

TRIPLE-SHAPE PROPERTIES OF MAGNETO-SENSITIVE NANOCOMPOSITES DETERMINED IN TENSILE TESTS

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Keywords: *magnetically active nanocomposite, shape-memory polymer, inductive heating, stimuli-sensitive polymer*

1 Introduction

Shape-memory polymers (SMP) are thermo-sensitive materials, which are capable of dual- or triple-shape effect having a high innovation potential in different application areas [1-5]. In contrast to a dual-shape effect, during a triple-shape effect two subsequent shape changes from a first temporary shape (A) to a second temporary shape (B) and from there to a third, permanent shape (C) were obtained. Two essential components of shape-memory polymers (SMP), which exhibit a thermally induced shape-memory effect (SME), are at least one kind of switching domain related to a thermal transition (T_{trans}) e.g. glass transition (T_g) or melting transition (T_m) and netpoints, which can be either of physical nature (thermoplastics) or chemical nature (polymer networks). In contrast to intrinsic material properties the shape-memory is a functionality, which must be created by a specific thermomechanical treatment of the polymer called shape-memory creation procedure (SMCP), where the temporary shape is fixed after deforming the material [6]. The activation of SME is typically achieved by heat, where the desired shape change is achieved when the environmental temperature T_{env} exceeds T_{sw} . If triggering of SME by environmental heating is not possible, non-contact activation is required. One opportunity for realization of non-contact SMP systems is the incorporation of magnetic particles (e.g. iron(III)oxide based particles) into a SMP matrix [7-11]. Activation of the SME in such polymer composites can be achieved by exposure to an alternating magnetic field. The inductive heating capability of such magnetically active SMP composites is a result of energy absorption by iron(III)oxide particles from the alternating magnetic field via hysteresis loss and/or superparamagnetism

related processes, which is transformed into heat. At the same time, potential changes in the surface to volume (S/V) ratio of the test specimen during the movement of the sample [8, 11], needs to be considered with respect to heat dissipation (heat loss) at the contact surface exposed to the surrounding environment.

Recently excellent triple-shape properties could be obtained when a two-step bending SMPC was applied for magneto-sensitive switchable triple-shape nanocomposites named MACLC, which were prepared by copolymerization of crystallizable poly(ϵ -caprolactone) diisocyanatoethyl methacrylate (PCLDIMA), cyclohexyl methacrylate (CHM) and silica coated magnetite nanoparticles (SNP) [8]. Such multiphase polymer network nanocomposites exhibited an AB polymer network structure.

In this work we investigated the triple-shape properties of MACLC using uniaxial-tensile tests, where the SME was activated by environmentally heating, whereby stress-free as well as constant strain recovery modules were utilized.

2 Experimental Part

2.1 Materials

MACLC polymer networks were prepared by copolymerization of PCLDIMA ($T_{\text{m,PCL}} = 55 \text{ }^\circ\text{C}$) with 60 wt% CHM with different SNP nanoparticle content (0 wt% and 12.5 wt%) according to the method described in [8]. The telechelic crosslinker (PCLDIMA) was synthesized from poly(ϵ -caprolactone)diol (Solvay chemicals, UK) with a number average molecular weight of $M_n = 8.300 \text{ g}\cdot\text{mol}^{-1}$ and 2-isocyanatoethyl methacrylate (Sigma-Aldrich, Taufkirchen, Germany) following the method described in [12]. Benzyl peroxide (Sigma-Aldrich, Taufkirchen, Germany) and silica coated

magnetite nanoparticles (AdNano MagSilica, Degussa, Hanau, Germany) were used as received.

2.2 Methods

The thermomechanical properties of MACLC were analyzed by dynamic mechanical analysis at varied temperatures (DMTA).

Cyclic thermomechanical shape-memory tests were performed on tensile testers Zwick Z1.0 and Z005 (Zwick, Ulm, Germany) equipped with a thermo chamber and temperature controller (Eurotherm Regler, Limburg, Germany) using test specimens type 1BB ($I_0 = 20$ mm, width 2 mm). Every cyclic thermomechanical experiment consisted of a programming module (SMCP), where the temperature-memory is created (see Fig. 1), and a recovery module for activation of SME. For each sample 4 cycles were conducted, whereby the 1st cycle was maintained as preconditioning and the shape-memory properties were determined as averaged values from cycle 2, 3 and 4.

SMCP: The specimen is heated to $T_{\text{high}} = 150$ °C (step 1) with a heating rate of $2 \text{ K}\cdot\text{min}^{-1}$ and elongated from ε_C to $\varepsilon_B^0 = 50\%$ at $T_{\text{high}} = 150$ °C with an equilibration time of 4 minutes (step 2). For fixation the sample is cooled to $T_{\text{low}} = -10$ °C with a cooling rate of $5 \text{ K}\cdot\text{min}^{-1}$ under constant stress resulting in $\varepsilon_B^{\text{load}}$ and after a waiting period of 10 minutes the stress was removed to obtain ε_B representing shape (B) (step 3). Afterwards, the sample was heated to $T_{\text{mid}} = 70$ °C with a heating rate of $2 \text{ K}\cdot\text{min}^{-1}$ (step 4), then the sample was deformed to $\varepsilon_A^0 = 100\%$ at T_{mid} (step 5), and subsequently cooled to $T_{\text{low}} = -10$ °C with a cooling rate of $5 \text{ K}\cdot\text{min}^{-1}$ under constant stress whereby the elongation decreases to $\varepsilon_A^{\text{load}}$. Shape (A), corresponding to ε_A , is obtained by unloading after a waiting period of 10 minutes (step 6).

Activation under stress-free conditions

The activation was induced by heating the programmed sample from T_{low} to T_{high} with a heating rate of $2 \text{ K}\cdot\text{min}^{-1}$ while the stress is kept at 0 MPa and the sample contracts to recovered shape (B) at $\varepsilon_B^{\text{rec}}$ and finally shape (C) at $\varepsilon_C^{\text{rec}}$ is recovered. The

activation module is completed by a waiting period of 10 minutes at T_{high} .

Activation under constant strain conditions

For the determination of the maximum stress σ_{max} and the corresponding temperature $T_{\sigma_{\text{max}}}$ an activation module under constant strain conditions, has been carried out after SMCP. The strain level ε_A was kept constant after programming and the temperature was increased from T_{low} to T_{high} with the heating rate of $2 \text{ K}\cdot\text{min}^{-1}$. The activation module was completed by releasing the stress to σ_0 to allow the sample to recover and a waiting period of 10 minutes at T_{high} .

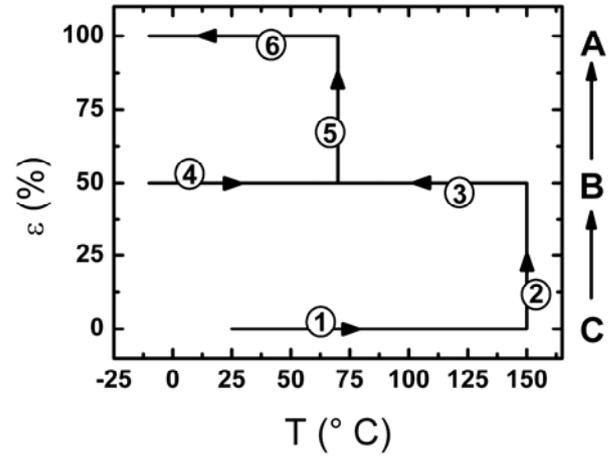


Figure 1: SMPC applied for programming of MACLC.

3 Results

Both MACLC materials with 12.5 wt% SNP (MACLC12) and without nanoparticles (MACLC00) showed high gel content values of $G > 95\%$, indicating an almost complete crosslinking reaction. The thermo-mechanical properties of the investigated polymer networks explored by DMTA were found to be almost identical. Here two glass transitions could be observed in the $\tan \delta$ vs. temperature curve at $T_{\text{max},\delta 1} = -55 \pm 3$ °C attributed to the amorphous PCL and at $T_{\text{max},\delta 1} = 146 \pm 3$ °C attributed to the glass transition of the poly (cyclohexyl methacrylate) domains (PCHM), while around 50 °C the melting of the PCL crystallites becomes obvious as displayed in Fig. 2.

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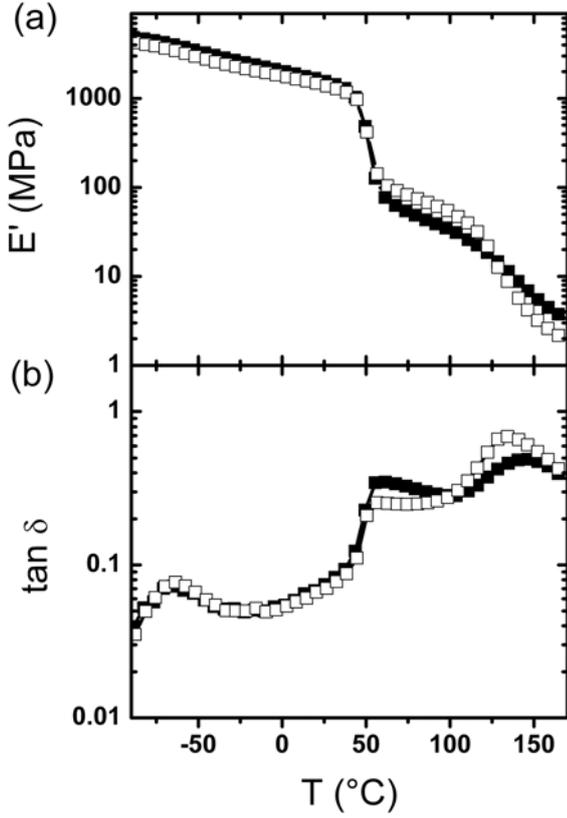


Figure 2: DMTA curves of MACLC composites containing 12.5 wt-% SNP nanoparticles (solid symbols) and without SNP (open symbols); **(a)** storage modulus E' - temperature curve. **(b)** $\tan \delta$ - temperature diagram.

For quantification of shape-memory properties the change in elongation ε was measured during SMPC and recovery under stress-free or constant strain conditions. Here the shape fixity ratios $R_f(C \rightarrow B)$ obtained after step 3 of SMCP and $R_f(B \rightarrow A)$ after completion of SMCP (step 6) were determined according to equations (1) and (2), while the shape recovery ratios were calculated $R_r(A \rightarrow B)$ and $R_r(A \rightarrow C)$ of the stress-free recovery curves by equations (3) and (4) [6, 13].

$$R_f(C \rightarrow B) = \frac{\varepsilon_B - \varepsilon_C}{\varepsilon_B^{load} - \varepsilon_C} \quad (\text{eq. 1})$$

$$R_f(B \rightarrow A) = \frac{\varepsilon_A - \varepsilon_B}{\varepsilon_A^{load} - \varepsilon_B} \quad (\text{eq. 2})$$

$$R_r(A \rightarrow B) = \frac{\varepsilon_A - \varepsilon_B^{rec}}{\varepsilon_A - \varepsilon_B} \quad (\text{eq. 3})$$

$$R_r(A \rightarrow C) = \frac{\varepsilon_A - \varepsilon_C^{rec}}{\varepsilon_A - \varepsilon_C} \quad (\text{eq. 4})$$

Additionally, two characteristic T_{sw} obtained during stress-free recovery was determined as inflection point from the angle ε vs. T_{env} plot, while under constant strain conditions, in the σ - T -diagram a stress maximum σ_{max} is observed during recovery at a characteristic temperature $T_{\sigma_{max}}$ [6].

Excellent shape-memory properties were obtained for MACLC nanocomposites in cyclic uniaxial tensile tests, when activated by environmentally heating whereby the results obtained from the 2nd, 3rd and 4th cycle were almost identical as summarized in Table 1.

Both samples MACLC00 and MACLC12 showed high shape fixity values of $R_f \geq 88\%$ and an almost complete overall shape recovery $R_r(A \rightarrow C) \geq 97\%$. Two distinct shape changes with $T_{sw}(A \rightarrow B) \approx 53$ °C and $T_{sw}(A \rightarrow B) \approx 120$ °C were obtained during thermally-induced recovery under stress-free conditions. In contrast under constant strain recovery conditions interestingly a single transition was observed with a recovery stress maximum σ_{max} at $T_{\sigma_{max}} \approx 74$ °C, as displayed in Fig. 3. In the σ - T curves for MACLC00 and MACLC12 (Fig. 3b) the recovery-stress initially decreased slightly in the temperature range from -10 °C to 10 °C, which might be attributed to the thermal expansion of the polymer network. During heating above 10 °C σ increased until σ_{max} was reached at $T_{\sigma_{max}} \approx 74$ °C, where the PCL domains are completely amorphous. At higher temperatures, while heating to T_{high} , σ decreased and the softening of the polymer dominates because of an increasing mobility of the PCHM segments, whereby an almost constant stress level of $\sigma \approx 0.5$ MPa was reached at temperatures > 120 °C indicating the fully rubbery elastic state of the polymer network. When 12.5 wt% SNP nanoparticles were embedded into the MACLC polymer matrix the achieved recovery stress increased significantly from $\sigma_{max} = 1.7$ MPa to $\sigma_{max} = 2.1$ MPa, which strongly indicates that the SNP act as additional physical netpoints within the polymer network matrix.

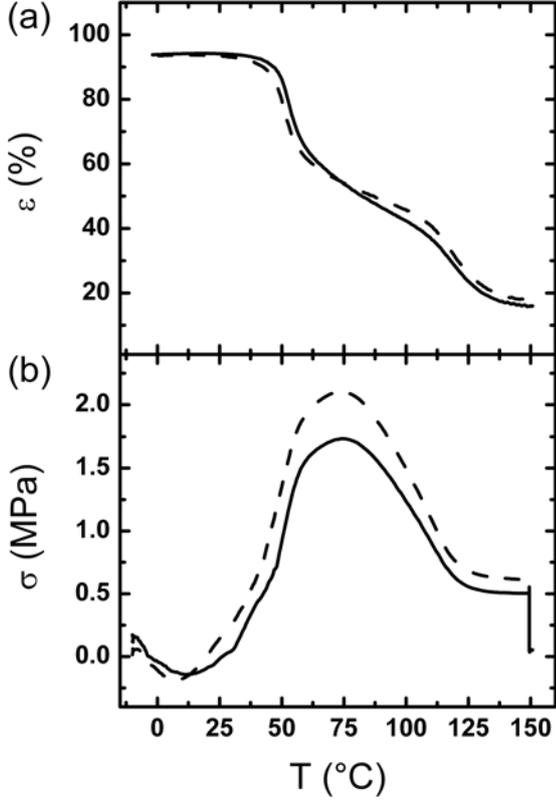


Figure 3: Stress-temperature-strain plots obtained for MACLC materials in the 2nd cycle of uniaxial tensile tests protocols with stress-free and constant strain recovery modules. MACLC00 (solid lines) and MACLC12 (dashed lines).

We assume that the resulting single step stress-recovery process might be related to the two-step programming procedure. Here in step 5 of SMCP, where the sample was deformed from $\varepsilon = 50\%$ to $\varepsilon = 100\%$ at $T_{\text{mid}} = 70\text{ }^{\circ}\text{C}$, the PCL segments are completely amorphous and the PCHM domains

remain in the glassy state forming physical netpoints, which are determining the overall mechanical properties of the polymer network. A relatively high loading stress is needed for deformation to $\varepsilon = 100\%$ at T_{mid} , whereby shape (A) was almost fixed instantaneously by the strained PCHM netpoints, as almost no recoiling of the PCHM chains should occur in the glassy state. While cooling the sample to $T_{\text{low}} = 0\text{ }^{\circ}\text{C}$, crystallization of the PCL switching domains takes places, whereby the developing crystalline PCL structures are constrained by the confinement of the cold drawn PCHM matrix. These newly formed PCL crystallites additionally stabilize shape (A). To our understanding the increase in σ in the temperature range from $20\text{ }^{\circ}\text{C}$ to $74\text{ }^{\circ}\text{C}$ during thermally-induced recovery under constant strain conditions, can be explained by a combination of at least two temperature dependent changes in the polymer network. First the melting of the crystalline PCL domains and the resulting increase in entropy elasticity is responsible for the observed increase in recovery stress in the temperature range from $20\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$. At temperatures above $60\text{ }^{\circ}\text{C}$ to $74\text{ }^{\circ}\text{C}$ the PCL domains are completely amorphous and stretched resulting in a negative expansion coefficient, which causes a further increase in σ until $74\text{ }^{\circ}\text{C}$ is reached. Here the softening of the glassy PCHM domains acting as strong physical netpoints starts, which is in accordance with the onset of the PCHM glass transition observed in DMTA. An internal stress compensation process between PCL and PCHM domains takes place at temperatures above $74\text{ }^{\circ}\text{C}$, and finally at temperature $> 125\text{ }^{\circ}\text{C}$ the polymer network reaches a completely viscoelastic equilibrium state.

Table 1: Shape-memory properties of MACLC materials

Sample ID	$\overline{R}_f(C \rightarrow B)$ [%]	$\overline{R}_f(B \rightarrow A)$ [%]	$\overline{R}_r(A \rightarrow B)$ [%]	$\overline{R}_r(A \rightarrow C)$ [%]	$\overline{T}_{\text{sw}}(A \rightarrow B)$ [°C]	$\overline{T}_{\text{sw}}(B \rightarrow C)$ [°C]	$\overline{T}_{\sigma, \text{max}}$ [°C]	$\overline{\sigma}_{\text{max}}$ [MPa]
MACLC00	95±2	91±3	88±3	98±2	53±2	120±2	74±2	1.7±0.05
MACLC12	89±2	91±2	91±3	98±2	51±2	119±2	73±2	2.1±0.1

* All denoted data are averaged values obtained from the 2nd, 3rd and 4th test cycle.

Here we could demonstrate that excellent triple-shape properties were obtained by environmentally heating during cyclic, thermomechanical tensile tests for MACLC materials with different SNP content, when activated under stress-free conditions. Whereas during constant strain recovery a single

step stress-recovery process was observed, with a stress maximum σ_{\max} at 74 °C.

In the future, we will further investigate the underlying mechanism for controlling the constant strain recovery process and explore the influence of different SMPC procedures on the σ - T behavior.

References

- [1] M. Behl, M. Y. Razzaq, A. Lendlein. "Multifunctional Shape-Memory Polymers". *Advanced Materials*, Vol. 22, No. 31, pp 3388-3410, 2010.
- [2] M. Behl, J. Zotzmann, A. Lendlein. "Shape-Memory Polymers and Shape-Changing Polymers". *Advances in Polymer Science*, Vol. 226, pp 1-40, 2010.
- [3] S. A. Madbouly, A. Lendlein. "Shape-Memory Polymer Composites". *Advances in Polymer Sciences*, Vol. 226, pp 41-95, 2010.
- [4] P. T. Mather, X. Luo, I. A. Rousseau. "Shape Memory Polymer Research". *Annual Review of Materials Research*, Vol. 39, No. 1, pp 445-471, 2009.
- [5] D. Ratna, J. Karger-Kocsis. "Recent advances in shape memory polymers and composites: a review". *Journal of Materials Science*, Vol. 43, No. 1, pp 254-269, 2008.
- [6] W. Wagermaier, K. Kratz, M. Heuchel, A. Lendlein. "Characterization Methods for Shape-Memory Polymers". *Advances in Polymer Science*, Vol. 226, pp 97-145, 2010.
- [7] R. Mohr, K. Kratz, T. Weigel, M. Lucka-Gabor, M. Moneke, A. Lendlein. "Initiation of shape-memory effect by inductive heating of magnetic nanoparticles in thermoplastic polymers". *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 103, No. 10, pp 3540-3545, 2006.
- [8] U. Narendra Kumar, K. Kratz, W. Wagermaier, M. Behl, A. Lendlein. "Non-contact actuation of triple-shape effect in multiphase polymer network nanocomposites in alternating magnetic field". *Journal of Materials Chemistry*, Vol. 20, No. 17, pp 3404-3415, 2010.
- [9] M. Y. Razzaq, M. Behl, K. Kratz, A. Lendlein. "Controlled Actuation of Shape-Memory Nanocomposites by Application of an Alternating Magnetic Field". *Mater. Res. Soc. Symp. Proc.*, Vol. 1140, pp 185-190, 2009.
- [10] G. Vialle, M. Di Prima, E. Hocking, K. Gall, H. Garmestani, T. Sanderson, S. C. Arzberger. "Remote activation of nanomagnetite reinforced shape memory polymer foam". *Smart Materials & Structures*, Vol. 18, No. 11, pp, 2009.
- [11] T. Weigel, R. Mohr, A. Lendlein. "Investigation of parameters to achieve temperatures required to initiate the shape-memory effect of magnetic nanocomposites by inductive heating". *Smart Materials & Structures*, Vol. 18, No. 2, pp 025011, 2009.
- [12] U. Narendra Kumar, K. Kratz, M. Behl, A. Lendlein. "Triple-Shape Capability of Thermo-Sensitive Nanocomposites from Multiphase Polymer Networks and Magnetic Nanoparticles". *Mater. Res. Soc. Symp. Proc.*, Vol. 1190, pp 55-61, 2009.
- [13] I. Bellin, S. Kelch, R. Langer, A. Lendlein. "Polymeric triple-shape materials". *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 103, No. 48, pp 18043-18047, 2006.