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Vegetable oil/styrene thermoset copolymers with shape memory behavior and damping capacity

Cintia Meiorin, Mirta I Aranguren and Mirna A Mosiewicki*

Abstract

The mechanical and damping properties as well as the shape memory behavior of copolymers obtained by cationic copolymerization of tung oil with styrene with different stoichiometric ratios are presented and analyzed in this work. The glass transition temperatures are close to room temperature for all the copolymers, and generally increase with the content of styrene. A similar trend is observed for the modulus, which exhibits values from 4.89 MPa for the copolymer with 30 wt% styrene to 13.92 MPa for the copolymer with 70 wt% styrene. These hard elastomers present shape memory behavior with high recovery and fixity ratios, as well as high damping quality (damping factors 0.4 and 1.38 at 28.9 and 43.3 °C, for the tung oil homopolymer and the copolymer with 70 wt% styrene, respectively), opening possibilities for practical applications that require material response close to room temperature.
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Keywords: vegetable oil; styrene; shape memory effect; damping properties; cationic copolymerization

INTRODUCTION

Although at present polymer production is mainly a petroleum-based industry, the high price and the non-renewable character of the fossil sources in addition to new policies focused on sustainability are driving the search for alternative raw materials. During the last few years, the preparation of polymeric materials from readily available, renewable, biodegradable and inexpensive natural resources has become gradually more significant.

Eco-friendly polymers present many advantages such as comparatively low cost, wide availability and renewable nature of the sources, offering an ample scope of alternatives for the synthesis of new materials.[1–3] In particular, tung oil (TO) is available as the major product from the seeds of the tung tree (*Aleurites fordii*).[4,5] It 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.[5–7]

This high concentration of unsaturated bonds is responsible for the outstanding drying properties of this oil which result from its fast polymerization in the presence of oxygen. This characteristic makes it one of the most used oils, together with linseed oil, in the paint and varnish industry.[6]

In general, the use of oils for polymer production consists in the chemical modification of triglycerides to obtain different products with properties comparable with those of the synthetic ones, as in the case of the synthesis of polyurethanes (from oil-based polyols) or oil-based resins used in radical copolymerization with unsaturated synthetic comonomers.[7–12] However, the free radical copolymerization of unmodified oils has proven to be unfeasible, even using styrene (St) comonomer.[13] Larock *et al*. have reported the production of rigid plastics by cationic polymerization of several unmodified unsaturated oils and St and/or divinylbenzene initiated by boron trifluoride diethyl etherate.[14–16] These materials can exhibit shape memory properties depending mainly on the polymerization conditions.

Materials that show shape memory behavior are capable of fixing a transient shape and recovering their original dimensions by the application of an external stimulus. These materials present a switch temperature, T_{switch} (generally, the glass transition temperature, T_g, or the melting temperature, T_m, of the polymer), which is higher than the application temperature. The material can reversibly recover from a deformed state when exposed at a temperature higher than T_{switch}. The permanent shape (remembered shape) is fixed in the material through chemical or physical crosslinks that are stable in the range of temperature used.[17] These materials have unusual properties, such as shape memory behavior, pseudoelasticity or large recoverable strain, high damping capacity and adaptive properties which derive from the reversible transition of the materials.[17]

On the other hand, good damping properties with high energy dissipation are searched-for characteristics in polymers used to control noise or mechanical vibration.[16,18]

The aim of this work was to synthesize new materials by cationic polymerization of TO with St and to analyze the mechanical properties, shape memory behavior and damping properties of these copolymers formulated with different chemical compositions.

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EXPERIMENTAL

Materials

TO composed of α-elaeostearic acid (main component, 84 wt%) was supplied by Cooperativa Agrícola Limitada de Picada Libertad, Argentina. St was purchased from Cicarelli Laboratory, Argentina. Boron trifluoride diethyl etherate (BF$_3$.OEt$_2$) with 46%–51% BF$_3$ obtained from Sigma-Aldrich was the catalyst of the cationic reaction. Tetrahydrofuran 99% (THF), used as a modifier of the catalyst, was acquired from Cicarelli Laboratory.

Methods and techniques

Cationic copolymerization of tung oil and styrene

A selected quantity of St was added to the TO and the mixture was stirred. The cationic polymerization of vegetable oils with St results in heterogeneous reactions mainly due to the poor miscibility of the catalyst in the oils.[14–16] However, homogeneous copolymerization can be carried out by modifying the catalyst with different oil ethyl esters, oil methyl esters or with THF[14–16,19] before it is incorporated in the reactive mixture of St and TO. In this work, a homogeneous reaction mixture was achieved by adding the catalyst, previously prepared by mixing the THF (5 wt%) with boron trifluoride diethyl etherate (3 wt% with respect to the weight of the reactants), to the St–TO mixture. The mixture was vigorously stirred and finally poured onto glass plates of 13 mm × 18 mm separated by a rubber cord 1 mm thick 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. St/TO weight ratios of 0/100, 10/90, 30/70, 40/60, 50/50, 60/40 and 70/30 were prepared.

The scheme of the copolymerization between TO and St is shown in Fig. 1.

Soxhlet extraction

A Soxhlet apparatus was used to extract soluble material from a cured sample by refluxing with methylene chloride for 24 h. After extraction, the soluble fraction was isolated for further characterization. The insoluble solid was dried under vacuum for several hours before weighing.

Chemical characterization of the materials

Fourier transform infrared (FTIR) spectra of the samples before and after curing, as well as the spectrum of the soluble fraction extracted by Soxhlet, were recorded by the attenuated total reflection (ATR) method using a Thermo Scientific Nicolet 6700 FTIR spectrometer. The spectra were recorded over the range 500–4000 cm^{-1} with a resolution of 2 cm^{-1} and averaged over 32 scans.

The substances extracted by Soxhlet were also characterized by ^{1}H NMR (Bruker AM-500 spectrometer), using CDCl$_3$ as solvent.

Differential scanning calorimetry

A Perkin Elmer differential scanning calorimeter, Pyris 1, with an internal coolant (Intracooler IIP) and nitrogen purge gas was used to investigate the thermal behavior of the materials. Each sample consisting of a specimen of 6–8 mg sealed in an aluminum pan was heated from −40 to 150 °C. The glass transition temperature of each specimen was determined from the midpoint of the inflexion change in the heat flux $versus$ temperature curve, at a heating rate of 10 °C min^{-1}.

Dynamic mechanical tests

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 a 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 × 5 × 0.5 mm^3. At least two tests for each sample were carried out in order to ensure reproducibility of the results.

According to the kinetic theory of rubber elasticity, the crosslinking density of the samples (ν_e, mol m^{-3}) was calculated
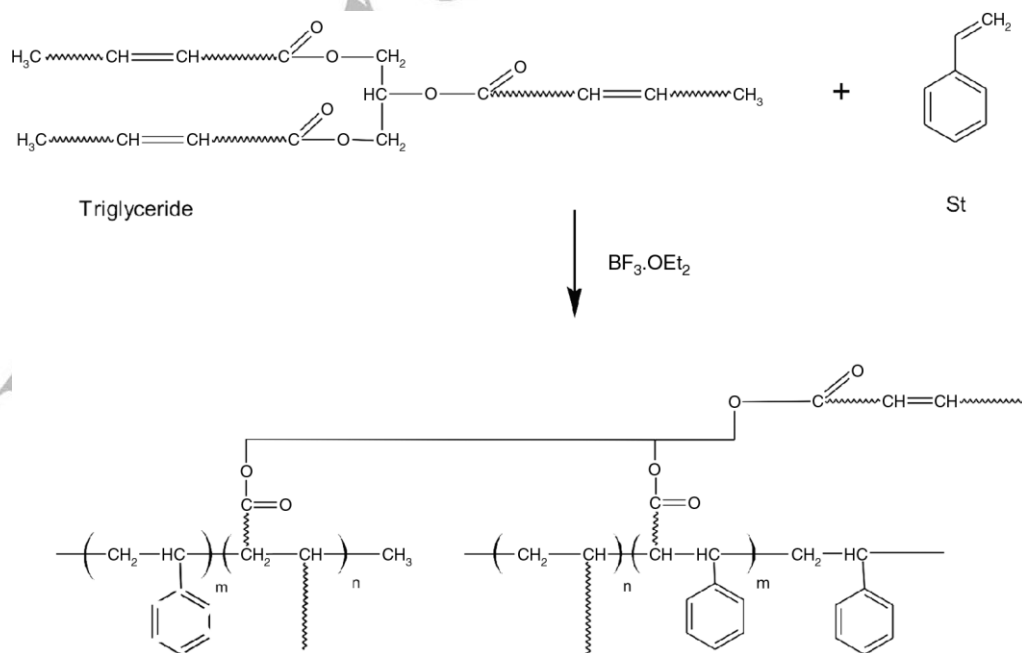

Figure 1. Scheme of copolymerization between the TO and St.

from the experimental values of the rubbery moduli using the following equation:[20–22]

$$E'_r = 3\nu_e RT$$

where E'_r (Pa) represents the storage modulus of the crosslinked copolymer in the rubbery plateau region above the glass transition temperature (T_g), R (J mol^{-1} K^{-1}) is the universal gas constant and T (K) is the absolute temperature. The values of the storage moduli used for the calculations were the values experimentally determined at 25 °C above T_g.

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 a universal testing machine (Instron 8501) in accordance with ASTM D 1708-93 using a crosshead speed of 5 mm min^{-1}. Young's modulus (E), the ultimate stress (σ_u) and the elongation at break (ε_b) were determined from the average values of at least four replicates for each sample.

Thermomechanical cyclic tensile tests (shape memory behavior) were performed on microtensile specimens of 5 mm × 35 mm × 1 mm using a universal testing machine equipped with a heating chamber (Instron 8501). Samples were conditioned at 25 °C and subsequently elongated to different percentages of the original length at a speed of 5 mm min^{-1}. Then the samples were cooled below the glass transition temperature (0 °C) and unloaded. To measure the recovery stress the samples were heated to 25 °C, maintaining the strain constant and equal to ε_u, while the stress developed was recorded by the load cell. Finally, the samples underwent the recovery process by heating for 10 min at 25 °C and zero stress.

The strain maintained after unloading and the residual strain at the end 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:

$$R_f(\%) = \frac{\varepsilon_u}{\varepsilon_m} \times 100 \qquad R_r(\%) = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \times 100$$

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

RESULTS AND DISCUSSION

Cationic● copolymerization

A detailed study of the composition and other characteristics of the TO based on SEC, FTIR and ^{1}H NMR techniques has already been presented in previous work.[7] For the following discussion it is important to state that the analysis by ^{1}H NMR indicated that the main fatty acid present in the TO is elaeostearic (83.6 mol%) with the rest being mostly (but not exclusively) oleic acid.[7]

After the synthesis, the sample containing 70 wt% TO was Soxhlet extracted. The insoluble fraction, composed of the crosslinked styrene triglyceride network, was determined as 89.9 wt% by weighing the dried residue, while the soluble material (material not attached to the network and catalyst fragments) was characterized by FTIR and ^{1}H NMR.

Figure 2 shows the FTIR spectrum of the soluble fraction after extraction with methylene chloride and that of the original TO, for comparison. The spectrum suggests that the major extracted
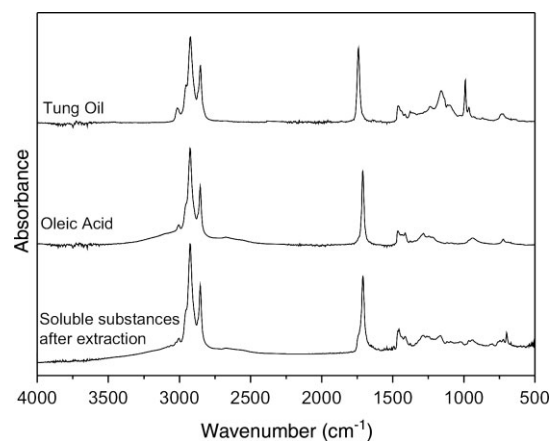
Figure 2. FTIR spectrum of the soluble fraction of the crosslinked copolymer after extraction with methylene chloride and that of the original TO.

components in this phase are unreacted oil derivatives. There is a peak at 1710 cm^{-1}, corresponding to the absorption of the carbonyl stretch ν(C=O), denoting that free acids are generated during curing or Soxhlet extraction from the triglyceride structures. Additionally, the rather high peak at 991 cm^{-1} that appears in the TO spectrum corresponding to the wag of the conjugated unsaturations of the elaeostearic chains is absent in the spectrum of the soluble fraction. The analysis of this spectrum suggests that the fraction contains mainly residues from oleic acid, which is less reactive than the elaeostearic acid (the FTIR spectrum of oleic acid is also included in the figure for comparison). Additionally, there is a very small peak at 698 cm^{-1} which suggests that some fractions may have very minor contributions of reacted St moieties. This assumption was further analyzed by ^{1}H NMR (not shown), which confirms that there is a high content of oleic acid derived structures in the soluble fraction and apparently none based on elaeostearic acid. On the other hand, only small spikes at 1.6 and 1.9 ppm could be related to St moieties.

In particular, the absence of peaks at 5.7, 6, 6.17 and 6.45 ppm, which would correspond to hydrogens from the conjugated double bonds in the elaeostearic chains,[7] supports the idea that these chains have more unsaturations that are also more reactive than unsaturated chains from oleic acid and thus they are mostly attached to the network.

Curing reaction

Figure 3 shows the FTIR spectra corresponding to the sample with 50/50 weight ratio of St/TO before and after curing (curves A and B, respectively), together with the spectra of St and TO. Curves A and B are normalized by the peak at 698 cm^{-1} corresponding to the deformation of the C–H bond in the aromatic ring of the St The FTIR spectrum of the uncured sample is a combination of the bands corresponding mainly to TO and St reactives. The peaks at 3081, 3058 and 3025 cm^{-1} corresponding to the aromatic ring of the St due to =C–H stretching vibrations are present in both spectra, although with changed intensities.

The peak at 3010 cm^{-1} corresponding to C–H bonds in the unsaturations of the TO and St is clearly observed in the unreacted mixture (curve A). The peaks at 2921 and 2852 cm^{-1} are attributed to C–H bonds of single C–C bonds present in the structure of the TO. The peak at 1740 cm^{-1} corresponds to the ester groups from triglyceride molecules. After the reaction a shoulder appears
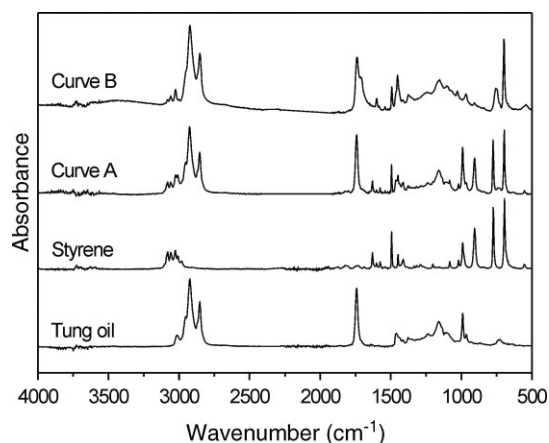
Figure 3. Comparison of FTIR spectra corresponding to the sample with 50/50 weight ratio of St/TO before and after curing (curves A and B, respectively) together with the spectra of St and TO.
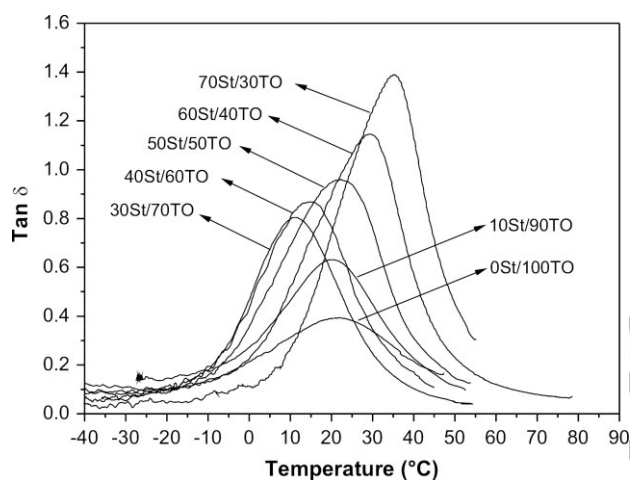
Figure 4. Tan δ versus temperature for TO based copolymers with different St concentrations.

at 1710 cm^{-1}, which indicates the presence of free acids. The high peak at 991 cm^{-1} is assigned to the wag of the conjugated unsaturations of the elaeostearic chains and absorption of the double bonds in the vinyl group of St and can be seen in the spectra of the two monomers and in curve A (before reaction).

The bands at 3010 and 991 cm^{-1}, corresponding to the carbon–carbon double bonds of the TO and St, which are present in the spectra of both comonomers and in that of the mixture before reaction (curve A), disappear completely after reaction (curve B), confirming the participation of the unsaturations of both comonomers in the cationic polymerization. The sharp peaks corresponding to the absorption bands of vinyl groups in St at 906 and 774 cm^{-1} also disappear due to the reaction.

Dynamic mechanical properties

Figure 4 shows tan δ as a function of temperature for copolymers with different St/TO weight ratios. The transitions begin below room temperature and show a broad relaxation region for all the analyzed compositions. Although the peaks in tan δ are wide, each sample displays only one relaxation peak indicating that the copolymers are not phase separated.
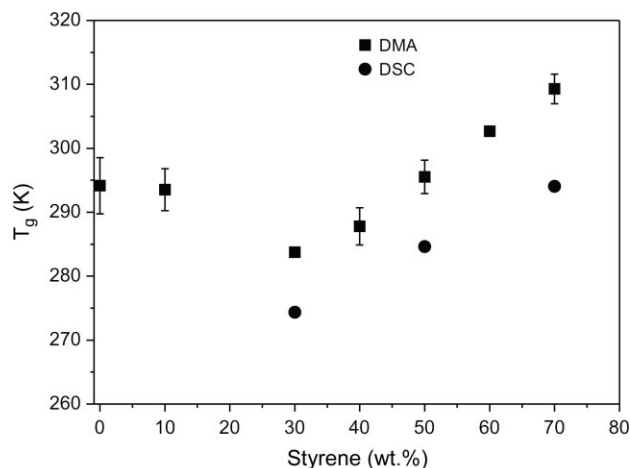
The error bars associated to some of the results are smaller than the size of the symbols.

Figure 5. Glass transition temperatures (T_g) measured by DMA and DSC.

The maximum in the tan δ curve, related to the sample glass transition temperature T_g, shifts to higher temperatures as the St concentration increases (St concentrations above 30 wt%), while the peak height increases. TO chains can contribute to the observed features with two opposite effects: plasticizing the network because of the relatively more flexible structure of dangling chain ends compared with that of an St molecule and increasing the rigidity of the network because of the large number of functional groups per molecule. Thus, the increase in TO concentration increases the amount of crosslinking points in the copolymer, but it also increases the concentration of dangling chain ends with high mobility. Although the two factors contribute to the properties of these copolymers, the plasticizing action of the fatty acid chains in the structure is the dominant effect (at St concentrations above 30 wt%). The higher St percentages decrease the proportion of mobile chains.[23,24] At the other end of the series, the TO homopolymer and the copolymer containing 10 wt% St present higher T_g values than the 30 wt% St copolymer because of the important effect of the crosslinking density.

Figure 5 shows the glass transition temperatures (T_g) obtained by dynamic mechanical analysis (DMA) and DSC as functions of the St concentration in the copolymer. The T_g (DMA) increases almost linearly with the content of St for percentages higher than 30 wt%. The trend obtained by DSC is in agreement with the T_g obtained by DMA but the absolute values are approximately 10 °C below those obtained from the tan δ peaks.

All the samples show a rubbery modulus at high temperatures, denoting the presence of stable crosslinks in the polymer structures (not shown). The magnitude of this property is proportional to the amount of TO in the sample compositions and also to the crosslinking densities calculated using rubber elasticity theory from the experimental values[25] (Table 1). A higher amount of TO in the copolymer correlates with higher crosslinking density of the material and with increased rigidity of the crosslinking points, due to the high functionality of the triglyceride molecules. As more St is introduced into the copolymer the diluent effect of the St is dominant, because longer St–St sequences are incorporated between the resin crosslinking points. Thus, the crosslinking density of the material decreases and consequently the rubber modulus decreases, as found experimentally (Table 1).

Table 1. Properties of the TO/St copolymers

Sample	$E'(T = T_g + 25\,^{\circ}C)$ (Pa)	Crosslinking density, ν_e (mol m^{-3})	(tan δ)$_{max}$	ΔT^* ($^{\circ}$C)
0St/100TO	2.68E + 07	3633.0	0.40	28.9 (6.0–34.9)
10St/90TO	1.32E + 07	1802.8	0.61	32.9 (2.8–35.7)
30St/70TO	7.00E + 06	908.7	0.80	31.9 (−4.3 to 27.6)
40St/60TO	4.90E + 06	627.9	0.86	37.1 (−4.2 to 32.9)
50St/50TO	3.30E + 06	413.7	0.96	41.8 (−1.8 to 40.0)
60St/40TO	1.95E + 06	238.5	1.14	42.5 (3.9–46.4)
70St/30TO	1.30E + 06	156.1	1.38	43.3 (11.2–54.6)

ΔT^*, temperature interval with height of tan $\delta \geq 0.3$.
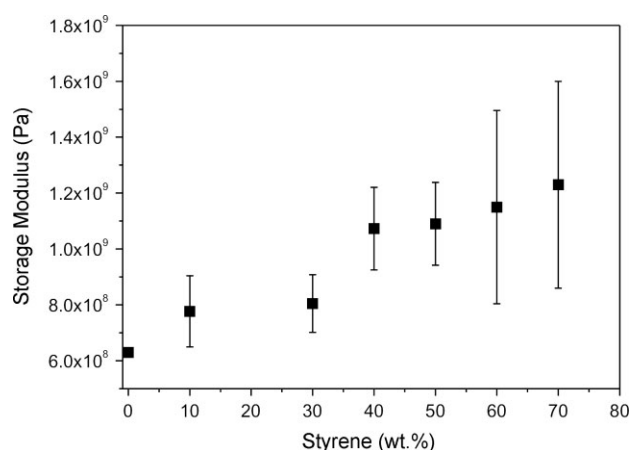
Figure 6. Storage modulus at −20 $^{\circ}$C as a function of the St content in the copolymer.

Figure 7. Tensile stress–strain curves of the copolymers tested at room temperature (18 ± 1 $^{\circ}$C) until failure.

Figure 6 shows the storage modulus at −20 $^{\circ}$C (in the glassy state) as a function of the St content. The glassy modulus is dependent on the cohesion density of the material, and higher concentrations of TO lead to a higher free volume because of the dangling chains effect, while increasing St concentration allows a better packing of the molecules in the network, a feature that also controls the trend observed in the T_g of the materials. Thus, it is seen from the experimental data that the low temperature modulus is directly proportional to the weight percentage of St, which also contributes with its aromatic nature to increasing the rigidity of the polymer and to decreasing the concentrations of dangling chains and soluble moieties from TO.

Damping properties

The factor tan δ, which is the ratio between the loss modulus (mechanical dissipation of energy) and the storage modulus (storage energy), indicates the damping capacity of the material. It has been suggested that good damping capacity correlates with tan $\delta > 0.3$ over a wide temperature range.[15]

Table 1 shows that the maximum in the loss factor increases with the St content and all the values are considerable higher than 0.3. The temperature intervals for the glass–rubber transition of these samples are between 28.9 and 43.3 $^{\circ}$C and close to room temperature, which is acceptable for applications requiring energy absorption at ambient conditions. As the St content increases in the copolymer formulation, the crosslinking density decreases. The crosslinking density restricts the segmental

mobility of the polymer and consequently reduces the ability to dissipate energy, which is the reason for lower peaks at lower St concentrations.

Mechanical properties

Figure 7 shows the tensile stress–strain curves of the copolymers tested at room temperature (18 ± 1 $^{\circ}$C) until failure. As expected, the stress increases linearly with the strain at the beginning of the test and the initial slope corresponds to the elastic modulus.

The samples with less that 70 wt% St behave like elastomers due to their proximity to the rubbery region at the test temperature. They present low modulus without yield point. Yield behavior is only observed in the sample with 70 wt% St which shows a nonlinear stress–strain functionality beyond this point until failure.

A summary of the mechanical properties in tensile tests is presented in Table 2. It can be observed that, as more St is introduced in the copolymer and longer St–St sequences are incorporated between the resin crosslinking points, the crosslinking density of the material decreases and the modulus decreases. However, at room temperature the sample with the highest St content (70 wt%) is in the glass–rubber transition zone, while the other copolymers are almost in the rubbery state, which is clearly reflected by modulus values in the range of elastomers. As a consequence, the 70 wt% St sample shows a much higher modulus than the rest of the series.

Table 2. Tensile properties of TO/St copolymers

Sample	E (MPa)	σ_u (MPa)	ε_u (mm mm^{-1})
30St/70TO	4.89 ± 0.55	0.52 ± 0.24	0.11 ± 0.04
40St/60TO	3.76 ± 0.20	1.31 ± 0.20	0.43 ± 0.06
50St/50TO	3.30 ± 0.36	1.36 ± 0.41	0.46 ± 0.10
60St/40TO	1.74 ± 0.09	1.21 ± 0.07	0.66 ± 0.06
70St/30TO	15.20 ± 2.33	1.05 ± 0.10	1.30 ± 0.21

The comparatively small value of the tensile strength (σ_u) of the sample with 30 wt% St can be attributed to the more non-uniform network structure present in this highly crosslinked elastomer.

The deformation at break (ε_b) increases as the St concentration increases in agreement with the fact that the density of crosslinking decreases. Besides, increasing the TO concentration in the copolymer formulation is equivalent to increasing the number of dangling chain ends that can generate defects in the crosslink structure and initiate microcracks during mechanical testing.[25] On the other hand, for the sample with 70 wt% St the deformation at break decreases because its behavior is closer to the glass performance.
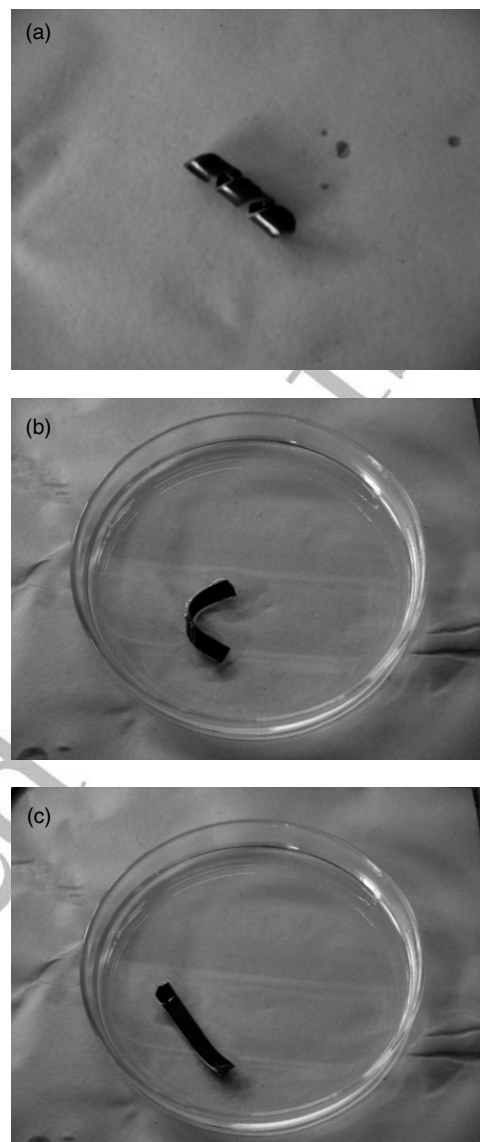
Shape memory behavior

Figure 8 shows the sequence of shape recovery of a bar (70St/30TO) initially deformed at a temperature above T_g to adopt a curly shape. The series of images shows the recovery of the sample after fixing the deformed shape by cooling below T_g. By immersing the curly piece in hot water (40 °C) the original bar shape is recovered after 40 s.

The production of copolymers with different glass transition temperatures and various degrees of crosslinking allows copolymers to be tailored to exhibit different shape memory properties. Thus, the shape memory behavior of the copolymers at 25 °C (above the glass transition temperatures obtained by DSC) was studied through thermomechanical experiments by varying the percentage of strain in the samples prepared with 40, 50, 60 and 70 wt% St.

Figure 9 gives the tensile stress–strain plots, showing the thermal cycle for the copolymer with 70 wt% St with maximum strain of 100%. In this, as in all the cases studied, rubber elasticity was observed at 25 °C. This phenomenon takes place from the micro-Brownian motion of mobile segments and the restricted molecular mobility caused by stable crosslinks. After deformation at 25 °C and subsequent cooling below T_g under constraint, the deformed shape was retained to a large extent because of the frozen micro-Brownian movement. When the samples were reheated to 25 °C, the original shape was substantially restored by the elastic energy stored during the deformation process. The stress–strain response showed an elastic region followed by nonlinear deformation. During unloading at low temperature, a small recovery occurred because the material cannot maintain the maximum deformation achieved. Upon heating, the imposed strain was almost completely recovered, leaving a residual deformation (ε_p). In all cases, the stress–strain behavior of the first cycle was distinct from the behavior in subsequent cycles,[26,27] which is the typical case for all shape memory polymers.

The main shape memory features of the copolymers with 30, 40, 50, 60 and 70 wt% St are presented in Table 3 (shape recovery and fixity). Different values of the maximum load were used depending on the copolymer composition. While the sample with 40 wt% St

Figure 8. Sequence of the shape recovery of a bar (70St/30TO) initially deformed at a temperature above T_g to adopt a curly shape: (a) before heating, and (b) after 20 s and (c) after 40 s in hot water.
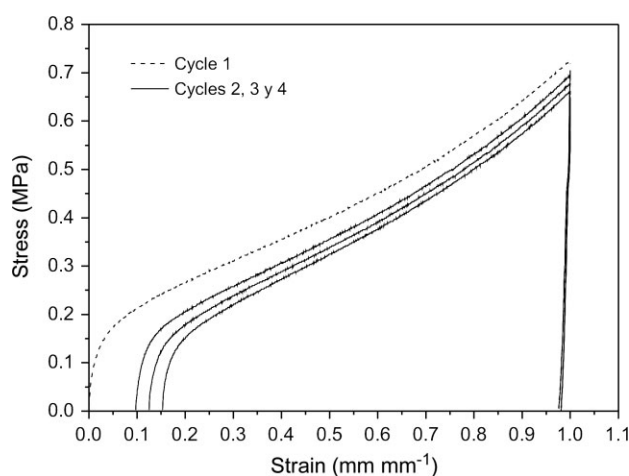
Figure 9. Results from thermal tensile cycles of a sample of 70 wt% St with a maximum strain of 100%.

cannot be deformed at maximum strains higher than 20% without breaking during the second cycle (at 25 °C), the sample with 70 wt% St allows strains as high as 100% to be achieved at 25 °C.

As could be observed with the samples with 60 and 70 wt% St the fixity reaches a value of 100% at all the maximum strains used in the study, indicating a perfect fixity.[28] When the sample is cooled under stretching, the shape is preserved by freezing molecular conformation below the glass transition temperature. However, a certain fraction of the chain segments keeps its mobility and consequently the maximum fixed deformation ε_m cannot be perfectly maintained after ●renewed motion of the load. Lin and Chen reported that the reduction of the crosslinking density can lead to incomplete recovery of the deformed sample.[29] In the case of these two copolymers (60 and 70 wt% St), the fact that their T_g is higher than that of the rest of the copolymers explains the better shape fixity. Of course this higher T_g is related to the structure of the polymers: lower concentration of dangling chains, longer St–St sequences that have relatively higher rigidity (compared with the triglyceride fatty acid chains) and overall higher uniformity of the network. The copolymers show a high recovery of the fixed deformation upon reheating to 25 °C indicating that the crosslinking density is high enough to allow for storing and releasing the elastic energy in the shape memory process.

The recovery force measured at the fixed maximum strain, while increasing the temperature, is also reported in Table 3. Rising temperature causes the amorphous chains to return back to their original random configuration of higher entropy. In this stage, preventing the chain motion by keeping the sample at constant strain generates the measured force.

For a given material, as the maximum strain increases, the stored energy increases and there is a larger driving force for the material to recover its original shape, which is reflected in the higher recovery force.

The comparison of the recovery forces for samples with different percentages of TO and the same maximum strain shows that higher TO content increases the recovery force. This behavior is related to the fact that TO generates multifunctional crosslinking points during curing. Tensile and dynamic mechanical results show that increasing TO content increases the elastic modulus in the rubbery state due to the increase in crosslinking density. The higher is the crosslinking density, the higher is the stored energy that generates the exerted recovery force.

CONCLUSIONS

Novel copolymers obtained by cationic copolymerization of unmodified TO with St were studied. Infrared spectroscopy confirms the copolymerization reaction of the carbon–carbon double bonds of TO and St.

The glass transition temperatures of the copolymers increase with increase in the St content for percentages higher than 30 wt%. The same trend was observed in the Young's modulus values. The properties of the copolymers are related to the degree of crosslinking, the length of St homopolymer sequences and the mobility of the TO dangling chains. Crosslinking increases the elastic modulus in the rubber region.

The complex chemical structures of these crosslinked networks are responsible for the good damping properties observed over a broad temperature range around T_g.

These materials can exhibit shape memory behavior in a low temperature range. The fixity and recovery ratios reach values higher than 85% for all the analyzed compositions and elongations.

Table 3. Shape memory properties of the TO/St copolymers

Sample	T (°C)	Elongation (%)	nth cycle	R_f (%)	R_r (%)	Recovery force (N)
40St/60TO	25	20	1	93.74	94.40	3.42
			2	86.80	89.60	3.60
			3	87.40	91.40	3.61
50St/50TO	25	40	1	84.70	94.70	5.25
			2	95.70	93.10	6.04
			3	96.30	96.10	6.09
		50	1	89.68	95.52	7.39
			2	92.56	94.80	7.65
			3	91.44	94.40	7.55
		60	1	92.33	93.93	9.45
			2	94.60	93.13	9.63
			3	89.47	92.93	9.00
60St/40TO	25	40	1	100.00	92.70	3.77
			2	100.00	90.50	3.75
			3	100.00	90.80	3.74
		50	1	100.00	93.28	4.00
			2	100.00	92.08	4.07
			3	100.00	92.00	4.10
		60	1	100.00	98.53	5.34
			2	100.00	98.07	5.09
			3	100.00	93.60	5.09
		70	1	100.00	100.00	5.82
			2	100.00	99.99	5.54
			3	100.00	99.83	5.62
70St/30TO	25	40	1	100.00	99.90	1.43
			2	100.00	91.40	1.30
			3	100.00	95.10	1.38
		50	1	100.00	95.04	1.80
			2	100.00	98.88	1.78
			3	100.00	91.36	1.62
		60	1	100.00	94.47	2.62
			2	100.00	94.27	2.53
			3	100.00	91.40	2.45
		70	1	100.00	87.49	3.27
			2	100.00	88.74	3.18
			3	100.00	87.20	3.11
		80	1	100.00	74.10	3.16
			2	100.00	65.90	3.02
			3	100.00	86.10	3.00
		90	1	100.00	89.78	2.69
			2	100.00	100.00	2.72
			3	100.00	99.78	2.69
		100	1	100.00	90.28	3.22
			2	100.00	87.48	3.12
			3	100.00	84.68	3.09

Modifications of the network formulations are currently being studied in order to increase the T_g of the materials and widen the scope of possible applications.

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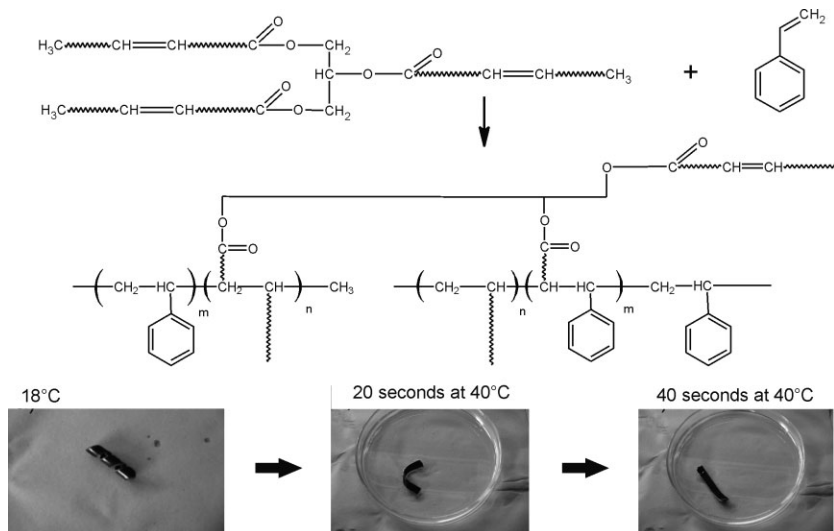
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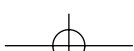
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