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Material properties

Ageing of thermosets based on tung oil/styrene/divinylbenzene

Cintia Meiorin, Mirna A. Mosiewicki, Mirta I. Aranguren*

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata – National Research Council (CONICET),
Av. Juan B. Justo 4302, 7600 Mar del Plata, Argentina

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ABSTRACT

New thermoset polymers prepared by cationic co-polymerization of tung oil with styrene and/or divinylbenzene were evaluated at different times after their preparation. The changes in the properties were correlated with the composition of the copolymers. The action of atmospheric oxygen on the fatty acid unsaturations produced chemical changes in these polymers, which affected the properties of the cured materials. These changes were analyzed by FTIR, dynamic mechanical properties and mechanical testing. An increase in the modulus with time for all the analyzed samples was observed, as well as a large effect on the glass transition temperature and, consequently, in the shape memory properties.

1. Introduction

The manufacture of polymeric materials from natural sources has been growing significantly in the last decade as an answer to the search for new raw products that can replace petroleum based ones [1–4]. In this context, vegetable oils represent a very interesting alternative, since they are raw materials from renewable resources widely available all over the world and at relatively low cost [5–9]. Vegetable oils are triglycerides of fatty acids which have between 0 to 3 carbon-carbon double bonds. In particular, tung oil contains a high percentage of elaeostearic acid, presenting 3 conjugated unsaturations per fatty acid chain, which are capable of reacting with atmospheric oxygen to form a three-dimensional network [10,11]. For this last reason, tung oil has been widely used in the paint and varnish industry as a “drying oil” [12–14].

The unmodified tung oil can be mixed with a reactive diluent such as styrene or divinylbenzene to be then cured in the presence of an initiator by cationic polymerization [15–17]. After reaction, some carbon-carbon double bonds can remain unreacted, hence the chains that did not react to become elastic network chains remain as dangling chains and have a plasticizing effect on the thermoset.

Given enough time to allow diffusion of oxygen (from the surrounding air) into the sample, chemical reactions that produce changes in the properties of these materials can occur [18]. Oxidative polymerization and degradative processes are among the most important chemical reactions related to the unsaturated vegetable oil structure [19–22].

Oxidative degradation might produce chain scission and formation of volatile products. Otherwise, the dangling segments of the fatty acid chains that act as plasticizers in a recently prepared sample can become part of the network after oxidative chemical reactions, and the mechanical performance of the materials can be remarkably enhanced [22]. These processes with opposite effects on the material properties can occur at the same time, making the analysis of the results difficult.

In view of these processes, the study of the behaviour of new polymeric materials with time is of large significance for prediction of their performance in potential final applications. Thus, the aim of this paper is to investigate the change in properties of tung oil/styrene and/or divinylbenzene copolymers with time.

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* Corresponding author. Tel.: +54 223 481 6600; fax: +54 223 481 0046.

E-mail address: marangur@fi.mdp.edu.ar (M.I. Aranguren).

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2. Experimental

2.1. Materials

Tung oil (TO) composed mainly of α-elaeostearic acid (component content 84 wt.%) was supplied by Cooperativa Agrícola Limitada de Picada Libertad, Argentina. Styrene (St), divinylbenzene (DVB) and tetrahydrofurane (THF) were purchased from Cicarelli laboratory, Argentina. Boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) with 46–51% BF_3 was obtained from Sigma-Aldrich and used as the initiator of the cationic reaction.

2.1.1. Cationic copolymerization of TO/St, TO/DVB and TO/St/DVB copolymers

Styrene and/or divinylbenzene in the selected ratio were added to the tung oil. The mixture was stirred, followed by the addition of 3 wt.% of modified initiator ($BF_3 \cdot OEt_2$ plus 5 wt.% of THF). The initial immiscibility of the reactive mixture was solved by modification of the initiator with tetrahydrofurane. The mixture was vigorously stirred and, finally, cast between 13 mm × 18 mm glass plates separated by a 1 mm thick rubber cord 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/St, TO/DVB and TO(50 wt.%)/St/DVB copolymers were prepared with different weight ratios. After curing, the samples were conditioned at room temperature in a dissicator containing silica gel to maintain low humidity, in a normally illuminated area.

2.2. Characterization

2.2.1. FTIR spectroscopy

FTIR spectra of the cured samples were recorded by the attenuated total reflection method (ATR) using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. The spectra were recorded over the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}, and averaged over 32 scans.

2.2.2. Dynamic mechanical tests

A Perkin Elmer dynamic mechanical analyzer (DMA 7) was used to determine the dynamic mechanical behaviour of the samples. The tests were carried out under nitrogen atmosphere using the temperature scan mode and a tensile fixture. The chosen dynamic and static stresses were 50 and 100 Pa, respectively. The average sample dimensions were $20 \times 5 \times 0.5$ mm^3. The frequency of the forced oscillations was fixed at 1 Hz and the heating rate was of 10 °C/min. At least two tests for each sample were carried out to check repeatability of the measurement.

2.2.3. Mechanical tests

2.2.3.1. Microtensile testing.

This 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 at a crosshead 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.

2.2.3.2. Thermomechanical cyclic tensile testing shape memory behaviour.

Thermal-mechanical cyclic tests 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 or 40 °C and, subsequently, elongated to different percentages of the original length at a speed of 5 mm/min. Then, the samples were cooled (at $T = 0$ °C) below the glass transition temperature and unloaded. To measure the recovery stress, the samples were heated to 25 or 40 °C maintaining the strain constant and equal to ε_r, while the stress developed was recorded by the load cell. Finally, the samples underwent recovery by heating for ten minutes at 25 or 40 °C and zero stress.

The remaining strain 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:

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

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

3. Results and discussion

Differential scanning calorimetry (DSC) was carried out on the recently prepared and aged samples to evaluate changes related to physical changes in the samples (not shown). No endothermic peak due to densification of the material was observed in any of the thermograms, indicating that negligible physical ageing occurred in the samples [23].

In order to evaluate chemical changes, infrared spectroscopy was used. Fig. 1 shows the comparison of the FTIR

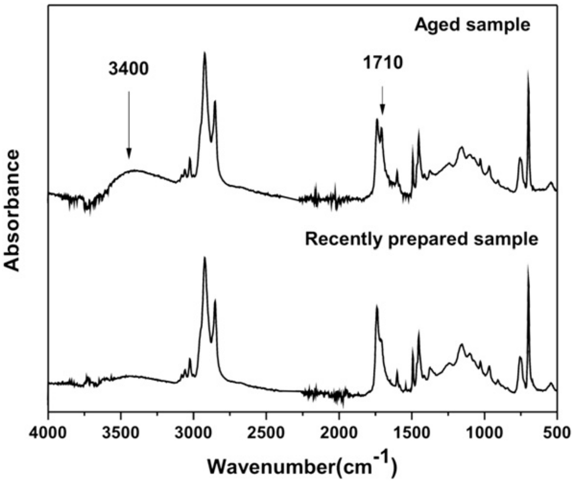

Fig. 1. Comparison of the FTIR spectra of the 50TO/50St copolymer at different times after preparation.

spectra of the 50TO/50St copolymer obtained at different times after preparation (recently prepared and 2 years ageing, respectively). 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 most important difference between the spectra is the presence of a wide band with a maximum at 3400 cm^{-1} in the aged sample, attributed to hydroxyl absorbance as a result of the formation of oxidized products during storage. Also, there is a change in the width of the carbonyl band at 1740 cm^{-1} (shoulder at 1710 cm^{-1}), probably due to the formation of aldehydes and acids in the aged sample, as was reported in the literature by other authors studying the oxidative polymerization of unsaturated oils [19,21,24].

3.1. Dynamic mechanical analysis

Fig. 2 shows the glass transition temperature, Tg (determined as the temperature of the maximum in the tanδ curve obtained in DMA tests), for the copolymers prepared with TO and St. As discussed in a previous publication, the Tg decreases as the tung oil concentration increases for the analyzed compositions, and this trend is also displayed by the aged samples (Fig. 2). This result is justified by the high mobility of the dangling chains ends, whose concentration increases with that of the tung oil in the copolymer structure. On the other hand, the values of Tg of the samples increase with time lapsed from the preparation for all the compositions tested. However, it can be noted that the increase becomes more significant as the percentage of tung oil increases in the copolymer. This fact indicates that the ageing is mainly related to changes in the tung oil chains that are part of the crosslinked network.

Fig. 3 shows the glass transition temperature, Tg, of the copolymers prepared with TO and DVB with weight ratios of 90/10, 80/20 and 70/30, respectively. The results show the same trend as that of the TO/St copolymers, the Tg decreases with the TO concentration for the recently prepared samples as well as for the aged samples. As in the case of TO/St copolymers, the Tg increases noticeably with ageing.

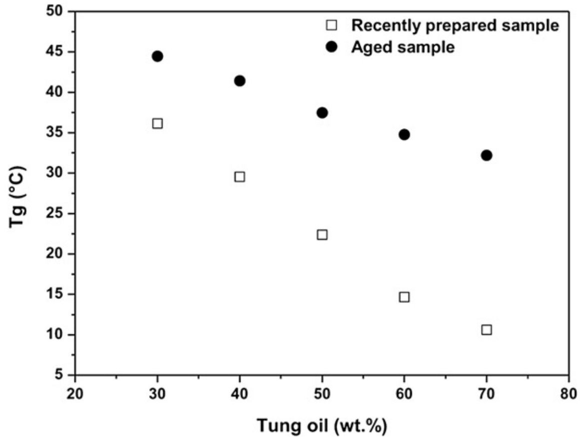

Fig. 2. Glass transition temperatures of the recently prepared and aged (2 years) samples for copolymers of TO/St.

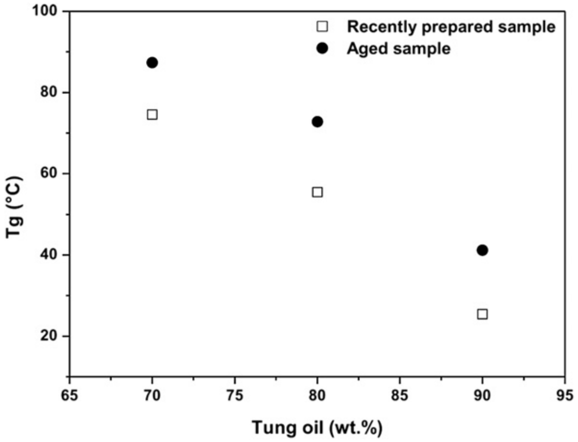

Fig. 3. Glass transition temperatures of the recently prepared and aged (2 years) samples for copolymers of TO/DVB.

However, the Tg-differences between old and new samples do not appear to depend on the composition, as discussed for the St-crosslinked samples. The DVB is a very effective crosslinking agent even at a concentration of 10 wt.%, significantly reducing the mobility of the chains. In this respect, Mallegol et al. have reported that increased crosslink density reduces the permeability of oxygen in the outer layers of the sample and, consequently, reduces the reaction rate [19,22].

3.2. Mechanical characterization

Table 1 and Fig. 4 show the tensile properties of the recently prepared and aged (2 years) samples for copolymers of TO and St.

The elastic modulus and ultimate stress at room temperature (18 °C) increase for all the aged samples in comparison with the recently prepared and tested samples.

The crosslink density increases with ageing because the dangling chains corresponding mainly to TO become less mobile, and the rigidity of the copolymer increases. The atmospheric exposure produces various changes in this

Table 1
Tensile properties of the recently prepared and aged (2 years) samples for TO/St copolymers.

Sample	E (MPa)	ε_u (%)
30TO/70St		
Recently prepared	15.20 ± 2.33	14.27 ± 7.15
Aged	74.93 ± 29.29	94.36 ± 4.27
40TO/60St		
Recently prepared	1.74 ± 0.09	65.7 ± 5.90
Aged	37.47 ± 11.45	93.5 ± 6.50
50TO/50St		
Recently prepared	3.30 ± 0.36	45.9 ± 10.50
Aged	20.56 ± 4.21	88.0 ± 6.00
60TO/40St		
Recently prepared	3.76 ± 0.20	42.77 ± 6.16
Aged	6.65 ± 1.09	74.47 ± 5.52
70TO/30St		
Recently prepared	4.89 ± 0.55	10.55 ± 3.55
Aged	2.40 ± 0.38	47.27 ± 7.35

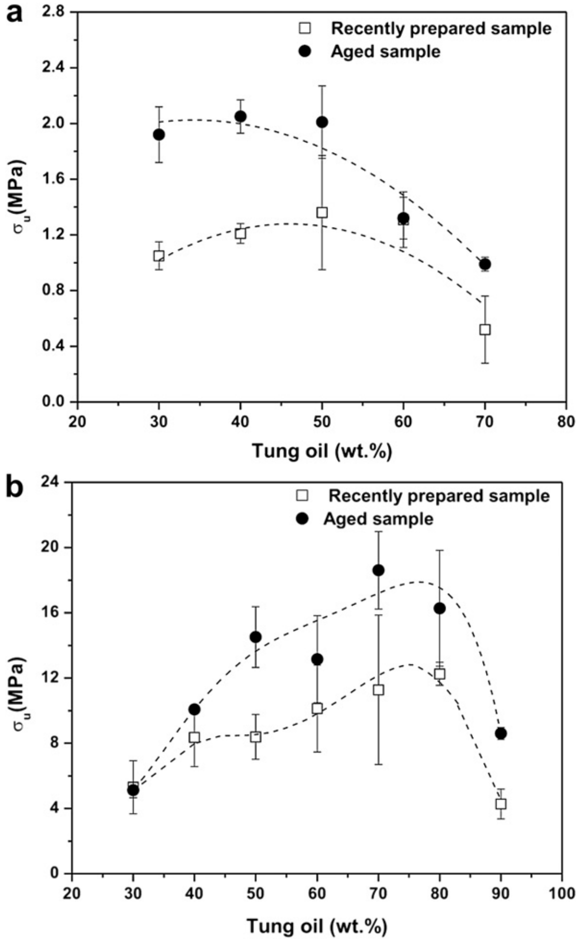

Fig. 4. a) Ultimate stress for the recently prepared and aged (2 years) TO/St samples. b) Ultimate stress for the recently prepared and aged (2 years) TO/DVB samples.

type of material, such as polymerization, oxidation and chain scission, among others. In many cases, these changes provoke opposite effects on the mechanical properties. The increase in modulus can be explained by the prevailing effect of polymerization reactions leading to the formation of a more crosslinked network.

The samples are close to the glass-rubber transition zone at the test temperature, and this may be related to the observation that the trend in some properties of the recently prepared and aged samples is different. As was explained in a previous work, the modulus in the recently prepared samples decreases with St content with the exception of the sample with 70 wt.% St. This behaviour was attributed to the fact that as more St is present in the copolymer, longer styrene-styrene sequences are incorporated between the crosslinking points, the cross-link density of the material decreases and, consequently, the modulus also decreases. On the other hand, the sample with 70 wt.% St presents the highest Tg of the series. At the test temperature, the sample is in the glass-rubber transition zone, while the others copolymers are closer to or in the rubbery state (see Fig. 2). As a result, the 70 wt. % St sample shows a much higher modulus than the rest of the series.

The moduli of the aged samples present a different trend, always increasing with the St content in the copolymer. As a result of the ageing, the Tg values are above room temperature (test temperature) for all the aged samples (as was discussed above). In this condition, the modulus is closely related to the cohesion of the sample, thus the lower concentration of TO dangling chains as the St concentration increases leads to lower free volume, higher cohesion and higher modulus of the sample.

Fig. 4a shows the ultimate stress for the recently prepared and aged (2 years) TO/St samples. The curves show a maximum as a result of the competing mechanisms already mentioned. At low TO concentrations, the crosslink density is low and the material shows low strength that increases with the oil concentration in the reactive initial mixture. However, at high TO concentrations the structure of the crosslinked network is heterogeneous, with regions of high and low crosslink density due to the steric hindrance produced by the direct TO-TO reactions. There is also a higher concentration of dangling chains that do not contribute to the cohesion of the material. As a result, the strength is low and, consequently, the strength curve shows a maximum at intermediate TO concentrations, in the range of 50–60 wt.% TO.

As a consequence of the ageing effect, the strength increases because of the increased crosslinking of the network due to oxidative polymerization, although a maximum in the curve still appears. Similar behaviour was observed for the strength of the samples crosslinked with DVB (Fig. 4b).

The deformation at break (ε_u) decreases as the TO concentration increases for the recently prepared and aged samples (Table 1). This is in agreement with the fact that the crosslink density and the number of dangling chain ends (that can generate defects in the network and initiate microcracks during mechanical testing) increases [15,25].

However, the values of this property are higher for the aged samples, which would be in agreement with higher crosslink density and a lower concentration of dangling chains because of oxidative polymerization.

Table 2 presents the mechanical properties of the TO/DVB copolymers. The modulus of the recently prepared samples increases with the DVB content, with the largest changes observed at low DVB content. The value of the modulus of the 10 wt.% DVB sample is lower than the values reported for the rest of the series. The reason for this behaviour is that the Tg of that sample is close to room temperature, while the Tg's of the rest of the samples are well above this and, consequently, the rigidity of the samples is higher. The reduction of the ultimate elongation above 20 wt.% DVB is related to the increase of Tg and reduced flexibility of the samples as more DVB is incorporated in the formulations.

Ageing produces the increase of the modulus of the materials, although there is a maxima around 50 wt.% of DVB. As the DVB concentration further increases, the modulus drops, which may be related to DVB unsaturations that remained unreacted due to steric hindrance in a highly crosslinked system. This effect could be more important in

Table 2
Tensile properties of the recently prepared and aged (2 years) samples of TO/DVB copolymers.

Sample	E (MPa)	ε_u (%)
30TO/70DVB		
Recently prepared	913.09 ± 23.57	1.05 ± 0.14
Aged	1175.43 ± 258.76	0.91 ± 0.10
40TO/60DVB		
Recently prepared	774.37 ± 33.74	1.44 ± 0.28
Aged	1235.19 ± 122.26	1.32 ± 0.17
50TO/50DVB		
Recently prepared	742.29 ± 33.51	1.38 ± 0.27
Aged	1419.17 ± 33.55	1.98 ± 0.20
60TO/40DVB		
Recently prepared	681.29 ± 39.58	2.16 ± 0.46
Aged	908.15 ± 94.69	2.64 ± 0.23
70TO/30DVB		
Recently prepared	549.20 ± 44.44	2.98 ± 0.96
Aged	899.72 ± 77.35	3.84 ± 0.42
80TO/20DVB		
Recently prepared	327.76 ± 21.98	8.32 ± 1.25
Aged	665.41 ± 122.87	4.99 ± 1.59
90TO/10DVB		
Recently prepared	74.5 ± 19.28	8.18 ± 1.43
Aged	109.230 ± 10.37	21.29 ± 3.44

the aged samples, in which TO unsaturations are already polymerized, than in the initial system in which the role of DVB as crosslinking agent is enough to increase the modulus above that of the TO rich systems.

The elongation at break is affected by ageing, especially at high TO content, and, as might be expected, the oxidative polymerization has little effect on the highly crosslinked samples at DVB concentrations higher than 30–40 wt.% (Table 2).

Table 3 shows the tensile properties of the 50TO/St/DVB copolymers. In this case, when the DVB content increases (and St content decreases) in the copolymer, the concentration of crosslinking points increases and, consequently, the modulus and strength also increase. The elongation at break decreases at increasing percentages of DVB because the material becomes stiffer and more fragile at the same time. The aged samples presented the same trend for all properties but with higher values in all cases.

Table 3
Tensile properties of the recently prepared and aged (2 years) samples of TO/St/DVB copolymers.

Sample	E (MPa)	ε_u (%)
50TO/48St/2DVB		
Recently prepared	3.10 ± 0.58	20.46 ± 4.30
Aged	85.42 ± 24.03	79.79 ± 3.73
50TO/45St/5DVB		
Recently prepared	6.48 ± 0.20	32.81 ± 4.15
Aged	215.27 ± 21.58	52.78 ± 1.89
50TO/40St/10DVB		
Recently prepared	38.50 ± 6.67	26.16 ± 5.14
Aged	550.59 ± 32.89	29.81 ± 5.99
50TO/30St/20DVB		
Recently prepared	476.22 ± 28.88	6.92 ± 1.56
Aged	935.30 ± 63.53	7.04 ± 0.36
50TO/20St/30DVB		
Recently prepared	650.20 ± 38.27	4.17 ± 1.63
Aged	899.72 ± 77.35	3.84 ± 0.42

3.3. Shape memory behaviour

As discussed above, ageing produces changes in glass transition temperature and mechanical properties of the analyzed copolymers. As a consequence, the shape memory behaviour is also modified. Tables 4 and 5 report the shape memory properties of the recently prepared and aged (2 years after preparation) samples of TO/St copolymers, respectively. A previous publication reported that the recently prepared and tested materials had switch temperatures too close to room temperature [15]. The change in glass transition temperatures of the copolymers with time (ageing) allows increasing the shape memory actuation temperature from 25 to 40 °C for the compositions 50TO/50St, 40TO/60St and 30TO/70St with different percent elongation.

For the recently prepared samples, the shape memory properties measured using a triggering temperature of 25 °C are reported. Higher temperatures resulted in premature breakage of the samples because of excessive softening. On the other hand, the aged samples could not be tested at a triggering temperature of 25 °C because the ageing process lead to an increase in the rigidity of the materials at room temperature and, consequently, the large deformations (which are preferred for testing the shape memory behaviour of elastomers) could not be achieved.

The aged sample 50TO/50St tested using 40 °C as the high temperature in the shape memory cycle can be stretched up to 40 and 50% with respect to the original length of the sample repeatedly (after the reported third cycle, the samples kept their integrity and could be deformed again). In the aged sample, although an

Table 4
Shape memory properties of the recently prepared samples of TO/St copolymers (High temperature of the cycle = 25 °C).

Sample	Elongation (%)	Nth cycle	R_f (%)	R_r (%)	F_r (N)[a]
50TO/50St	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
40TO/60St	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
30TO/70St	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

[a] Recovery force.

Table 5
Shape memory properties of the aged (2 years after preparation) samples of TO/St copolymers (High temperature of the cycle = 40 °C).

Sample	Elongation (%)	Nth cycle	R_f (%)	R_r (%)	F_r (N)[a]
50TO/50St	40	1	98.50	97.00	2.31
		2	98.50	92.70	2.28
		3	99.00	91.70	2.28
	50	1	98.72	99.12	2.90
		2	97.52	96.00	2.98
		3	98.72	99.84	3.01
	60	1	99.47	84.47	3.02
		2	96.60	100.00	2.77
		3	–	–	–
40TO/60St	40	1	100.00	100.00	1.23
		2	100.00	100.00	1.30
		3	100.00	100.00	1.32
	50	1	99.64	84.64	1.46
		2	99.76	84.48	1.49
		3	99.76	84.48	1.51
	60	1	99.67	90.20	1.73
		2	99.73	94.53	1.77
		3	99.47	90.47	1.78
30TO/70St	40	1	99.70	80.30	0.68
		2	99.70	69.60	0.67
		3	99.70	59.90	0.57
	50	1	100.00	63.28	0.71
		2	100.00	59.28	0.69
		3	100.00	60.72	0.65
	60	1	99.80	83.07	0.75
		2	99.80	77.80	0.70
		3	99.80	60.33	0.66

[a] Recovery force.

elongation of 60% is possible at 40 °C, the sample breaks down during the third cycle.

The recovery and fixity ratios increase with respect to the recently prepared samples. During ageing, the crosslink density and the rigidity of the samples increase, so the micro-Brownian motion of the mobile segments can be more effectively frozen and the fixity is high. Analogously, the higher crosslink density of the aged material favours the recovery of the sample when it is reheated at the triggering temperature.

It is quite remarkable that the 40TO/60St aged sample tested at 40 °C and elongated at 40% strain showed fixity and recovery values of 100%, indicating perfect fixing and recovery.

For higher elongation percentages, the shape memory properties of the aged samples are good with fixity ratio higher than 99.4% and recovery ratio higher than 84.4% in all cases.

The recovery forces measured at a fixed maximum strain and different temperatures are also reported in Tables 4 and 5. High temperature favours amorphous chains snapping back to their original equilibrium conformation. Reduction of the chain mobility achieved by keeping the sample under a fixed strain generates the measured force reported as recovery 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 recently and aged samples with different percentages of TO and the same maximum elongation shows that higher TO content increases the recovery force. This behaviour is related to the fact that TO generates multifunctional crosslink points during curing. Tensile and dynamic mechanical results showed that increasing tung oil content increases the elastic modulus in the rubbery state due to the increase in crosslink density [15]. The higher the crosslink density, the higher is the stored energy that generates the exerted recovery force.

However, the different temperature of the tests does not allow further comparison, for example the recovery force is lower for the aged samples because it was measured at 40 °C instead of 25 °C. Since the aged samples were tested to higher temperatures than the recently prepared samples, the recovery force was lower for the higher temperature tests, even when the samples were aged.

Tables 6 and 7 show the shape memory properties of the 50TO/St/DVB copolymers. In a previous publication, the shape memory capabilities of these recently prepared copolymers were reported [16]. The aged materials with 2 and 5 wt.% of DVB were evaluated not only at 25 °C as high temperature in the shape memory cycles (as the recently prepared samples) but also at 40 °C and increasing the elongation from 20 to 35%. The fixity and recovery ratios present much higher values that the recently prepared sample.

The aged copolymers with 10 wt.% of DVB could be tested in load-unload cycles with triggering temperatures of 40 and 50 °C and at 35% of elongation in both cases. For the test at 40 °C the maximum elongation of work was 50%.

The comparison between the shape memory behaviour of the 50TO/40St/10DVB copolymer using 40 and 50 °C as the high temperatures in the cycle and 35% of deformation shows that the fixity and recovery ratios as well as the recovery force decrease with increasing temperature.

The trend in the recovery ratio is in agreement with the gained mobility of the elastically active chains at higher temperature, which leads to better "snap-back" response of the material. Increasing the deformation temperature from 25 and 40 °C for the same copolymer at a fixed deformation (35%) results in a lower recovery force (Table 4), which is related to the softening of the material as the temperature is increased.

Table 6
Shape memory properties of the recently prepared samples of TO/St/DVB copolymers.

Sample	T (°C)[b]	Elongation (%)	Nth cycle	R_f (%)	R_r (%)	F_r (N)[a]
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	10.70
			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	14.50
	40	35	1	95.59	98.66	10.79
			2	92.27	98.67	10.29
			3	94.66	98.40	10.56

[a] Recovery force.
[b] High temperature used in the shape memory cycle.

Table 7
Shape memory properties of the aged (2 years after preparation) samples of TO/St/DVB copolymers.

Sample	T (°C)[b]	Elongation (%)	Nth cycle	R_f (%)	R_r (%)	F_r (N)[a]
50TO/48St/2DVB	25	35	1	99.87	75.60	2.25
			2	99.07	65.87	2.87
			3	99.20	60.48	3.03
	40		1	99.70	73.83	1.88
			2	99.83	55.95	1.63
			3	98.87	48.33	1.33
50TO/45St/5DVB	25	35	1	98.30	100.00	6.71
			2	98.43	99.33	6.53
			3	98.30	99.33	6.36
	40		1	97.73	92.53	7.34
			2	96.80	88.53	7.26
			3	98.13	86.80	7.35
50TO/40St/10DVB	40	35	1	97.50	100.00	7.69
			2	98.27	100.00	7.61
			3	98.03	100.00	7.02
		50	1	98.20	86.72	9.88
			2	97.70	82.88	10.62
			3	97.60	80.80	10.02
	50	35	1	96.57	85.20	6.37
			2	96.00	83.60	5.99
			3	96.83	80.93	5.78

[a] Recovery force.
[b] High temperature used in the shape memory cycle.

Additionally, for the 50TO/40St/10DVB sample, the comparison between the results for maximum deformations of 20 and 30% (not aged sample) or 35 and 50% (aged sample) shows that in both cases the recovery force increases with the deformation, since the material is farther from the equilibrium configuration.

Comparison of the recovery force for the different copolymers (recently prepared or aged samples) shows that it increases with the DVB content at fixed temperature (25 or 40 °C) and deformation (20 or 35%), which is due to the increased crosslink density of the material and, consequently, its higher rigidity.

4. Conclusions

The ageing of tung oil based copolymers was evaluated. Changes in mechanical and dynamic mechanical properties revealed the effect of a crosslinking reaction taking place with time. This reaction is identified as corresponding to oxidative mechanisms that involve the unreacted unsaturations of the tung oil chains.

The observed increase of the glass transition temperatures of these materials results in the possibility of increasing the switch temperature of the shape memory behaviour keeping high fixity and recovery ratios at similar elongation values.

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