C/mol and ME: 2.644 mol C=C/mol from ^{1}H NMR results).

The addition of DVB (5 wt.%) to the sample of 70TO/30ME also generates an increase in the stiffness (storage modulus), which becomes more significant as the temperature of the test increases (Fig. 7). Furthermore, the material with higher content of DVB presents higher storage modulus throughout the temperature range used, which is related to the high crosslinking density and high rigidity contributed by DVB to the structure of the copolymer.

Table 1 shows the properties of the copolymers obtained from DMA testing. All the samples show values of the loss factor considerably higher than 0.3 at the maximum of the peak, with temperature intervals for the glass transition close to room temperature. This characteristic would be an asset for the use of these materials in sound insulation and in vibration damping for mechanical engineering applications.[21,45].



Scheme 1. Graphic representation of the reaction between TO and ME by cationic polymerization. The structures that represent TO and ME are a simplification considering that the main fatty acid in both reactants is α-elaeostearic acid.

3.3.2. Mechanical properties

Table 2 reports the mechanical properties determined in tensile tests. The 70TO/30ME sample has mechanical properties comparable to those obtained for 70TO/30St copolymer.

The elastic modulus at the test temperature is higher when the ME is used instead of St as comonomer. The ME is a monomer with higher concentration of carbon–carbon double bonds than St, leading to a material with higher rigidity. In turn, the addition of DVB generates a considerable increase in tensile modulus. These results confirm the results of dynamic -mechanical tests.

The samples of 70TO/30ME and 70TO/30St do not show significant differences with respect to tensile strength, while ultimate strain decreases slightly for the copolymer

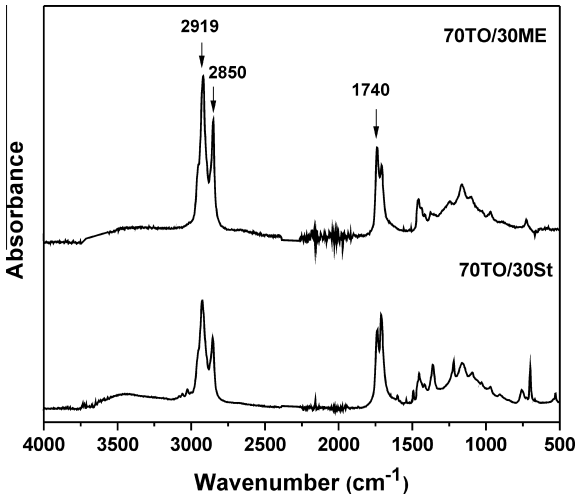


Fig. 5. Comparison of FT-IR spectra of the copolymers 70TO/30St and 70TO/30ME.

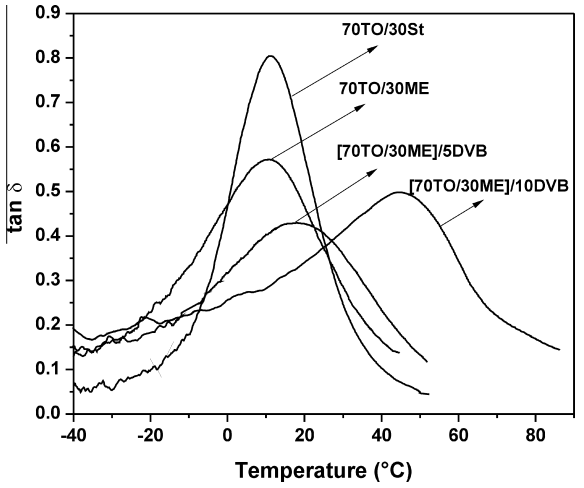


Fig. 6. Tan δ vs. temperature of the copolymers 70TO/30St, 70TO/30ME and [70TO/30ME]/DVB.

Table 1
Glass transition characteristics of the 70TO/30St, 70TO/30ME and [70TO/30ME]/DVB copolymers.

Sample	Tg (°C)	$(\tan\delta)_{max}$	ΔT^* (°C)
70TO/30St	11.50	0.80	31.9 (−4.3 to 27.6)
70TO/30ME	11.07	0.57	42.1 (−13.1 to 29.0)
[70TO/30ME]/5DVB	18.22	0.43	36.5 (−1.6 to 34.9)
[70TO/30ME]/10DVB	45.11	0.50	49.6 (12.9 to 62.5)

ΔT^*, temperature interval with height of tan $\delta > 0.3$.

with ME in comparison with the copolymer with St, because of the increased rigidity and fragility of the copolymer. The addition of 5 and 10 wt.% of DVB greatly improves tensile strength (580 and 1030%, respectively) and the ultimate strain increases from 8 to 13% with the addition of 5 wt.% of DVB possibly due to the improvement

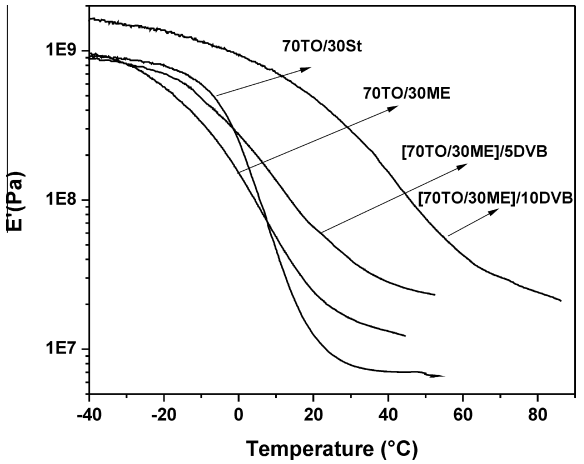


Fig. 7. Storage modulus (E') vs. temperature of the copolymers 70TO/30St, 70TO/30ME and [70TO/30ME]/DVB.

Table 2
Tensile properties of the 70TO/30St, 70TO/30ME and [70TO/30ME]/DVB copolymers.

Sample	E (MPa)	σ_u (MPa)	ε_u (%)
70TO/30St	4.89 ± 0.55	0.52 ± 0.24	10.55 ± 3.55
70TO/30ME	5.87 ± 0.31	0.49 ± 0.09	8.04 ± 1.41
[70TO/30ME]/5DVB	32.46 ± 1.87	2.86 ± 0.56	13.00 ± 2.17
[70TO/30ME]/10DVB	65.57 ± 16.34	5.54 ± 0.95	13.65 ± 3.02

in the cohesion of the material due to increased crosslinking density. No significant changes are noted when comparing the strains at break of the samples with 5% and 10 wt.% of DVB.

3.3.3. Shape memory behavior

Thermal cycles were performed to evaluate tensile shape memory properties of the copolymers obtained and the results are summarized in Table 3.

As in the case of the 70TO/30St copolymer (reported in previous publication [14]), the copolymer formulated with ME instead of St does not show shape memory behavior. Instead, the copolymer [70TO/30ME]/10DVB shows shape memory when using 20% of maximum deformation and 25 °C as switch temperature. The addition of 10 wt.% of DVB in the sample with 30 wt.% of ME results in an increase of the glass transition temperature (Fig. 6), which favors the development of shape memory properties. It could be noted that increasing the number of cycles seems not to significantly affect the fixity factor (in the three cycles the value exceeds 90%).

3.4. Polymers of tung oil (TO) modified with acrylated epoxidized soybean oil (AESO)

FT-IR spectroscopy was used to characterize the samples prepared with 90/10 ratio of TO to St or AESO. Fig. 8 shows the FT-IR spectra for the sample of 90TO/10St and 90TO/10AESO.

Table 3
Shape memory properties of the [70TO/30ME]/10DVB copolymer.

Muestra	T (°C)	Elongation (%)	Nth cycle	R_f (%)	R_r (%)	Recovery force (N)
[70TO/30ME]/10DVB	25	20	1	91.20	100	11.75
			2	93.00	100	11.61
			3	90.60	100	9.96

An important difference between the curves is the appearance of a broad band in the 3500 cm^{-1} in the sample with AESO that is attributable to the absorbance of the hydroxyl group derived from the epoxy ring opening. Furthermore, comparison of the relative intensities of the ester absorption band at 1740 cm^{-1} indicates a higher concentration of ester groups in the sample 90TO/10AESO, which was expected considering the molecular structure of the bio-modifier. As can be observed in Fig. 8 and discussed above, small peaks at 3025–3080 cm^{-1} appear in the spectra of the sample with St related to vibrations in bonds of the aromatic ring.

3.4.1. Dynamic-mechanical tests (DMA)

Fig. 9 shows the variation in tan δ as a function of temperature for the polymers prepared with different weight ratios of TO/AESO.

The maximum in the curve of tan δ shifts to higher temperatures with the decrease in the concentration of AESO (or increase the TO content), as it could be expected from the addition of this modifier, that acts mainly as a plasticizer of the TO crosslinked network. Additionally, the tan δ peak is lower and wider for the polymer with lower AESO concentration, which is related to the heterogeneous and highly crosslinked structure of tung oil network.

When comparing the tan δ curves of 90TO/10St and 90TO/10AESO, it can be seen that the maximum in the curve occurs at higher temperature, while the peak is lower and wider for the last polymer; all these characteristics of the heterogeneous structure resulting from the cationic homopolymerization of tung oil. This is also the reason for the higher Tg of the TO/AESO material, despite the lubricant action of the AESO. This last effect is more clearly illustrated with increasing the AESO concentration, which confers mobility to the structure.

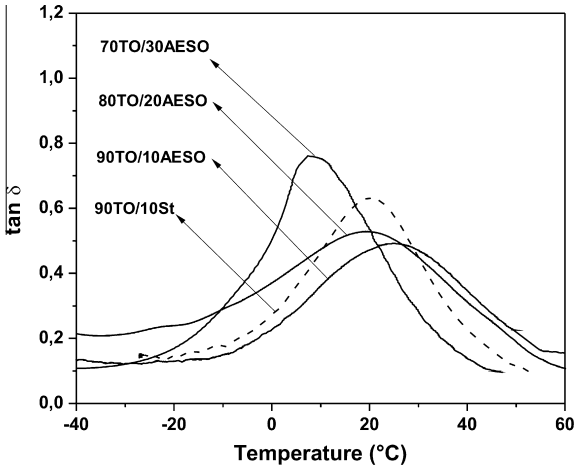


Fig. 9. Tan δ vs. temperature of the polymers of 90TO/10St and TO/AESO.

Fig. 10 shows the storage modulus as a function of temperature for the TO polymers modified with AESO. Samples containing 10 and 20 wt.% of AESO show similar behavior and in both cases, higher modulus than the St copolymer, because the high crosslinking density resulting from the cationic homopolymerization of TO has a strong effect on the properties. On the other hand, further addition of the modifier results in the reduction of the storage modulus, due to the plasticizing and dilution action of the AESO.

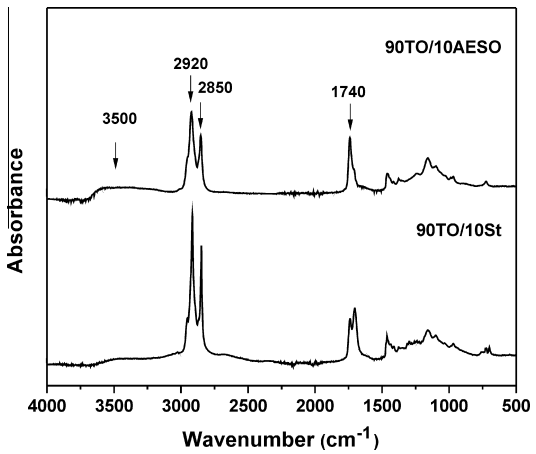


Fig. 8. Comparison of FT-IR spectra of the polymers 90TO/10St and 90TO/10AESO.

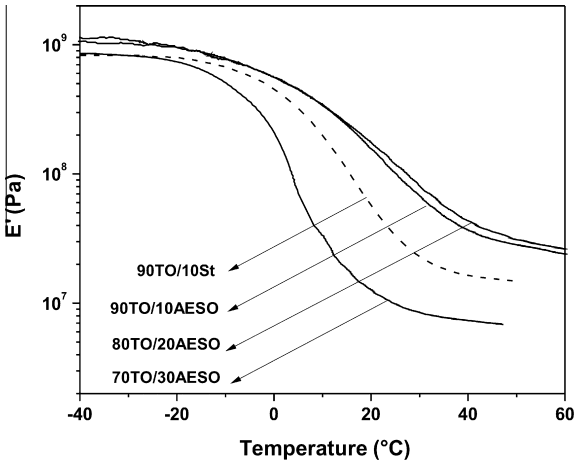


Fig. 10. Storage modulus (E') vs. temperature of the polymers based on 90TO/10St and TO/AESO.

Table 4
Glass transition characteristics of the TO/St, TO/AESO and [TO/AESO]/DVB polymers.

Sample	Tg (°C)	$(\tan\delta)_{max}$	ΔT^* (°C)
70TO/30AESO	7.94	0.76	39.04 (−9.80 to 29.24)
80TO/20AESO	19.24	0.53	48.87 (−8.31 to 40.56)
90TO/10AESO	25.62	0.49	37.32 (6.12 to 44.08)
90TO/10St	20.18	0.61	32.90 (2.80 to 35.70)
[90TO/10AESO]/5DVB	26.90	0.62	46.90 (2.07 to 48.97)
[90TO/10AESO]/10DVB	39.02	0.53	46.73 (12.19 to 58.92)

ΔT^*, temperature interval with height of $\tan\delta > 0.3$.

Table 5
Tensile properties of the TO/AESO and [TO/AESO]/DVB polymers.

Sample	E (MPa)	σ_u (MPa)	ε_u (%)
70TO/30AESO	4.91 ± 0.65	0.34 ± 0.13	9.08 ± 3.39
80TO/20AESO	15.88 ± 2.21	0.93 ± 0.68	9.02 ± 1.33
90TO/10AESO	10.28 ± 2.74	0.54 ± 0.10	8.90 ± 1.16
[90TO/10AESO]/5DVB	30.92 ± 8.77	3.52 ± 0.68	15.14 ± 1.73
[90TO/10AESO]/10DVB	81.05 ± 12.93	6.33 ± 0.50	13.67 ± 1.67

Table 4 summarizes the dynamic - mechanical properties of the TO polymers modified with AESO. All materials showed good damping properties with maximum values in the loss factor higher than 0.3, similarly to copolymers TO/St. The maximum height of the loss factor increased with the content of AESO. The higher mobility of the structure incorporated by the AESO leads to the increase in energy dissipation.

On the other hand, Table 4 also shows that the Tg increases with the addition of DVB, as a result of the increase in the crosslinking density of the network structure.

3.4.2. Mechanical properties

Table 5 summarizes the tensile mechanical properties. Overall, the increase of the TO content increases the modulus and the ultimate stress since the TO incorporates more crosslinking points into the network (as mentioned previously). The ultimate strain does not seem to change significantly with TO content.

However, at high TO content (90%) the modulus and strength decrease. This can be attributed to a more heterogeneous network and the possibility of leaving unreacted unsaturations of TO due to steric hindrance.

The addition of 5–10% by weight of DVB, leads to the increase of the modulus and the stress at break as a result of the increase in the crosslinking density of the material and the rigidity provided by the DVB. As to the strain at break, this property increases with the addition of DVB, although not significant changes were noticed by varying the concentration of 5–10%.

4. Conclusions

Two green modifiers (one reactive and one non reactive) allowed to vary the properties of tung oil networks obtained by cationic polymerization. While a methyl ester synthesized from tung oil resulted an efficient comonomer in the cationic copolymerization with tung oil, a commercial acrylated epoxidized soybean oil (AESO) acted as plasticizer.

The analysis of the results showed that the dynamical–mechanical and mechanical properties of these polymers based on green monomers from vegetable oil are comparable with those obtained using styrene.

The addition of a small proportion of divinylbenzene (5–10 wt.%) allowed increasing the glass transition temperature and improving the mechanical properties of the resulting materials, thus, extending the range of application.

All the materials obtained presented good damping properties over a broad temperature range around Tg and close to ambient temperature.

The [70TO/30ME]/10DVB copolymer presented shape memory behavior (maximum strain of 20% and T_{switch} = 25 °C) with high fixity and recovery ratios.

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