Reversible Stress-Driven and Stress-Free Two-Way Shape Memory Effect in a Sol-Gel Crosslinked
Polycaprolactone

(Article begins on next page)

29 June 2024

Reversible Stress-Driven and Stress-Free Two-Way Shape Memory Effect in a Sol-Gel Crosslinked Polycaprolactone

Nicoletta Inverardi, Stefano Pandini, Gabriele Gemmo, Maurizio Toselli, Massimo Messori, Giulia Scalet, and Ferdinando Auricchio*

The two-way shape memory effect is the ability of a material to change its shape between two configurations upon application and removal of a stimulus, and, among shape memory polymers, it is featured only by few systems, such as semicrystalline networks. When studied under tensile conditions, it consists of elongation–contraction cycles along cooling and heating across the crystallization and melting region, typically under the application of a constant load. However, recent studies on crosslinked semicrystalline co-polymers demonstrate that also a completely stress-free, or self-sustained, two-way effect may be achieved through specific thermomechanical cycles. This effect is currently regarded with interest for the development of intrinsically reversible sensors and actuators, and it may also be displayed by simpler materials, as homopolymer-based semicrystalline networks. Only seldom articles investigate this possibility, therefore in this work the two-way shape memory behavior is studied on a poly(ε-caprolactone) system, crosslinked by means of a sol-gel approach. The effect is studied both under stress-driven and stress-free condition, by applying properly set-up thermo-mechanical histories. The results allow to describe the effect as a function of temperature, to reveal the dependence on specific testing parameters and to compare the extent of the reversible strain variation under these two conditions.

N. Inverardi, S. Pandini
Department of Mechanical and Industrial Engineering
University of Brescia
via Branze 38, Brescia 25133, Italy
E-mail: stefano.pandini@unibs.it

G. Gemmo, M. Toselli
Department of Industrial Chemistry "Toso Montanari"
University of Bologna
Viale Risorgimento 4, Bologna 40136, Italy

M. Messori
Department of Applied Science and Technology
Politecnico di Torino
Corso Duca degli Abruzzi 24, Torino 10129, Italy

G. Scalet, F. Auricchio
Department of Civil Engineering and Architecture
University of Pavia
via Ferrata 3, Pavia 27100, Italy

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/masy.202100254

1. Introduction

Thermally-activated shape memory polymers (SMPs) are a class of stimuli-responsive materials able to undergo significant shape variation as response of specific changes in temperature.[1,2] This peculiar response may be defined, for most of the polymers, as the possibility to be deformed in a temporary shape, and to maintain this configuration until the exposure to certain temperatures activate the recovery of the pristine, or "permanent," shape. Such a behavior is also known as "one-way" shape memory effect, a term that clearly underlines that the only shape transformation activated by temperature regards the temporary-to-permanent one. By contrast, the term "two-way" shape memory effect describes the ability of a material to change its shape between two configurations upon application and removal of a stimulus.[3,4] This reversible effect is regarded as a promising feature in polymeric materials in order to obtain materials intrinsically capable of reversible actuation.[4,5] However, not all shape memory polymers are capable of this behavior, but only few families such as liquid crystalline elastomers and crosslinked networks[3] and under a specific condition, that is the application of constant load through the shape memory cycle.

This latter condition may be regarded as a limitation for many applications, and therefore great interest was reserved in recent studies which showed that a reversible two-way response may be obtained in a fully stress-free, or self-sustained, manner, based on internal stresses developed on polymer chains by a preceding thermo-mechanical deformation cycle. Further, while most of the pioneering work concentrated on materials having a specific architecture (crosslinked co-polymers with two crystalline domains[6,7]) or requiring crosslinking after deformation,[8,9] only few works focused on materials with relatively easy structure, as in the case of homopolymer-based semicrystalline networks.[10]

In the present work the two-way shape memory behavior of a crosslinked semicrystalline material was investigated, taking as reference a sol-gel crosslinked poly(ε-caprolactone), whose one-way and stress-driven two-way shape memory behavior was well assessed in previous investigations.[11] The polymer was subjected to specific thermo-mechanical tests in order to verify the
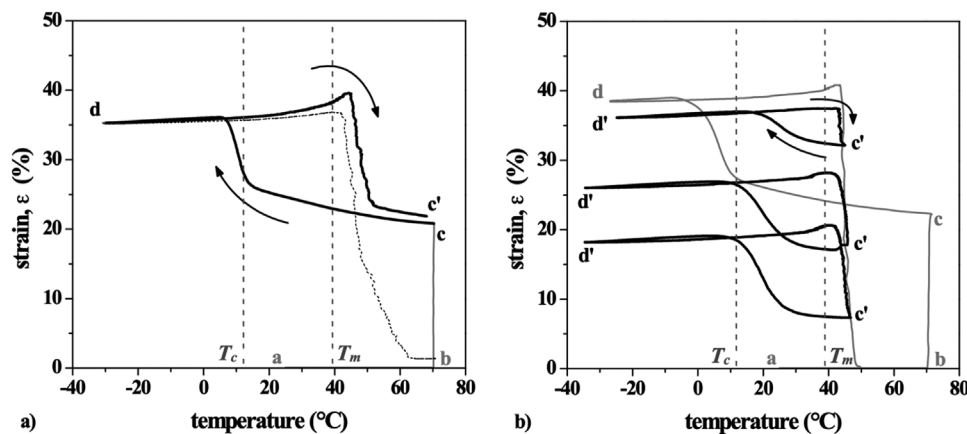
Figure 1. a) Two-way shape memory cycle under stress-driven condition (shaded line: stress-free recovery); b) two-way shape memory cycles under stress-free conditions for various values of T_{act} (top cycle: T_{act} = 44.8 °C; middle cycle: T_{act} = 45 °C; bottom cycle: T_{act} = 46.5 °C).

possibility to achieve a stress-free two-way shape memory response and to compare it with the stress-driven results.

2. Results

The thermal and thermo-mechanical characterization of the material provides useful information concerning its microstructure as a semicrystalline network. DSC experiments allow to quantify melting and crystallization temperature (T_m = 39 °C and T_c = 12 °C, respectively) and a crystallinity content estimated close to 27% (calculated by assuming the melting enthalpy of a 100% crystalline PCL equal to 134.9 J g^{-1} [12]). DMA tests reveal that material stiffness, measured in terms of storage modulus, changes when crossing the melting temperature from about 190 MPa at 20 °C to about 0.6 MPa in the rubbery plateau. Noteworthy, once above T_m the storage modulus does not show significant variation with temperature, or just slightly increases with it, confirming the achievement of a crosslinked structure.

As a consequence of this particular structure the material presents both an excellent one-way and two-way shape memory response, as suggested by the curves of **Figure 1**a. In particular, here it is displayed a typical two-way shape memory cycle, articulated in various sub-steps, as follows: the specimen is heated above T_m (a–b; deformation temperature equal to 70 °C) and deformed up to a strain, ε_c, equal to 20% (b–c), corresponding to a stress level of about 300 kPa; by maintaining the applied stress constant, the specimen is first cooled well below T_c (c–d), and later heated up to the deformation temperature (d–c').

As expected, during the cooling–heating cycle and under the presence of an applied stress, a significant, and practically fully reversible, elongation–contraction effect occurs. In particular, a significant elongation can be observed upon cooling, along a continuous process whose major contribution occurs simultaneously with the crystallization process; the contraction, which onsets at temperature close to T_m, almost completely brings the specimen back to the deformation displayed before cooling. The process is thus strongly related to the evolution of the crystalline structure, and its extent under this condition, was evaluated as:

$$\Delta\varepsilon_{stress-driven}\ (\%) = \varepsilon_d\ (\%) - \varepsilon_c\ (\%) \tag{1}$$

where ε_d and ε_c represent the strain in point d (after the induced elongation) and c (after the applied deformation), respectively. By carrying out the test under different stress values, and thus at different ε_c, it was shown that the overall elongation extent, $\Delta\varepsilon_{stress-driven}$, is strongly influenced by the loading conditions, as shown by the data reported in **Table 1**. The induced elongations, which not surprisingly increases with the applied stress, assume values comparable to the amount of deformation displayed at beginning of the cycle ($\Delta\varepsilon_{stress-driven} \sim 0.75\varepsilon_c$).

In addition, in Figure 1a is reported also the dashed line representing the stress-free recovery of the specimen after the cooling induced elongation: in fact, if the stress is removed the specimen is able to undergo complete recovery, in a process that onsets close to the melting temperatures and that reveals a good one-way shape memory response for this system. In fact, by carrying out the typical one-way shape memory cycles (not displayed here), it is shown that the system is capable of fully fixing the applied deformation and to completely recover it by heating above melting temperature, in a process narrowly distributed around T_m.

The typical appearance of the two-way shape memory cycles under stress-free condition is displayed in Figure 1b. The cyclic history involves the same initial step as in the previous test: heating up to 70 °C (a–b), deformation up to 20% (b–c), cooling under load below T_c (c–d). Afterwards, the load is removed and the specimen is heated up to a higher temperature, called actuation temperature, T_{act} (d–c'). While approaching T_{act} the strain is partially recovered to a value $\varepsilon_{c'}$. Finally, the specimen is subjected to a cooling–heating cycle between T_{act} and a temperature well below T_c (c'–d'–c''). The various cycles of Figure 1b refer to different heating up to various T_{act}. A new type of elongation–contraction cycle is thus observed, spreading again across the melting–crystallization region, but this time fully free from external load, and presumably exerted by internal forces between the stretched chains. The shape of the self-sustained two-way cycle is seen to greatly vary depending on the values of T_{act}, and thus of the different values of residual strain preceding the cycle, $\varepsilon_{c'}$. The extent of the elongation–contraction cycle under this condition, was evaluated as:

$$\Delta\varepsilon_{stress-free}\ (\%) = \varepsilon_{d'}\ (\%) -- \varepsilon_{c'}\ (\%) \tag{2}$$

Table 1. Correlation between the experimental parameters and the deformation induced by the two-way shape memory effect under stress-driven condition and under stress-free condition.

Two-way under stress-driven condition			Two-way under stress-free condition[a)]		
Applied stress [kPa]	Deformation preceding the cycle, ε_c [%]	Induced elongation, $\Delta\varepsilon_{\text{stress-driven}}$ [%]	Actuation temperature, T_{act} [°C]	Deformation preceding the cycle, $\varepsilon_{c'}$ [%]	Induced elongation, $\Delta\varepsilon_{\text{stress-free}}$ [%]
100	5	1.9	46.5	7	13.9
180	10	7.4	46	12	12.5
300	20	15.4	45	16	11.3
430	30	22.6	45	28	6.7
500	40	28.6	44.8	32	4.9

[a)] Measured for various T_{act} but for a same value of $\varepsilon_c = 20\%$.

where $\varepsilon_{d'}$ and $\varepsilon_{c'}$, represents the strain in point d' (maximum strain for each cycle) and c' (starting strain for each cycle), respectively.

The estimated values of $\Delta\varepsilon_{\text{stress-free}}$ are reported in Table 1 for various values of T_{act} and $\varepsilon_{c'}$, showing that the larger is the recovered strain achieved through heating up to T_{act} (i.e., the lower is $\varepsilon_{c'}$), the higher is the two-way effect. Further, it is interesting to see that the reversible strain measured under stress-free condition are typically lower than those measured under an applied load (see as comparison $\Delta\varepsilon_{\text{stress-driven}} = 15.4\%$ for $\varepsilon_{c'} = 20\%$), although, remarkably, the maximum $\Delta\varepsilon_{\text{stress-free}}$ measured (for $T_{\text{act}} = 46.5$ °C and $\varepsilon_{c'} = 7\%$) is closely comparable ($\Delta\varepsilon_{\text{stress-free}} = 13.9\%$).

3. Conclusion

A semicrystalline network, based on poly(ε-caprolactone) and crosslinked by means of a sol-gel reaction, was subjected to specific thermomechanical histories, aimed at revealing its two-way shape memory response both under the application of a constant non-zero stress and under a stress-free, or self-sustained, condition. Under both conditions the material was capable of the typical two-way response measured under tension, that is a reversible elongation–contraction cycle induced by cooling and heating across a thermal region related to crystallization and melting. In the case of the stress-driven cycle, the extent of the elongation–contraction cycle was remarkable, at least for the application of a stress above 100 kPa, and strongly increases with the applied stress. In the case of the stress-free approach, the material requires a more complex thermo-mechanical cycle to prepare the material for the two-way response. The extent of the two-way cooling–elongation cycle measured under this condition is typically lower than those measured under corresponding stress-driven conditions. However, this extent is strongly dependent on the temperature T_{act} at which the polymer is heated before the cyclic response, and for the highest T_{act} explored the elongation induced under stress-driven or stress-free approach is comparable.

4. Experimental Section

Materials: Crosslinked semicrystalline networks were obtained starting from α,ω-hydroxyl-terminated PCL ($M_w = 3400$ g mol^{-1}; purchased from Sigma-Aldrich, Milan, Italy). α,ω-trialkoxysilane-terminated PCL was obtained upon reaction with 3-(triethoxysilyl) propyl isocyanate, while a sol-gel reaction of the terminal groups, by inducing the formation of cross-linked silica domains, was employed in order to achieve a crosslinked structure. The material was prepared by casting as a thin sheet (approximate thickness of 200–300 µm). Further details about the material preparation could be found elsewhere.[11]

Thermal and Thermo-Mechanical Testing: Differential scanning calorimetry was performed by means of a DSC Q100 (TA Instruments) on about 8 mg of material. The thermal program consisted of heating/cooling/heating runs, scanning the region between −30 and 70 °C at 2°C min^{-1}. Dynamic mechanical analysis was carried out under tensile conditions with a DMA Q800 analyzer (TA Instruments) on rectangular specimens (overall length: 20 mm; gauge length: 10 mm; width: 5 mm). A displacement amplitude equal to 15 µm at 1 Hz was applied on a cooling and heating cycle covering the thermal region between 70 and −30 °C at 2 °C min^{-1}.

Shape-Memory Testing: The two-way shape memory ability of the material was quantified both in presence of an applied stress or under stress-free conditions. The test was carried out with a DMA Q800 analyzer (TA Instruments) under tensile conditions on rectangular bars (overall length: 20 mm; gauge length: 10 mm; width: 5 mm) cut from the sheets.

To measure the two-way shape memory response, the following thermomechanical cycle was applied: i) heating above T_m (at 70 °C); ii) application of a tensile strain equal to 20% at a loading rate of 0.5 N min^{-1}; iii) cooling under fixed load below T_c (at −20 °C) at a constant cooling rate of 5 °C min^{-1}; iv) heating up to 70 °C at 5 °C min^{-1}.

To explore the self-sustained two-way shape memory response, the following thermomechanical cycle was applied: i) heating at 70 °C; ii) application of a strain equal to 20% at a loading rate of 0.5 N min^{-1}; iii) cooling under fixed load below T_c (to −20 °C) at a constant cooling rate of 5 °C min^{-1}; iv) load removal; v) heating ramp up to a given temperature called T_{act} which was approached at 5 °C min^{-1}; vi) cooling to −20 °C; and vii) heating to T_{act} at 5°C min^{-1}. Various values of T_{act} (44.8; 45; 46; 46.5) were investigated in order to identify the best value towards a significant stress-free two-way shape memory effect.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

[1] M. Behl, A. Lendlein, *Mater. Today* **2007**, *10*, 20.

[2] J. Leng, X. Lan, Y. Liu, S. Du, *Prog. Mater. Sci.* **2011**, *56*, 1077.

[3] M. Zare, M. P. Prabhakaran, N. Parvin, S. Ramakrishna, *Chem. Eng. J.* **2019**, *374*, 706.

[4] K. Wang, Y.-G. Jia, C. Zhao, X. X. Zhu, *Prog. Mater. Sci.* **2019**, *105*, 100572.

[5] G. Scalet, *Actuators* **2020**, *9*, 10.

[6] K. Wang, Y.-G. Jia, X. X. Zhu, *Macromolecules* **2017**, *50*, 8570.

[7] W. Yan, T. Rudolph, U. Noechel, O. Gould, M. Behl, K. Kratz, A. Lendlein, *Macromolecules* **2018**, *51*, 4624.

[8] L. F. Fan, Y. N. Huang, M. Z. Rong, M. Q. Zhang, *eXPRESS Polym. Lett.* **2020**, *14*, 295.

[9] Y. Gao, W. F. Liu, S. P. Zhu, *eXPRESS Polym. Lett.* **2020**, *14*, 295.

[10] O. Dolynchuk, I. Kolesov, D. Jehnichen, U. Reuter, H.-J. Radusch, J.-U. Sommer, *Macromolecules* **2017**, *50*, 3841.

[11] S. Pandini, F. Baldi, K. Paderni, M. Messori, M. Toselli, F. Pilati, A. Gianoncelli, M. Brisotto, E. Bontempi, T. Riccò, *Polymer* **2013**, *54*, 4253.

[12] R. L. Miller, *Polymer Handbook*, 3rd ed. John Wiley and Sons, New York, USA **1992**.