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Shape memory epoxies based on networks with chemical and physical crosslinks

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ABSTRACT

Epoxies are an important family of shape memory polymers (SMP) due to their excellent stability and thermo-mechanical endurance and the high values of shape fixity and shape recovery. Actuators based on these materials can be designed for large tensile elongations (e.g., 75% or higher) or large recovered stresses (e.g., 3 MPa or higher). However, meeting these requirements simultaneously is a difficult task because changes in the crosslink density affect both variables in opposite ways. We show that an SMP based on an epoxy network with both chemical and physical crosslinks could be strained up to 75% in four repeated shape memory cycles with tensile stresses close to 3 MPa. Shape fixity and shape recovery values were close to 98% and 96%, respectively, for everyone of the cycles, without any significant change between the first and subsequent cycles.

1. Introduction

Shape memory polymers (SMP) are stimuli-sensitive materials that can be deformed and temporarily fixed in a second shape, and can recover the original shape when exposed to a suitable stimulus. The change in the shape can be triggered by heat, light, humidity, solvents, electric or magnetic fields, ionic strength or pH [1–11]. These smart materials are the basis of a large number of actual and potential applications in packaging, textiles, electronics, medicine, transportation, construction and aerospace.

Thermosets are an important family of SMP. When they are heated above their glass transition temperature (T_g) they can be deformed to a temporary shape by applying a relatively small stress. By fixing the deformation and cooling below T_g, a glass is obtained that stores elastic energy in chain conformations removed from their equilibrium values. When the material is released from any constraint and is heated again above T_g, a rapid recovery of the original shape is obtained as chains recuperate their equilibrium conformations. But if the heating step is performed keeping the initial deformation, the thermoset develops a recovery stress that depends on the rubbery modulus and is close to the stress necessary to produce the initial deformation [12,13]. Actuators based on thermosets can make use of the shape recovery or the stress recovery. It is possible to design thermoset formulations that can undergo large deformations (e.g., 75% or higher) in the rubbery region, or that develop large recovery stresses (e.g., 3 MPa or higher) when heated beyond T_g. However, it is not easy to rich both targets simultaneously [14,15]. The reason is that large deformations require low values of the elastic modulus and, therefore, low values of stresses. Reinforcements can be used to increase the recovery stress at the expense of reducing the recoverable strain [16,17]. Selecting the chemical structure of thermoset precursors can provide some increase in the recovery stress as discussed for a variety of meth(acrylate)-based thermosets [14]. Our study is focused on a particular epoxy formulation that combine relatively large values of tensile deformation and recovery stress.

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Shape memory epoxies are commercially available, e.g., Veriflex™, provided by Cornerstone Research Group (CRG) [12,13,18], and Tembo® composites, provided by Composite Technology Development (CTD) [16]. Reported properties for two CRG products are comprised in the range of large deformations (shape memory cycles carried to 25%, 50% and 75% strains) and low recovery stresses (0.15–0.6 MPa) [12,13]. Shape memory properties of a variety of stoichiometric epoxy formulations based on diglycidylether of bisphenol A (DGEBA) (eventually mixed with a fraction of diglycidylether of neopentylglycol), cured with mixtures of mono- and diamines [19–21], or with a defect of a diamine [22], have been reported. The variety of combinations enabled to shift the T_g of cured materials in a broad temperature range. Shape memory cycles were performed at a maximum tensile strain less than 10% [19,20], or about 20% [21]. However, in this last case a relatively large strain hysteresis was observed between the first thermomechanical shape memory cycle and the subsequent cycles, reducing the strain to less than 15% for the second and following cycles.

The aim of this study was to design a shape memory epoxy that could combine large strains (e.g., 75%) in repeated shape memory cycles, with relatively large recovery stresses (e.g., 3 MPa, a value significantly higher than those reported for commercial formulations at 75% strain [12,13]). The strategy was based on two different concepts: (a) selection of a chemical formulation with an elastic modulus in the rubbery state enabling to attain the desired value of the recovery stress but, at the same time, permitting relatively large tensile strains without failure, (b) selection of convenient conditions for straining the material in the rubbery region. Both concepts are analyzed separately.

Thermoplastic epoxies synthesized by reacting a diepoxide with a monoamine behave as conventional thermoplastics and can undergo large deformations in the melt [23]. To use these materials as the basis of an SMP it is necessary to introduce crosslinks. An interesting alternative is to use a thermoplastic epoxy that forms strong physical crosslinks between chains. An example of such an epoxy is the one synthesized by the reaction of diglycidylether of bisphenol A (DGEBA) with an *n*-alkylamine. These linear polymers form strong physical crosslinks by tail-to-tail associations among alkyl chains and exhibit the behavior of a physical network [24–26]. As an example, Fig. 1 shows the evolution of the storage and loss modulus of the physical network formed by reacting stoichiometric amounts of DGEBA and *n*-dodecylamine (DA). During the heating scan the physical network undergoes devitrification (defined at the onset of the decrease in the storage modulus), followed by a continuous decrease of the rubbery modulus as a consequence of a corresponding decrease in the fraction of physically associated dodecyl chains. At about 150 °C, a crossover between storage and loss modulus is observed meaning that the physical gel was turned into a liquid. Cooling produced the reconstruction of physical associations and turned again the liquid into a physical gel. This material exhibits convenient values of elastic modulus and can, presumably, be strained to higher values than an epoxy network with the same crosslink density but with chemical crosslinks instead of physical crosslinks. The DGEBA–DA formulation was therefore selected as a basis of the shape memory epoxy. In order to increase mechanical properties and allow a fast shape recovery, a small amount of a diamine (*m*-xylylenediamine, MXDA) was used while keeping an overall stoichiometric ratio between epoxy and amine functionalities. The selected amount of MXDA determined the T_g of the resulting epoxy network. It could be varied from about 14 °C, for 100% DA, to about 120 °C, for 100% MXDA. A particular MXDA/DA ratio was selected to give a T_g close to 40 °C. We will show that in spite of the MXDA addition introducing chemical crosslinks in the epoxy network, physical crosslinks were

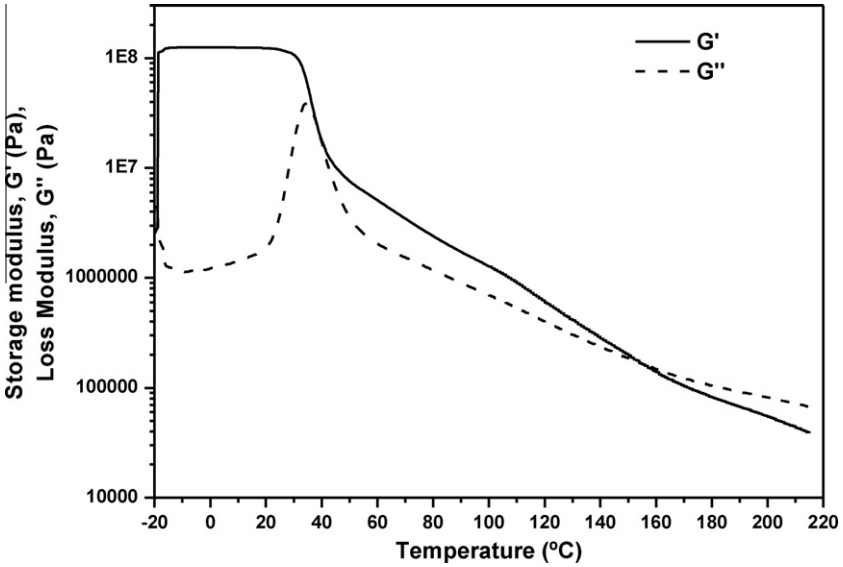

Fig. 1. Evolution of the storage and loss modulus of the physical network formed by reacting stoichiometric amounts of DGEBA and *n*-dodecylamine at 100 °C for 14 h. Reprinted with permission from [24].

also present. Therefore, the resulting epoxy network had both physical and chemical crosslinks.

The second concept enabling to produce large tensile strains in the rubbery state without failure of the material, is the adequate selection of operation parameters. In uniaxial tension tests the crosshead rate has a direct influence on the tensile properties of the material since the strain to failure and ultimate strength are generally observed to increase with increasing strain rate [13]. According to ASTM D638, a material with low rigidity such as a shape memory epoxy in the rubbery region, should be tested at 50 mm/min as opposed to the material in the glassy region which is typically tested at 5 mm/min [13]. However, we decided to use a crosshead rate of 5 mm/min for the low and high temperatures of the shape memory cycle to assure that large strains are not the result of arbitrarily fast strain rates. Another operation parameter that determines the strain to failure in the rubbery region is the selection of the maximum temperature of the shape memory cycle. It has been shown that the failure strain can be increased by producing the deformation at a temperature above but very close to the T_g onset [14,15,21]. A particular temperature in this suggested range was selected to quantify shape memory parameters although no specific analysis of the influence of temperature in the range close to T_g, was performed.

2. Experimental

The shape memory epoxy network was based on the reaction of diglycidylether of bisphenol A (DGEBA, DER 332, Dow), with a weight per epoxy group equal to 174.25 g/mol ($n = 0.03$ in the chemical structure shown in Fig. 2), with a stoichiometric amount of a blend of *n*-dodecylamine (DA, Fluka, 98 wt.%) and *m*-xylylenediamine (MXDA, Aldrich), Fig. 2. The selected molar ratio of the three monomers was DGEBA:DA:MXDA = 6:4:1. DA was heated at 130 °C for 30 min to remove the CO_2 content. Then it was mixed with DGEBA under vigorous stirring at 100 °C and MXDA was added. The mixture was placed between two Teflon-covered glass plates using a 1.4 mm-thickness rubber spacer. The polymerization was carried out at 60 °C for 1 h, followed by 2 h at 100 °C, to carry the reaction to full conversion [24,25]. Samples were then annealed at 100 °C for 72 h to increase the fraction of associated dodecyl groups [24,25].

The increase in the fraction of physical crosslinks produced by the annealing process was assessed by the increase in both the glass transition temperature (T_g) and the rubbery modulus. T_g was determined by differential scanning calorimetry (DSC, Pyris 1 Perkin-Elmer, rate = 10 °C/min), defined at the onset of the change in the specific heat. The variation of the storage (G') and loss modulus (G'') with temperature was followed using an Anton Paar rheometer (model Physica MCR-301), provided with a CTD 600 thermo chamber. A rectangular-solid configuration with probes of $40 \times 5 \times 1.4\ mm^3$ was used in oscillatory mode with 0.1% amplitude at a frequency of 1 Hz. Temperature scans were performed at 5 °C/min from −40 to 160 °C.

Uniaxial tensile tests were performed in an Instron 4467 universal testing machine equipped with a thermostatic chamber to determine mechanical properties of the epoxy glass at 20 °C and of the epoxy rubber at different temperatures above T_g. Dumb-bell shaped samples ($25 \times 4 \times 1.4\ mm^3$) were loaded in tension at a crosshead speed of 5 mm/min, at 20 °C (glassy state) and at 55, 75 and 100 °C (rubbery state). Raw load–displacement data were converted to engineering stress–strain curves (σ–ε), defining the strain by the crosshead displacement.

To quantify shape memory properties, uniaxial tensile-thermal cycles were carried out in the universal testing machine employing dumb-bell shaped specimens ($25 \times 4 \times 1.4\ mm^3$). In order to determine the actual deformation of the gage length (part of the specimen with constant width), two dots of 1 mm diameter, separated by 12.5 mm,

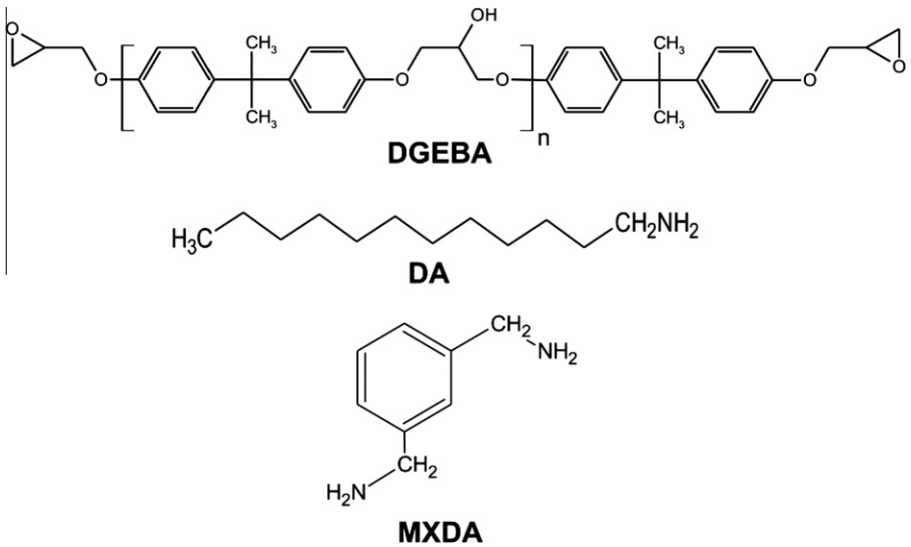

Fig. 2. Chemical structures of the epoxy monomer, the monoamine and the diamine.

were printed on the gage length along the stretching direction, using an acrylic ink. The dots deformed elastically following the sample deformation. Strain values were determined from the actual separation between the mass center of both dots determined using high resolution pictures taken with macro lens and analyzed using an image processor. Strains defined in this way can be compared with values reported in the literature for the characterization of shape memory epoxies [12].

The shape memory cycle consisted in the four steps schematized in Fig. 3. Specimens were held by the top grip, heated at 24 °C/min to 55 °C, and kept at this temperature for 40 min to attain thermal equilibrium. The heating rate was the maximum available and was used because preliminary tests showed that it had no influence on stress–strain curves obtained at 55 °C. Then, the specimen was fixed by both grips and loaded under uniaxial tension at 5 mm/min up to ε_{max} = 75% (step 1). This strain value, determined by the displacement between the ink marks, corresponded to a strain ε = 60%, determined by the crosshead displacement. Then, specimens were cooled down to 20 °C at 1 °C/min, keeping the strain constant at ε_{max} = 75%

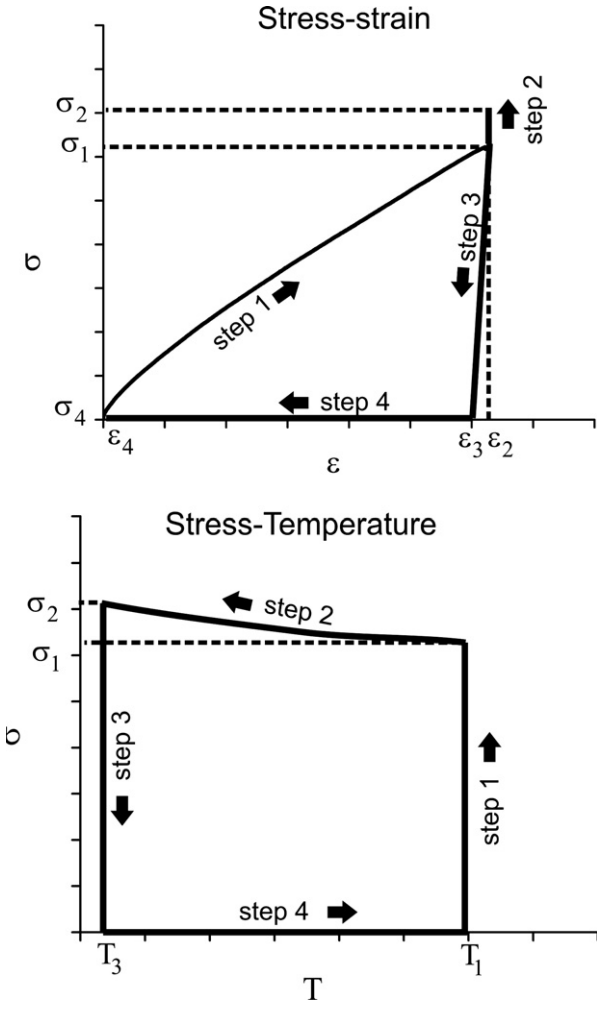

Fig. 3. Scheme of the shape memory cycle.

(step 2). In this step the sample was transformed from a rubber to a glass (T_g close to 41 °C). A very slow cooling rate was used to enable the sample equilibrate its temperature with the surroundings, avoiding generation of thermal stresses. The sample was held 40 min at 20 °C and unloaded by removing it from the bottom grip (step 3). The fixed strain, $\varepsilon_{unloaded}$, was determined. The cycle was closed by heating the specimen to 55 °C at 24 °C/min and holding at this temperature for 40 min (step 4). At $T > T_g$, sample contraction was observed as the elastic chains recovered their equilibrium conformations. After 40 min at 55 °C, the residual strain, $\varepsilon_{permanent}$, was determined and a new cycle was initiated. The cycle was repeated four times which is a standard practice for the determination of shape memory properties. The reason arises from the fact that any significant variation in results is usually observed between the first and second cycles with following cycles repeating the values of the second cycle.

From the strain values, ε_{max}, $\varepsilon_{unloaded}$ and $\varepsilon_{permanent}$, the shape fixity (R_f) and shape recovery (R_r) parameters were calculated for each cycle (N):

$$R_f = [\varepsilon_{unloaded}(N)/\varepsilon_{max}(N)] \times 100\%$$

$$R_r = [(\varepsilon_{unloaded}(N) - \varepsilon_{permanent}(N))/(\varepsilon_{unloaded}(N) - \varepsilon_{permanent}(N-1))] \times 100\%$$

3. Results and discussion

The epoxy network contains chemical crosslinks represented by MXDA units (a crosslink group with functionality four) and physical crosslinks represented by DA units involved in tail-to-tail associations. N atoms of associated DA units can be regarded as crosslink sites with functionality three. For the selected stoichiometry, the maximum ratio of physical crosslinks to chemical crosslinks was 4:1. When the cure reaction was followed in situ using the rheometer, a continuous increase of the rubbery modulus was observed during the annealing period at 100 °C, after the complete conversion of the epoxy monomer. The increase in the rubbery modulus is ascribed to the increase of the fraction of physical crosslinks produced during the annealing period, a similar result as the one observed for the DGEBA–DA polymerization [24,25]. The final result is shown in Fig. 4 representing the dynamic-mechanical thermal response of the epoxy networks obtained before and after the annealing period. Both T_g and the rubbery modulus increased with the annealing due to the increase in the fraction of tail-to-tail associations among dodecyl groups generating physical crosslinks. T_g measured by DSC also increased from 37.6 to 41.2 °C with the annealing.

Fig. 5 shows the tensile response of the material at 20 °C, in the glassy state. A maximum in the stress was observed (yield stress, σ_y = 42 MPa), and the strain at break was relatively high (ε_b >25%). The elastic modulus, determined using an extensometer, was E = 1.92 GPa. The ductility of the glass at room temperature should provide a convenient life-time for actuators based on this material.

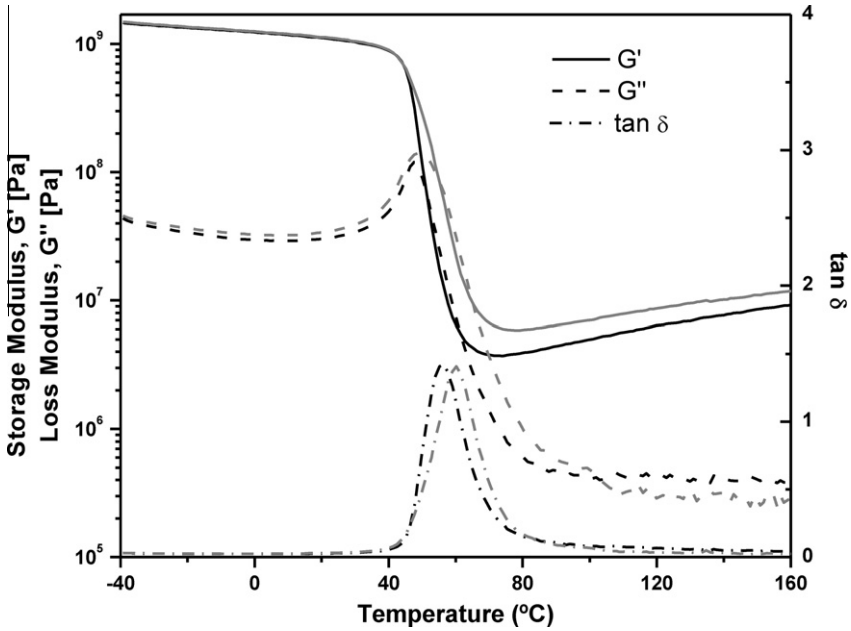

Fig. 4. Storage modulus, loss modulus and tan δ for the cured epoxy networks before and after the annealing period; curves for the annealed material are those shifted to the right.

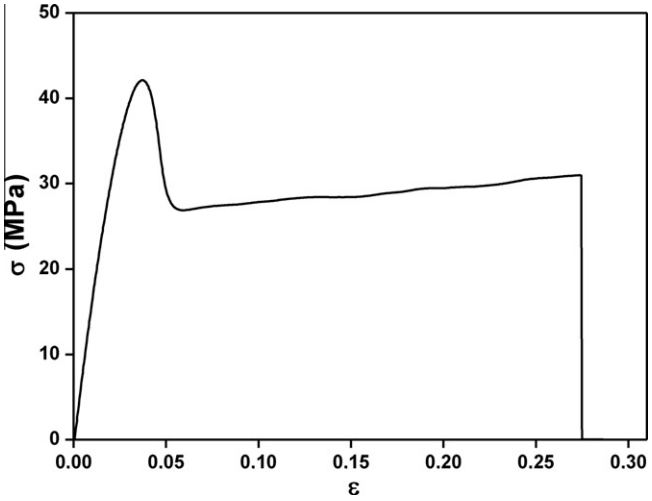

Fig. 5. Typical uniaxial stress–strain curve at 20 °C (glassy state).

Fig. 6 shows the uniaxial tensile behavior of the epoxy network in the rubbery state, at three different temperatures. The strain at break shows a significant increase when decreasing temperature approaching the glass transition, an effect previously reported in the literature [14,15,21]. The steep increase of the failure strain is observed at temperatures located in the transition region between glassy and rubbery states (Fig. 4). At 55 °C the material is located at about half of its transition while at 75 °C it is close to the end value. We can speculate that the presence of local glassy regions increases the toughness of the material.

Based on the results shown in Fig. 6, we selected a temperature of 55 °C as the high temperature of the shape memory cycle. At this temperature the elastic modulus was 11 MPa and the sample could be strained to the desired value of 75% (actual strain determined from the displacement of ink marks), corresponding to $\varepsilon = 60\%$, determined by the crosshead displacement. The required stress is close to 3 MPa, as results from the curve at 55 °C shown in Fig. 6, a value that represents the stress recovery of the SMP for the selected strain [12,13]. The stress recovery of our formulation is 5–20 times larger than

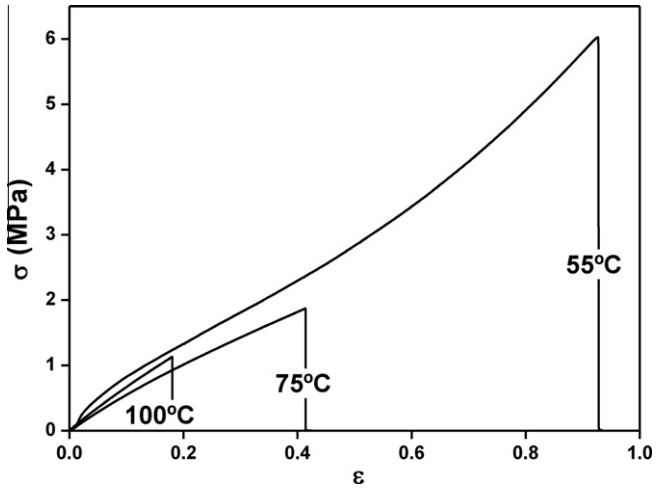

Fig. 6. Typical uniaxial stress–strain curves at different temperatures in the rubbery state.

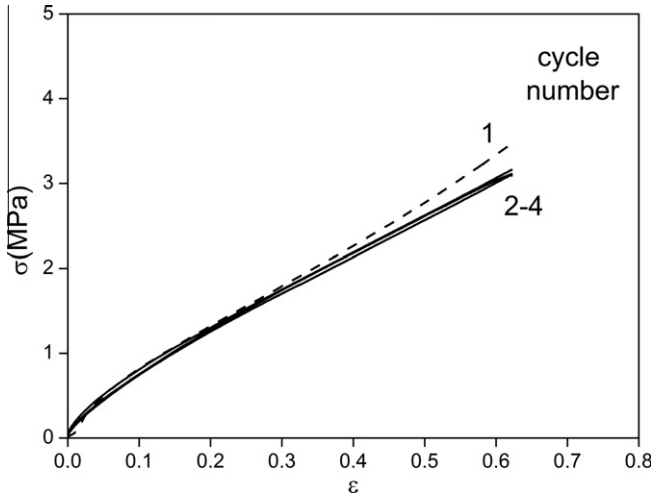

Fig. 7. Uniaxial stress–strain curves at 55 °C during the four cycles used to determine shape memory properties.

values reported for two commercial formulations using the same prescribed strain [12,13]. We could have increased the stress recovery to values in the range of 4–5 MPa by increasing the prescribed maximum strain at the risk of getting too close to the failure strain (a value showing a normal variability in repeated tests).

Shape memory properties were determined employing four thermomechanical cycles (Fig. 3), fixing 20 °C and 55 °C as the low and high temperatures of the cycle and 75% as the prescribed tensile strain. Fig. 7 shows the stress–strain curves at 55 °C for the four cycles. There is a small difference between the first and subsequent curves and almost no difference from the second to the fourth cycle. The resulting values of shape fixity and shape recovery are shown in Table 1. They were close to 98% and 96%, respectively, for the four cycles. A significant result is the absence of a strain hysteresis in the first cycle with respect to subsequent cycles, as reported for other shape memory epoxies [21]. Such behavior has been explained by the permanent plastic deformation produced in the first cycle arising from the molecular rearrangement of the pendant monoamine chains. The absence of this behavior in our system might be assigned to the fact that a significant fraction of pendant chains are not free but are associated by tail-to-tail bonds.

Table 1
Values of shape fixity and shape recovery for different cycles.

Cycle	1	2	3	4
R_f (%)	98.0	98.5	98.1	98.2
R_r (%)	96.8	95.7	95.5	95.5

The shape recovery was very fast. As an example, Fig. 8 shows a sequence of photographs of a pre-deformed bar immersed in a water bath held at 60 °C. The recovery of the initial shape took place in only 3 s.

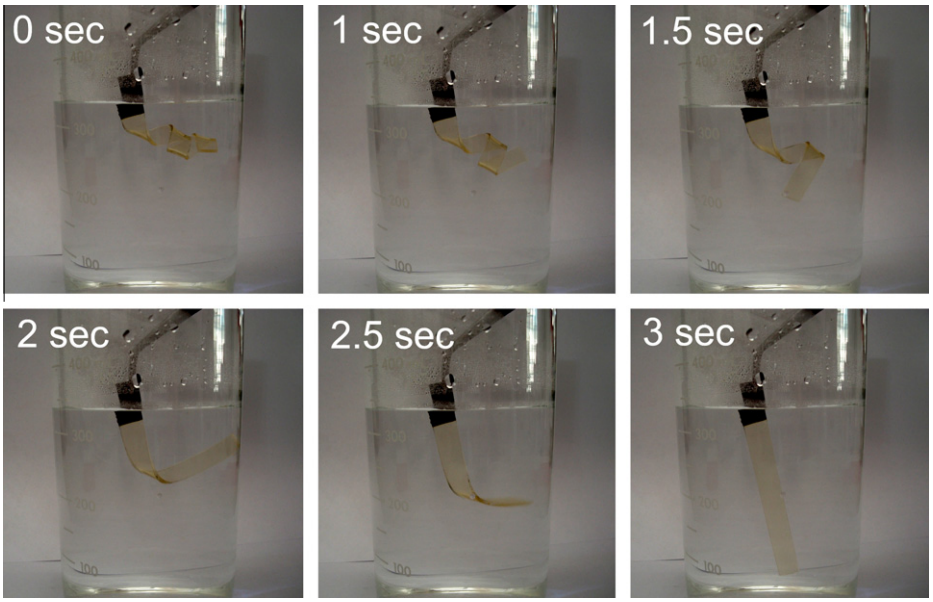

Fig. 8. Sequence of photographs of a pre-deformed bar immersed in a water bath held at 60 °C.

4. Conclusions

An epoxy network with chemical and physical crosslinks showed an excellent behavior as an SMP enabling a combination of relatively high tensile strains (75%) and recovery stresses (3 MPa). In the glassy state at room temperature, the SMP exhibited a ductile behavior with a yield stress of 42 MPa and a failure strain higher than 25%. Very good values of shape fixity (98%) and shape recovery (96%) were obtained and no shape hysteresis was observed between the first and subsequent cycles. This was assigned to the presence of physical associations among pendant alkyl chains.

Acknowledgements

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