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## ABSTRACT

The "two-way" shape memory effect consists in a cyclic elongation-contraction effect, achieved by subjecting semicrystalline networks a constant load and to a cooling-heating cycle from above melting temperature ( $T_m$ ) to below crystallization temperature ( $T_c$ ). The achievable elongations and the transformation temperatures may be tailored by varying the material network density. In this work we have explored the two-way shape memory response of poly( $\epsilon$ -caprolactone)-based networks presenting a large variation in crosslink density. A significant strain increment observed during cooling and is almost completely reversed by heating above  $T_m$ . By representing strain as a function of temperature it is possible to identify two different contributions to the overall elongation, one due to a rubber entropy process and the other due to a crystallization induced effect. These two processes have different importance on the materials response. Maximum elongation could be achieved by improving the balance between materials compliance and the resistance to applied stress.

## INTRODUCTION

The shape memory behavior of polymers is a stimuli-responsive feature by which significant dimensional changes may be triggered by a change in temperature, and it results from a proper combination of the polymer macromolecular architecture and of a particular thermo-mechanical history. All the materials classified as shape memory polymers (SMPs) possess, as common structural characteristic, a cross-linked structure, either chemical or physical, which is responsible for the materials "permanent" shape. The shape-shifting ability is possible by the remaining polymer chain mobility when heating/cooling them across their glass transition and/or melting and crystallization temperatures.

Most polymers are typically associated with the irreversible "one-way" shape memory effect (i.e. the ability to switch from a temporarily set shape to its permanent one). Recently, it was shown that semicrystalline networks are capable of a "two-way" response, which is of great interest for applications where reversible actuation is demanded. The "two-way" shape memory effect (TWSME) consists in a reversible cyclic elongation-contraction, which involves significant strain variation and is achieved by subjecting this class of polymers to a constant stress and to a cooling/heating cycle from above melting temperature to below crystallization temperature.

An interesting advantage of SMPs lies in the ease of tailoring

their shape memory capabilities and transformation temperatures through changes in the macromolecular architecture. In particular, the materials crosslink density plays an important role on the elongation capabilities related to the TWSME. In this work we explore the effect of a large variation in network density on the two-way shape memory response of poly( $\epsilon$ -caprolactone)-based materials.

## MATERIALS

The semicrystalline networks employed in our investigation are based on poly( $\epsilon$ -caprolactone) (PCL), and were obtained starting from reactive PCL precursors with methacrylic end-caps, thermally crosslinked in presence of an initiator (dicumyl peroxide). The crosslink density (i.e. the number of effective network chains per unit volume) was varied by changing either the structure of the precursors (linear, three- and four-arms branched precursors) or their methacrylation degree. As reported in Table 1, the materials were coded as PCL-x, where x may corresponds to: i. L, T, F, indicating linear, three-arm and four-arm branched architectures of fully methacrylated precursors; ii. m100, m78, m65, corresponding to linear precursors with different methacrylation degrees (100%, 78% and 65%, respectively). The materials were prepared by the group of Prof. Pilati and Prof. Messori of the University of Modena - Reggio Emilia and more details concerning their preparation can be found in reference [1]. The materials have a wide range of crosslink densities, which span over about one order of magnitude and display different thermal properties. Differential scanning calorimeter (DSC) experiments carried out by using a TA Instruments DSC Q1000 at a rate of 2°C/min over a temperature range -50°C to 75°C, allowed the melting ( $T_m$ ), crystallization temperature ( $T_c$ ) and the crystallinity content ( $\chi_c$ ) to be determined. The latter term was evaluated by considering 134.9 J/g as melting enthalpy of a 100% crystalline PCL [2]; the results are reported in Table 1.

A relevant effect of the network density is shown in Figure 1 and regards the materials mechanical behavior above the melting temperature (95°C), i.e. in the thermal region where load is applied in the TWSME experiments. A remarkable increase in compliance (~68%) was obtained for the least crosslinked material. Moderate, but significant changes were achieved by the other systems (5-30%).

Material Code	Precursor molecular architecture	Precursor molecular weight (g/mol)	Methacrylation degree	crosslink density (mol/cm <sup>3</sup> )	Crystallization, T <sub>c</sub> (°C)	Melting temperature, T <sub>m</sub> (°C)	Crystallinity content, $\chi_c$ (%)
PCL-L	Linear	7300	100	830	-10	50	32
PCL-T	Three-arm	15800	95	490	10	56	44
PCL-F	Four-arm	22800	96	670	6	52	34
PCL-m100	Linear	10000	100	430	15	53	40
PCL-m78	Linear	10000	78	260	23	53	47
PCL-m65	Linear	10000	65	12	31	55	53

Table 1. Structural and thermal characteristics of the various PCL-based systems.

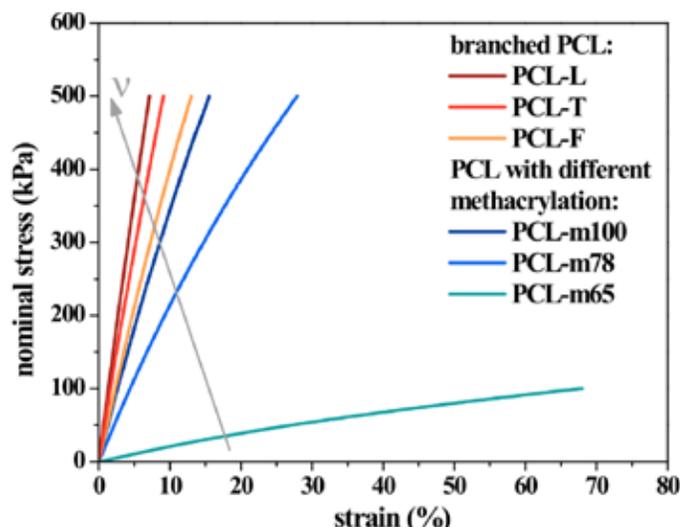


Figure 1. Stress vs. strain curves up to 500 kPa (100 kPa for PCL-m65) for the various materials tested above melting temperature.

## TWO-WAY SHAPE MEMORY BEHAVIOUR

The TWSME was investigated by employing properly designed thermo-mechanical cycles, carried out by means of a TA Instruments DMA Q800 under a tensile configuration. Samples were rectangular bars with average length of 10mm and average cross-section of 5x1.5mm<sup>2</sup>. The thermal history is represented in Figure 2 for the PCL-m78 system, and consists in an early application of stress above T<sub>m</sub> (95°C) and at a constant loading rate of 0.2 N/min up to a stress of 500 kPa (A→B); the stress was kept constant during the subsequent part of the test, during which the specimen was cooled at 2°C/min below T<sub>c</sub>, finally maintaining the temperature for 10 minutes (B→C), and then heated again to 95°C at a rate of 2°C/min, maintaining the final temperature constant for additional 10 minutes (C→D). During the test, the strain evolution was monitored and may be described as an early pre-stretch during the loading ramp, a subsequent elongation during cooling until an upper plateau is approached, and a final recovery stage during heating, in which, after an elongation due to thermal expansion, the specimen reduced in length to a value close to that displayed before cooling. The peculiarity of the TWSME consists in fact this elongation/contraction effect stimulated

by the heating/cooling cycle.

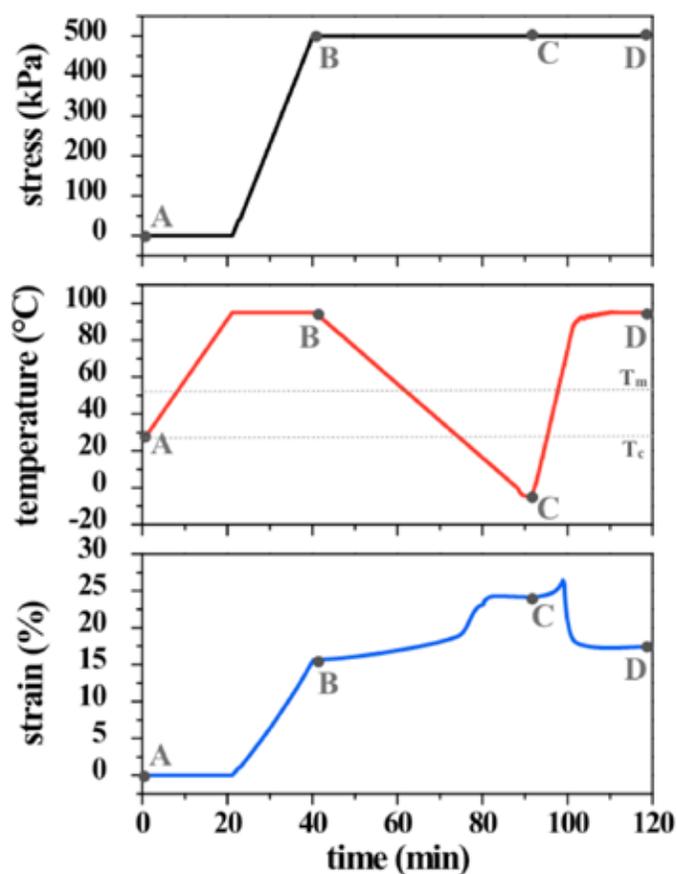


Figure 2. Time evolution of stress, temperature and strain during a two-way shape memory cycle for the material PCL-m78.

In Figure 3a the TWSME is represented for various systems subjected to a load of 500 kPa in terms of strain vs. temperature curves. The lower crosslink density regards the higher pre-stretch and cooling induced elongations displayed as well as an increased temperature of transformation. The representation also shows evidence that the elongation occurs as a two stage process, involving a steep increase in strain followed by a steeper and remarked effect on the crystallization region.

describing, with good experimental agreement [4], the dependence on temperature and suggesting that larger elongation capabilities may be shown by specimens subjected to a higher pre-stretch

$$\left( \lambda^2 - \frac{1}{\lambda} \right)_{prestretch}$$

Consistently, Figure 3a shows a steeper elongational trend for materials subjected to a larger pre-stretch.

The elongation taking place close to the crystallization temperature may be interpreted as a consequence of the crystal formation under a fixed stress condition: the creation of crystals allows a certain strain to be maintained under reduced amount of stress, but since the stress is kept constant the material has to undergo further elongation to satisfy the mechanical equilibrium conditions [6]. The effect of the crosslink density on the overall elongation as well as on their sub-components is represented in Figure 3b. The overall elongation is seen to increase as the network density decreases, and a similar dependence is reported also for the entropy driven component, as a consequence of the larger pre-stretch achieved by the more compliant materials. The crystallization induced component is seen to play a relevant role, being almost the only contribution for the more crosslinked materials, but does not present any dependence on the network density. Although these results deserve further elucidation, it may be concluded that the different total elongation capabilities may be mainly ascribed to the entropy-driven effect, and thus to the higher compliance of the less crosslinked systems.

It was thus interesting to investigate the two-way shape memory response for a significantly low crosslink density, as that presented by the system PCL-m65. This system could not be directly compared to the more cross-linked, since presenting failure for loads above 100 kPa. The results are presented in Figure 4, showing that significant elongations, approaching values of about 20% may be obtained under reduced stress levels. Further, by representing the strain evolution as a function of temperature, it is possible to see that the elongation seems to be almost completely ascribed to the entropy-driven process. The absence of a significant crystallization induced effect is probably due to the low stresses applied. This is consistent with the hypothesis, presented in reference [1] that a threshold stress of similar entity is required to induce crystallization.

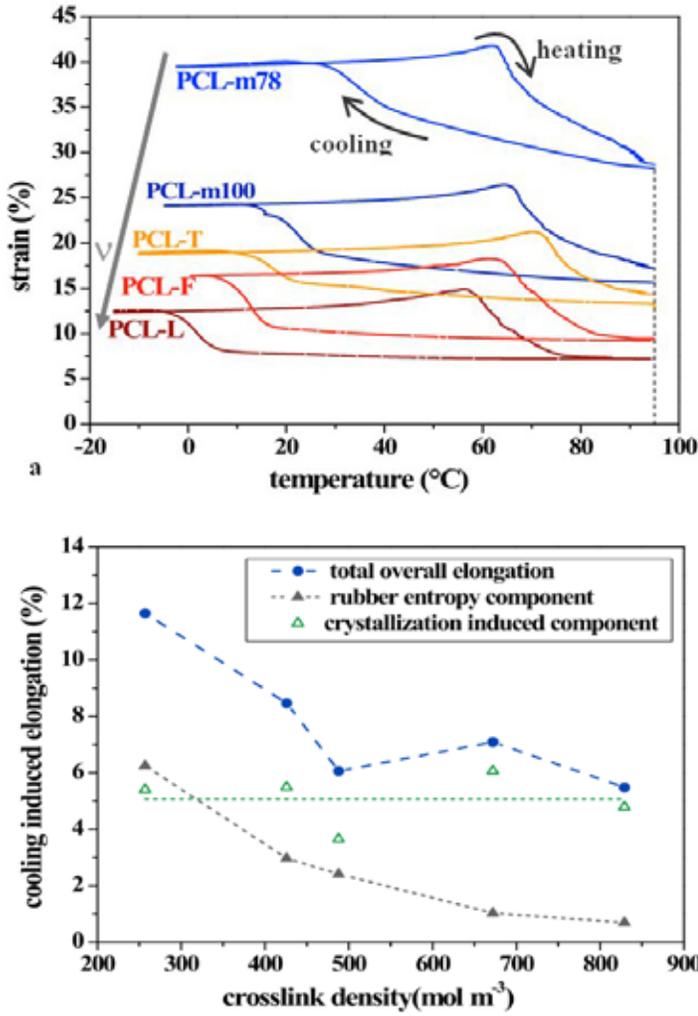


Figure 3. a) Strain evolution as a function of temperature for various materials subjected to a two-way shape memory cycle under a maximum load of 500 kPa, and b) overall elongation, entropy- and crystallization-driven subcomponents as a function of the crosslink density.

The high temperature process is due to an entropic elasticity behavior, proper of these materials in the rubbery region [4]. In fact, the rubber elasticity equation postulates that [5]:

$$\sigma = \nu RT \left( \lambda^2 - \frac{1}{\lambda} \right)$$

where  $\sigma$  is the nominal stress,  $\nu$  is the crosslink density,  $T$  is the absolute temperature and  $\lambda$  is the extension ratio ( $\lambda = l/l_0$ ;  $l$  and  $l_0$  are the actual and initial specimen length). By considering the pre-stretch condition obtained during the (A→B) stage, the equation may be rearranged as [1]:

$$\left( \lambda^2 - \frac{1}{\lambda} \right) = \left( \lambda^2 - \frac{1}{\lambda} \right)_{prestretch} \frac{T_{prestretch}}{T}$$

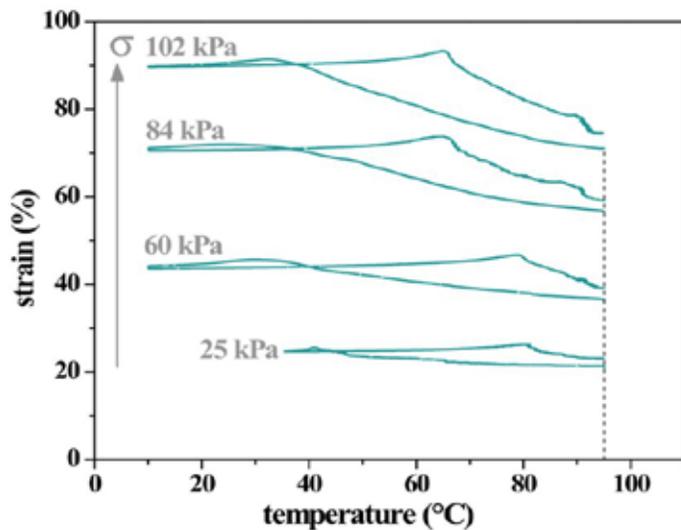


Figure 4. Strain evolution as a function of temperature for the system PCL-m65 subjected to a two-way shape memory cycle under various levels of stress.

To investigate the effect of the pre-stretching conditions on the elongation capabilities, the TWSME was investigated on specimens subjected to a same pre-stretch, under the application of various stresses. The two-way shape memory curves of three systems deformed at 30% before cooling are reported in Figure 5: it may be seen that the entropy driven process follows the same behavior for all systems since depending only on the pre-stretch conditions. The elongation experienced during crystallization is strongly dependent on stress, increasing as the applied stress increases. The results seem to suggest that tailoring a strategy aiming at enhancing the elongation capabilities have to focus on materials with high compliance (i.e. obtain high pre-stretch) and high resistance (i.e. higher load levels).

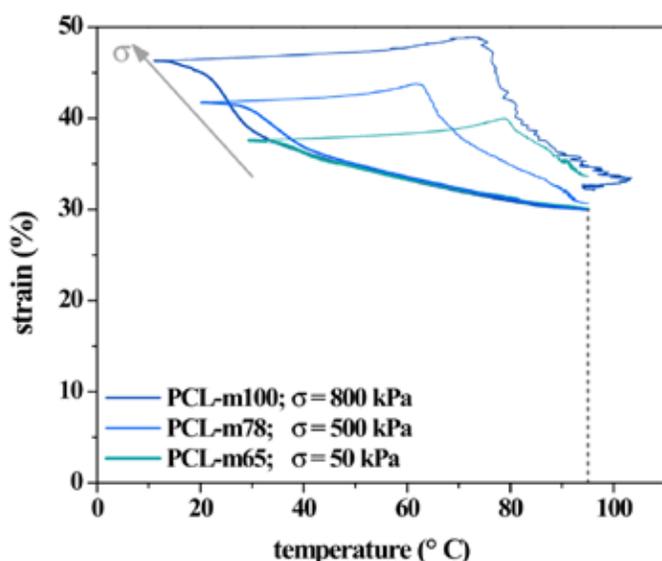


Figure 5: Strain evolution as a function of temperature for various materials subjected to a same pre-stretch level.

## CONCLUSION

The TWSME capabilities of semicrystalline networks were investigated on poly( $\epsilon$ -caprolactone)-based systems with different crosslink densities. Under the application of proper thermo-mechanical cycles a two-way shape memory response was possible. Significant elongation was observed when cooled below  $T_c$  under an applied load and a later contraction by heating above  $T_m$ . By focusing our analysis on the cooling induced elongation processes, two subcomponents were identified to contribute to the elongation, one ascribed to rubber elasticity and the other to a crystallization-driven effect.

When the same load is applied, a larger elongation may be obtained by systems with lower network density. By considering the sub-processes separately, this effect seems to be ascribed to the entropy-driven process and the materials compliance. Further, in presence of a significantly low crosslink density, large elongations may be obtained under reduced applied stresses and through a process that may be almost completely ascribed to the entropy-driven process. In these cases, absence of a crystallization induced effect may be due to the low stress applied.

The results seem to indicate that the system compliance, i.e. a large pre-stretch, plays an important effect in obtaining large cooling induced elongation. At the same time, further elongation during crystallization is enhanced by the application of large load levels. Both suggest that to obtain materials capable of large elongation levels, a good compromise between the material pre-stretch and load applied has to be attained.

## ACKNOWLEDGEMENT

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