Smart and Structural Thermosets from the Cationic Copolymerization of a Vegetable Oil

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ABSTRACT: Copolymers based on tung oil (TO) and presenting a very wide range of properties were obtained. Depending on the chemical composition, materials fitted for structural or functional applications were prepared. The use of divinylbenzene (DVB) as a comonomer in the cationic polymerization of the triglyceride allowed us to obtain polymers with a high thermal stability in an ample temperature range and with a room-temperature modulus close to 1 GPa for percentages of TO up to 40 wt % styrene (St) as a partial replacement of DVB in a copolymer containing 50 wt % TO resulted in a material with shape-memory behavior with switch temperatures in the range 25–40°C. The mechanical properties and shape-memory behavior of copolymers with different chemical compositions were analyzed. It was observed that an increase in the DVB content increased the glass-transition temperature and modulus, which was associated with an increase in the crosslinking density and the contribution of the rigid aromatic structure of the comonomer.
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Key words: cationic polymerization; copolymers; mechanical properties; renewable resources

INTRODUCTION

The use of renewable resources in the polymer industry is slowly gaining acceptance as an option for commercial and environmental interests that can reduce the need for polymers derived from the petrochemical industry. Biomass-derived polymers can exhibit a relatively low environmental impact, whereas the high availability of the raw materials at a relatively low cost is a clear advantage.[1,2] In this sense, vegetable oils are an interesting alternative, and in recent years, basic studies on the synthesis conditions of polymeric precursors from vegetable oils, physicochemical characterization, and determination of the thermal and mechanical characteristics of the final materials have been carried out.[3–7] Vegetable oils are triglycerides consisting of three fatty acids attached to a glycerol structure, offering a large variety and number of reactive sites.[8] In particular, tung oil (TO) is extracted from the seeds of the tree of the same name and is composed mainly of a glyceride of α-elaeostearic acid with a conjugated triene structure.[9,10] It has been reported that although TO is a highly unsaturated oil, polymers with good dimensional stability cannot be obtained by radical copolymerization because of the low reactivity of the carbon–carbon double bonds in this type of reaction.[11] On the contrary, the carbocationic mechanisms of highly unsaturated triglycerides are adequate for producing polymers with typical comonomers such as styrene (St) or divinylbenzene (DVB).[3,4,12] The use of different ratios between the triglycerides and comonomers leads to final materials with an ample range of properties from which different applications could benefit.

Shape-memory polymers are materials that are distinguished by their ability to self-recover from large strains imposed by mechanical loads after the application of an external stimulus without suffering any significant damage.[13,14] The transient shape is achieved by mechanical deformation and subsequent fixation of that deformation. After the application of an external stimulus, these polymers recover their initial shape, and the deformation cycles can be repeated several times.[15] These polymers have found applications as packaging films,[16] smart textiles,[17,18] intelligent medical devices,[19] and implants for minimally invasive surgery.[20,21] On the other hand, highly crosslinked polymer materials can be considered for structural applications with acceptable durability, low cost, and low density as well as good mechanical performance.

This article presents the synthesis by cationic polymerization of copolymers based on TO with St and DVB as comonomers with the aim of widening the

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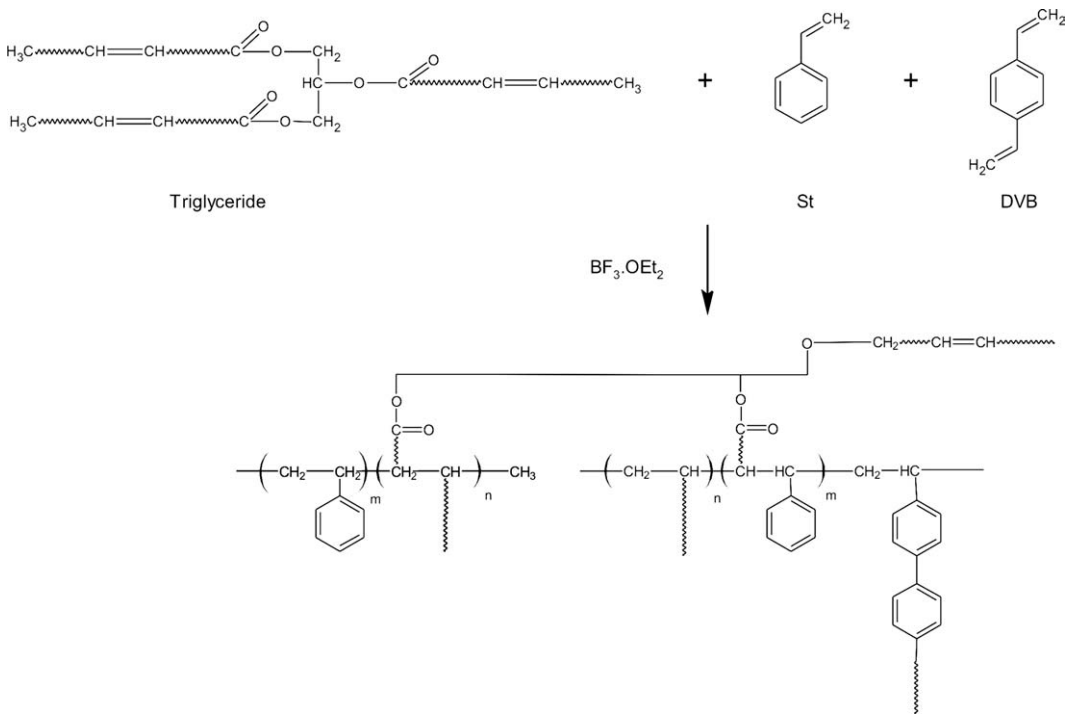

Figure 1 Scheme of the copolymerization.

field of applications covered by the TO/St copolymers previously reported.[22] These new copolymers displayed structural or shape-memory properties, depending on their compositions. Consequently, TO/DVB and TO/St/DVB copolymers with different initial weight ratios were prepared, and their thermomechanical and mechanical properties and shape-memory behaviors were analyzed.

EXPERIMENTAL

Materials

TO, composed mainly of α-elaeostearic acid (84 wt %) and minor percentages of oleic, linoleic, and linolenic acids, was supplied by Cooperativa Agrícola Limitada de Picada Libertad (Misiones, Argentina). St (99.5%), DVB (80%), and tetrahydrofuran (a modifier of the catalyst) were purchased from Cicarelli Laboratory (Argentina) and were used without further purification. Boron trifluoride diethyl etherate (BF_3OEt_2), used as a catalyst, was supplied by Sigma-Aldrich.

Methods and techniques

Cationic copolymerization of the TO/DVB and TO/St/DVB copolymers

Because of the poor miscibility of the catalyst in the oils, the cationic polymerization of vegetable oils and St or DVB results in a heterogeneous reaction. To solve the initial immiscibility, the catalyst must be modified to obtain a homogeneous initial solution.[3,4,12] In this work, St and/or DVB in the selected ratio were added to TO. The mixture was stirred, and this step was followed by the addition of 3 wt % modified catalyst ($BF_3.OEt_2$ plus 5 wt % tetrahydrofuran). The mixture was vigorously stirred and finally poured into glass plates 13 × 18 mm^2 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. TO/DVB and TO (50%)/St/DVB copolymers at weight ratios of 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, and 30/70 and 50/40/10, 50/30/20, 50/20/30, 50/45/5, and 50/48/2, respectively, were prepared.

Figure 1 shows schematically the cationic copolymerization of TO (50%)/St/DVB.

Differential scanning calorimetry (DSC)

A PerkinElmer Pyris 1 DSC instrument (Massachusetts, USA) with an internal coolant (Intracooler IIP) and nitrogen purge gas was used in the experimental work to determine the glass-transition temperatures (T_g's) of the materials. Each sample was heated from −40 to 150°C. Specimens of 6–8 mg sealed in aluminum pans were used for the tests. The T_g values of the polymers were determined at the midpoint of the observed change in the heat flux curve at a heating rate of 10°C/min.

Dynamic mechanical tests

A PerkinElmer dynamic mechanical analyzer (DMA 7, Massachusetts, USA) was used to determine the

dynamic mechanical behavior of the samples. The tests were carried out with tensile fixtures and a temperature scanning mode (10°C/min) under a nitrogen atmosphere with dynamic and static stresses of 50 and 100 kPa, respectively. The sample dimensions were approximately 20 × 5 × 0.5 mm^3 and were measured with an error in the linear dimensions of ±0.01 mm.

Mechanical tests

Microtensile testing was performed at 18°C on tensile specimens 5 × 35 mm^2 cut from the molded plaques with a universal testing machine (Instron 8501) in accordance with ASTM D 1708–93 with a crosshead speed of 5 mm/min. The Young's modulus (E), stress at break (σ_b), and elongation at break (ε_b) values were determined as the average values of at least four replicates of each sample.

To determine the shape-memory behavior, thermal cyclic tests were performed on microtensile specimens of 5 × 35 mm^2 with the universal testing machine mentioned previously, which was equipped with a heating chamber. Samples were conditioned at 25 or 40°C (both temperatures above the T_g of the copolymers, as determined by DSC, to ensure rubber elasticity and, consequently, the mobility of elastically active chains, which allowed large deformation of the samples to a preselected temporary shape) and subsequently stretched at a speed of 5 mm/min. Then, the samples were cooled below T_g (0°C) to fix the transient deformation. The cooled sample was released from the external stress, and the temporary shape was retained because the sample, although at a nonequilibrium state, could not recover its original shape because of the reduced mobility of the polymer chains in the glassy state. The sample snapped back toward its initial shape once the molecular recovery mechanism was thermally induced by an increase in the temperature back to the deformation temperature.

To measure the recovery stress, the samples were heated to 25°C (or 40°C) at a constant strain equal to the strain maintained after unloading (ε_u), and the developed stress in the sample was recorded by the load cell. Finally, the samples were unloaded and underwent the recovery process by heating for 10 min at 25°C (or 40°C).

The maximum strain in the thermal mechanical cycle (ε_m), ε_u, and the residual strain of each cycle (ε_p) were used to calculate the fixity ratio (R_f) and recovery ratio (R_r) with the following equations:[23,24]

$$R_f(\%) = \frac{\varepsilon_u}{\varepsilon_m} \times 100$$

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

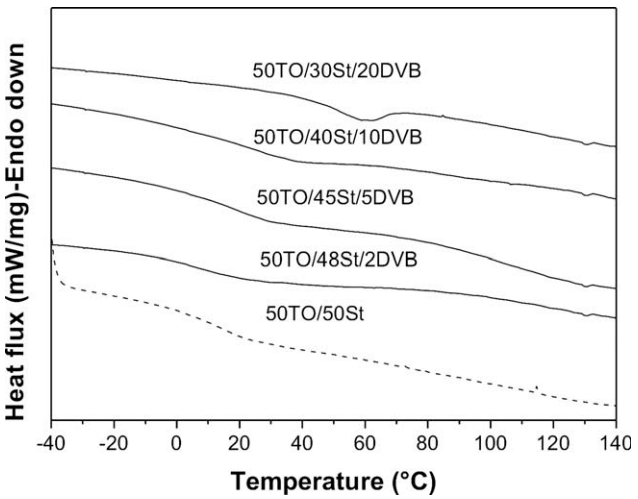

Figure 2 DSC curves corresponding to samples containing 50 wt % TO and different St/DVB ratios.

RESULTS AND DISCUSSION

Thermal transitions

The use of DSC to determine the T_g values of the copolymers was not successful in the case of the TO/DVB because of the very wide and shallow transitions for some compositions and the inability to show any transition in others. However, it allowed us to determine the T_g values of the TO (50%)/St/DVB copolymers. Figure 2 shows the DSC curves corresponding to these samples containing 50 wt % TO and different St/DVB ratios.

In general, the DSC traces of the copolymers showed a variation in the heat flux that started close to room temperature, which corresponded to the T_g. The increase in the DVB content in the copolymer increased the crosslinking density and produced a shift of the transition to higher temperatures (Fig. 2). Samples with DVB contents higher than 20 wt % showed shallow and wide transitions, which complicated the determination from the DSC curves (not shown). Table I summarizes the T_g values of the specimens determined at the midpoint of the transition.

Dynamic mechanical behavior

Dynamical mechanical measurements are more sensitive to changes at the glass–rubber transition, and thus, they could be used in the study of the TO/DVB and TO (50%)/St/DVB copolymers.

Figure 3 shows the dynamic mechanical properties of the TO/DVB copolymers with different compositions (no St was included in these preparations). The curves show the typical features of a thermoset: the storage modulus initially remained almost constant at low temperatures, and as the temperature increased, the storage modulus exhibited a sharp

TABLE I
T_g Values and Damping Properties of the TO/St/DVB Copolymers

	T_g (°C)		Damping results		
Sample	DSC	DMA	$(\tan\delta)_{max}$	ΔT (°C)[a]	Temperature range (°C)[a]
50TO/50St	11.5	22.4	0.96	42.3	−1.8 to 40.5
50TO/48St/2DVB	14.7	30.2	1.02	35.9	10.6 to 46.5
50TO/45St/5DVB	15.6	39.8	0.91	40.3	17.4 to 57.7
50TO/40St/10DVB	23.0	47.7	0.95	47.6	20.6 to 68.2
50TO/30St/20DVB	49.0	74.2	0.58	34.9	56.4 to 91.3
50TO/20St/30DVB		91.2	0.46	47.2	70.0 to 117.2
50TO/50DVB		—[b]	—	—	—

[a] Range of temperature with tan $\delta > 0.3$.
[b] Showed no maxima in the tan δ curve in the temperature range.

drop, followed by a rubbery plateau modulus at high temperatures. The modulus drop was associated with the beginning of segmental mobility in the crosslinked polymer network, whereas the constant modulus at high temperature was the result of the crosslinked structure of the copolymer.

Further analysis showed that the overall trend was an increase in the modulus as the DVB content increased, with the largest and clearest differences at temperatures above the glass transition [Fig. 3(a)]. It has been reported that TO and DVB have comparable reactivities in cationic polymerization and, like DVB, TO can be used as a crosslinking agent because of its multiple functionalities.[25] As the DVB content increased, the crosslinking density increased (Table I) and so did the rubbery modulus, as expected from rubber elasticity theory.[26–28] In addition to this effect, the molecular mobility also became more restricted because of the increased rigidity of the copolymer due to the aromatic structure of the DVB. Following this trend, the copolymers with the highest DVB content showed a very small reduction in the modulus with temperature because the high crosslinking densities led to glass transitions above the measured temperature range and, eventually, to materials that could thermally degrade before they reached such a transition.

The curves of the loss factor (tan δ) as a function of the temperature for the same copolymers are presented in Figure 3(b). The peak in tan δ corresponded to the main mechanical relaxation of the matrix, which was related to the T_g of the copolymer. Thus, it could be used to determine the temperature of the transition, although it usually appeared at temperatures higher than T_g, as measured by DSC.[29] The results show that the peaks shifted to higher temperatures, decreased in height, and became broader with increasing DVB content (from 10 to 40 wt %).[30,31] The curves corresponding to the highest percentages of this very effective crosslinking agent showed practically no maxima, with the transition being shifted above the temperature range observed because of the much reduced mobility of the chains. The widening and decrease in height of the tan δ peaks were associated with increasingly more crosslinked and heterogeneous networks with wider molecular weight distribution of the chains between crosslinking points.[32]

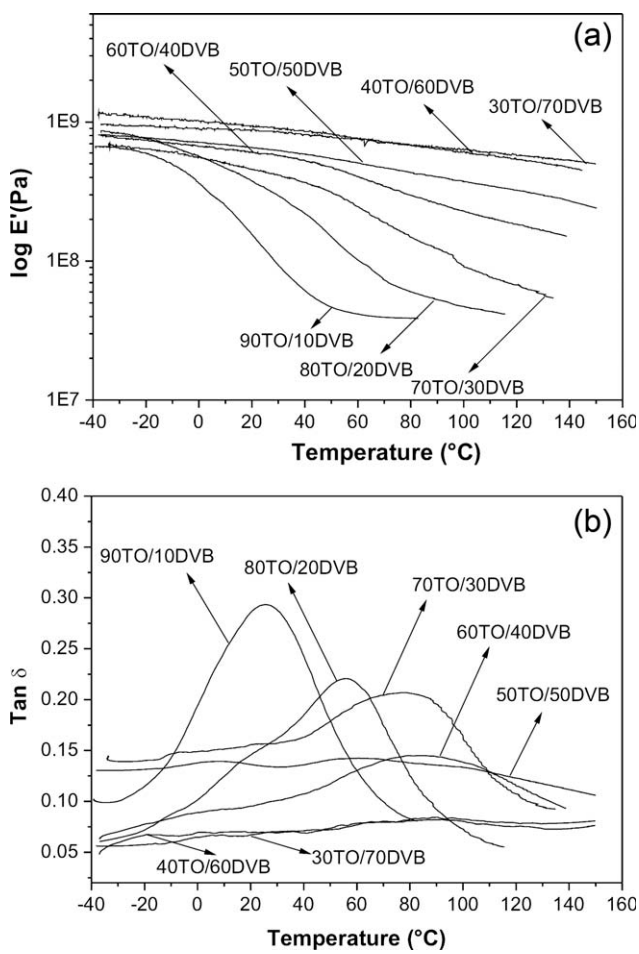

Figure 3 Dynamic mechanical properties of the TO/DVB copolymers as a function of the temperature: (a) storage modulus (E') and (b) tan δ.

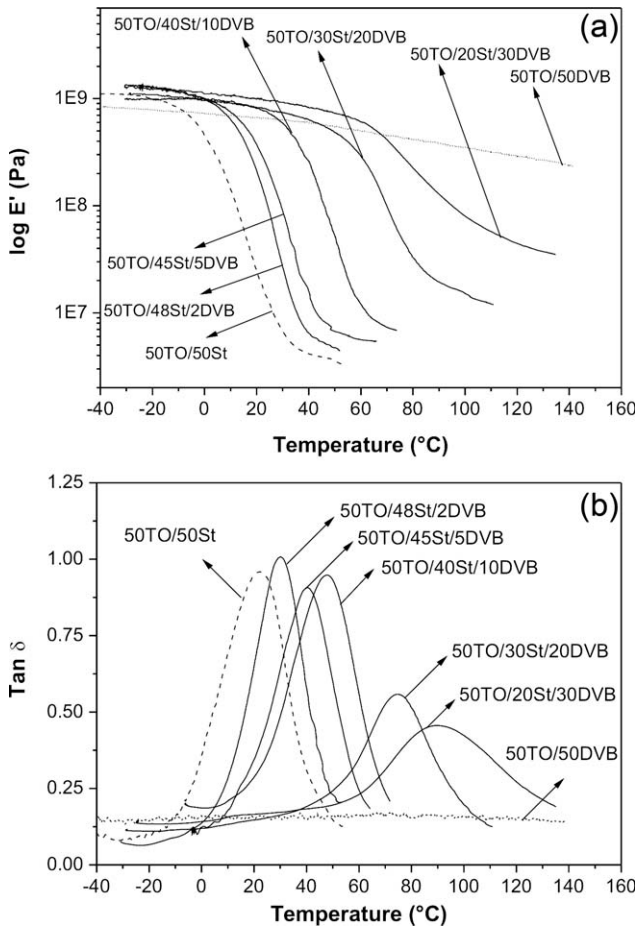

Figure 4 Dynamic mechanical properties of copolymers with 50 wt % TO and different St/DVB ratios as a function of temperature: (a) storage modulus and (b) tan δ.

The properties of the copolymers prepared from TO and St obtained by cationic polymerization were already reported in a previous work.[22] These materials presented good damping properties and shape-memory behavior, depending on their composition, but their use could be limited because of the low T_g values [$T_g = 22°C$ for TO (50%)/St, as measured by dynamic mechanical analysis (DMA)]. This prompted the incorporation of DVB into the formulation to shift the transition to higher temperatures, expand the temperature range for applications, and still retain the shape-memory properties.

Figure 4(a) shows the storage modulus versus temperature of the TO (50%)/St/DVB copolymers. The storage modulus did not show large differences in the glassy state; conversely, at temperatures above T_g, higher concentrations of DVB produced a higher rubbery modulus as the crosslinking density increased, as was previously discussed.

Figure 4(b) shows the curves of tan δ versus temperature for the TO (50%)/St/DVB copolymers. When a higher percentage of DVB with respect to St was incorporated into the copolymer, the higher functionality of the DVB crosslinker contributed to a reduction in the mobility of the structure, and T_g shifted to higher temperatures, 30 to 92°C for 2 and 30 wt % DVB, respectively. The increased rigidity of the network also resulted in the reduction of the peak height, whereas the broadening of the tan δ peak was related to the more heterogeneous structure of the network (different lengths of the elastically active chains and crosslinking points of different nature for TO and DVB).

DMA results also offer information regarding the damping capabilities of the materials. Depending on the application of the polymer, a high loss tangent value around the glass–rubber transition region may be required. For example, polymers used for vibration control need to have tan δ values as high as 1 close to the transition so that the impact energy can be efficiently absorbed.[33] In general, good damping capacity has been reported for materials that present tan δ values greater than 0.3 in a temperature interval larger than 60°C.[30,31,34,35] As shown in Table I, the TO (50%)/St/DVB copolymers showed a $(\tan \delta)_{max}$ value higher than 0.3, but the transition was not as broad as mentioned previously. However, these materials still exhibited a high relaxation peak over a relatively wide temperature range (35–47°C).

In thermoset polymers, the damping capacity is strongly dependent on the crosslinking density (V_e) because the crosslinking points restrict the movement, and consequently, the energy that could be dissipated decreases. Accordingly, there is an

TABLE II
Mechanical Properties in Uniaxial Tensile Tests of the TO/DVB Copolymers

Sample	E (MPa)	σ_b (MPa)	ε_b (%)	ν_e (mol/m^3)
90TO/10DVB	74.5 ± 19.3	4.27 ± 0.92	8.18 ± 1.43	5.83×10^3
80TO/20DVB	327.7 ± 22.0	12.25 ± 0.70	8.32 ± 1.25	7.30×10^3
70TO/30DVB	549.2 ± 44.4	11.27 ± 4.58	2.98 ± 0.96	1.07×10^4
60TO/40DVB	681.3 ± 39.6	10.13 ± 2.66	2.16 ± 0.46	—[a]
50TO/50DVB	742.3 ± 33.5	8.39 ± 1.37	1.38 ± 0.27	—[a]
40TO/60DVB	774.4 ± 33.7	8.36 ± 1.78	1.44 ± 0.28	—[a]
30TO/70DVB	913.1 ± 23.6	5.31 ± 1.63	1.05 ± 0.14	—[a]

[a] It was not possible to determine the rubbery modulus at $T_g + 25°C$ (DMA) to calculate ν_e.

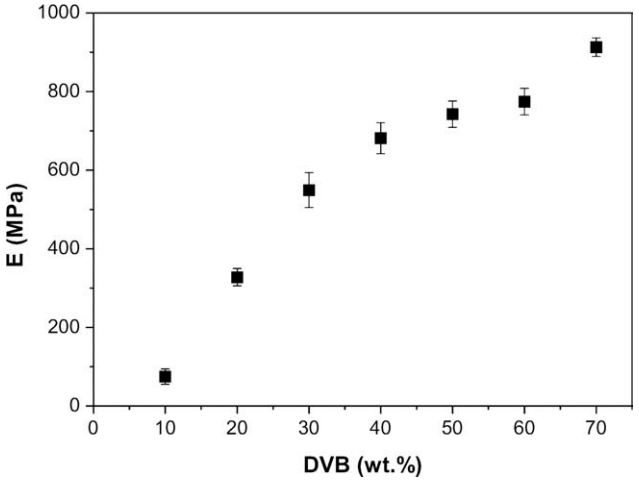

Figure 5 Storage modulus (E′) at −20°C as a function of the DVB content in the TO/DVB copolymers.

opposite relationship between the energy dissipation and the crosslinking density. Thus, in this study, the potentially best damping behavior for applications close to room temperature was displayed by the TO (50%)/St/DVB copolymers with DVB contents from 0 to 10 wt %.

Mechanical properties

Table II shows the mechanical properties of the TO/DVB copolymers measured at room temperature. The values of E of the materials were affected by the increase in the DVB content through more than one effect: (1) an increase in the crosslinking density, (2) an increase in the rigidity of the network chemical structure due to the increase in the aromatic content, and (3) an increase in the T_g of the network. This last effect was particularly strong at low DVB contents.

The TO/DVB copolymer with 10 wt % DVB was in the rubber state at room temperature, and consequently, it showed a relatively low modulus.

At low DVB contents, the values of the modulus showed a strong functionality with the DVB content but a much weaker functionality at concentrations of DVB above 30–40 wt %. Below 30 wt % DVB, the observed increase of the modulus was due to the increasing crosslinking density, which changed the material from an elastomer to a glass in this composition range.[36]

Above 40 wt %, the increase in the crosslinking density just increased the rigidity of the already glassy network (Fig. 5).

The copolymer with 10 wt % DVB presented the lowest crosslinking density of this copolymer series; its strength was low. The strength increased with crosslinking density (in the range of low DVB content) because of the higher cohesion density of the network, but at DVB contents higher than 20 wt %, the strength decreased again because of the increased rigidity of the structure. ε_b decreased with increasing percentage DVB because of the lower extensibility of the more crosslinked material.

Table III summarizes the tensile properties of the TO (50%)/St/DVB copolymers. In this case, when the DVB content was increased (and the St content was decreased) in the copolymer, the concentration of crosslinking points increased, and consequently, the modulus and strength also increased.[32] The ε_b decreased at increasing percentages of DVB because the material became stiffer and more fragile at the same time.

Shape-memory properties

In particular, the TO (50%)/St/DVB copolymers showed shape-memory properties at some of the investigated compositions. In a previous publication, the shape-memory capabilities of TO/St copolymers were reported.[22] However, the materials had switch temperatures too close to room temperature, which made the incorporation of DVB an interesting option to shift the memory response to higher temperatures. During the copolymerization with TO, St formed linear segment chains of homopolymer, whereas DVB contributed with crosslinking points, which led to an increase in three-dimensional networking.

Figure 6 shows the stress–strain plot for the thermal cycling of the copolymer TO (50%)/St (40%)/DVB (10%) wit an ε_m of 35%; this value was chosen because the ε_b of this material determined in uniaxial tensile tests at 40°C was 50%. The summary of the results obtained for copolymers containing 50 wt % TO and different concentrations of St and DVB is presented in Table IV.

The copolymers with high amounts of DVB, TO (50%)/St (20%)/DVB (30%) and TO (50%)/St

TABLE III
Mechanical Properties in the Uniaxial Tensile Tests of the TO/St/DVB Copolymers

Sample	E (MPa)	σ_b (MPa)	ε_b (%)	ν_e (mol/m^3)
50TO/48St/2DVB	3.1 ± 0.6	0.50 ± 0.15	20.46 ± 4.30	4.81×10^2
50TO/45St/5DVB	6.5 ± 0.2	1.46 ± 0.17	32.81 ± 4.15	7.00×10^2
50TO/40St/10DVB	38.5 ± 6.7	3.34 ± 0.56	26.16 ± 5.14	8.71×10^2
50TO/30St/20DVB	476.2 ± 28.9	12.36 ± 1.22	6.92 ± 1.56	1.80×10^3
50TO/20St/30DVB	650.2 ± 38.3	16.07 ± 3.25	4.17 ± 1.63	5.36×10^3

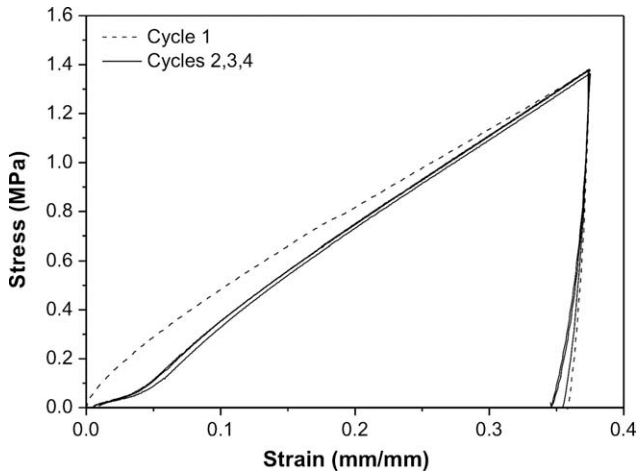

Figure 6 Stress–strain plot for the thermal cycling of the 50TO/40St/10DVB copolymer with an ε_m of 35% with a deformation temperature of 40°C.

(30%)/DVB (20%), did not present shape-memory properties. On the other end of the series, the 2 and 5 wt % DVB copolymers presented this characteristic behavior, but the allowable maximum deformation was relatively low (20%). Instead, TO (50%)/St (40%)/DVB (10%) had a usable switch temperature [T_g, Fig. 4(b)] and allows an increase in the maximum deformation to 35% and even a higher deformation temperature (40°C) in the shape-memory tests. The increase in the number of cycles did not seem to significantly affect R_f. Instead, R_r showed a slightly decreasing trend as the number of cycles increased.

The comparison between the shape-memory behavior of the TO (50%)/St (40%)/DVB (10%) copolymer with 25 and 40°C as the high temperatures in the cycle and 35% deformation showed that R_f decreased slightly and R_r increased with increasing temperature. The trend in R_r was in agreement with the gained mobility of the elastically active chains at higher temperatures; this led to a better snap-back response of the material. An increase in the deformation temperature from 25 and 40°C for the same copolymer at a fixed deformation (35%) resulted in a lower recovery force (Table IV), which was related to the softening of the material as the temperature was increased.

Additionally, a comparison between the results for maximum deformations of 20 and 30% for the TO (50%)/St (40%)/DVB (10%) sample showed that the recovery force increased with the deformation because the material was farther from the equilibrium configuration.

Like the TO/St copolymers reported in a previous publication,[22] the TO/St/DVB copolymers showed high fixation of the transient form after cooling. A comparison of the samples formulated with different concentrations of DVB and tested at the same high temperature (25°C) and maximum elongation (20%) showed that the higher the content of DVB was, the greater the fixing factor was because of the higher crosslinking density of the material. The recovery factor was negatively affected by the DVB content because the higher the crosslinking density was, the

TABLE IV
Shape-Memory Properties of the TO/St/DVB Copolymers in the Thermal Cycles

Sample	T (°C)	Elongation (%)	Nth cycle	R_f (%)	R_r (%)	Recovery force (N)
50TO/50St	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
50TO/48St/2DVB	25	20	1	89.20	92.00	3.64
			2	89.40	90.60	3.61
			3	88.18	87.98	3.48
50TO/45St/5DVB	25	20	1	87.80	94.40	4.63
			2	90.00	92.20	4.59
			3	90.00	91.00	4.55
50TO/40St/10DVB	25	20	1	96.80	76.00	10.7
			2	97.19	60.52	10.77
			3	96.99	56.31	10.72
		35	1	97.06	89.05	15.45
			2	96.75	77.60	15.01
			3	96.93	73.47	14.5
	40	35	1	95.59	98.66	10.79
			2	92.27	98.67	10.29
			3	94.66	98.40	10.56

more rigid the structure obtained was, and consequently, the sample was less able to recover its original shape because of this reduced flexibility.

A comparison of the recovery force for the different copolymers showed that it increased with the DVB content at a fixed temperature (25°C) and deformation (20%); this was due to the increased crosslinking density of the material and the related higher rigidity.

CONCLUSIONS

TO/DVB and TO/St/DVB copolymers were prepared with different compositions by cationic copolymerization. The mechanical, thermomechanical, and shape-memory properties of these copolymers could be tuned by variation of the crosslink density or chain flexibility between crosslinking points.

The T_g and elastic modulus of the copolymers increased with the content of DVB, whereas the resistance decreased because of the increasing rigidity of the materials. The TO/DVB copolymers with more than 30 wt % DVB were highly crosslinked materials with T_g values above the temperature range studied. The modulus reached a value of 913 MPa for the copolymer with 70 wt % DVB, and the mechanical properties were comparable to those of commercial polymers used for structural purposes.

Although good damping properties were observed in the copolymers with 50 wt % TO and different ratios of St to DVB, the shape-memory properties were only obtained with low DVB contents ($\leq$10 wt %). The thermal mechanical cyclic tests showed that the recovery force decreased with the increase in temperature because of the softening of the material, and it increased with the crosslinking density (higher DVB content). In general, R_f increased and R_r decreased with the DVB content in the copolymer.

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