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Influence of Compression Direction on the Shape-Memory Effect of Micro-Cylinder Arrays Prepared from Semi-Crystalline Polymer Networks

Yi Jiang[1,2], Liang Fang[1,#], Karl Kratz[1], Andreas Lendlein[1,2]
[1] Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz Zentrum Geesthacht, Kantstr. 55, 14513, Teltow, Germany
[2] Institute of Chemistry, University of Potsdam, 14476 Potsdam, Germany
[#] Present address: State Key Laboratory of Materials-Oriented Chemical Engineering, College of Material Science and Engineering, Nanjing Tech University, 210009, Nanjing, China.

ABSTRACT

Microstructured polymeric surfaces capable of a thermally-induced shape-memory effect (SME) can perform on demand changes of surface properties such as wettability or adhesion. In this study, we explored the influence of the applied compression direction during programming, i.e. vertical compression and tilted compression, on the SME of microstructured crosslinked poly[ethylene-*co*-(vinyl acetate)] (cPEVA) films comprising arrays of micro-cylinders with a height of 10 µm and different diameters of 10 µm, 25 µm, and 50 µm. The shape recovery of the microstructures during heating was visualized online by optical microscopy, while atomic force microscopy (AFM) was utilized to investigate the temperature-induced shape change of single micro-cylinders. Here, the changes in micro-cylinder height and the characteristic angle θ were followed and analyzed for quantification of the shape-memory performance. Both compression modes resulted in almost flat programmed surfaces as indicated by high shape fixity ratios of $R_f \geq 93\pm1\%$. A nearly complete recovery of the micro-cylinders was obtained for all investigated cPEVA samples documented by high shape recovery values of $R_r \geq 97\pm1\%$, while the obtained shape change of the micro-cylinders during recovery almost reversely recalled the applied deformation during programming. The presented capability of SMP microstructured substrates to memorize the way of deformation during programming could be a new tool for controlling particular shape changes of microstructures during recovery and in such a way the generated local recovery forces can be adjusted.

INTRODUCTION

Shape-memory polymers (SMPs) are a prominent class of thermo-sensitive materials, which are capable of active movements. While in the last decade the majority of SMP research was focused on the investigation of macroscopic effects [1], more recently micro- and

nanostructured SMP films have been explored as novel type of intelligent surface [2-9]. In this context smart films have been reported showing i.e. a switchable wettability [2] or adhesion [3, 9], allow controlled changes in optical elements [4, 5], can be applied as intelligent microfluidics [6] or utilized as active cell culture substrates [7, 8].

In this study, we explored, whether the application of different compression modes applied during programming, i.e. vertical compression and tilted compression can influence the shape-memory performance/behavior of microstructures prepared from crosslinked polymer networks with crystallizable switching units. Crosslinked poly[ethylene-*co*-(vinyl acetate)] (cPEVA) with a vinyl actetate content of 18 wt% having a broad melting transition in the temperature interval from 30 to 85 °C [9] related to crystalline polyethylene domains, was selected as polymer matrix exhibiting excellent shape-memory properties [10]. A soft lithography approach was chosen for fabrications of cPEVA microstructured films comprising arrays of micro-cylinders with different diameters of 10, 25, and 50 µm. The temperature-induced shape recovery of the differently programmed microstructure arrays was recorded online by optical microscopy, while atomic force microscopy (AFM) was applied to follow the related shape changes of the single micro-cylinders represented by the cylinder height H and the angle θ.

The presented shape-memory polymer micro-cylinder arrays might be applicable as smart surfaces showing a drastic change in water wettability when the temperature is increased. In the programmed flat shape such surfaces should exhibit hydrophobic contact angles related to the nature of the polymer, while the recovered micro-structured surface, which represents the Cassie state, will be hydrophilic.

EXPERIMENT

Materials and preparation of microstructured films

Poly[ethylene-*co*-(vinyl acetate)] (PEVA) with a vinyl acetate content of 18 wt% (data of the supplier) was obtained from DuPont de Nemours (Neu-Isenburg, Germany). Crosslinking agent dicumyl peroxide (DCP) and toluene (99.8%) were purchased from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany) and Sylgard® 184 silicone elastomer kit from Dow Corning Corp. (Midland, USA). All chemicals were used as received. Smooth and custom made microstructured Si-wafers with arrays of cylindrical micro-wells with diameters of 10, 25 or 50

μm and a spacing of two-times the micro-well diameter was purchased from IMS CHIPS (Stuttgart, Germany).

In a first step, a poly(dimethylsiloxane) (PDMS) soft mold replicate of the microstructured Si-Wafer was synthesized from a precursor mixture of 90 wt% prepolymer sylgard 184 and 10 wt% curing agent by curing at 80 ºC for 24 hours. The achieved microstructured PDMS mold was utilized as negative template for fabrication of a second PDMS soft mold comprising micro-wells following the afore-mentioned procedure. This PDMS mold was applied for generation of microstructured crosslinked poly[ethylene-*co*-(vinyl acetate)] (cPEVA) films. First, a solution casted film of PEVA with 2 wt% DCP was prepared from toluene. In a next step the obtained PEVA/DCP film is placed on the micro-well-structured PDMS mold and the sandwich is covered from both sides with a glass plate and a weight of 2 kg is placed on top. By heating to 140 ºC for 10 minutes the PDMS micro-cavities should be completely filled with PEVA/DCP. For crosslinking of the PEVA/DCP mixture the temperature was raised to 220 ºC and kept for 30 minutes. After cooling to 0 °C the PDMS mask was removed and microstructured cPEVA films with a thickness in the range of 400 to 500 μm and different micro-cylinder arrays with diameters of 10 μm (cPEVA_10), 25 μm (cPEVA_25), and 50 μm (cPEVA_50) were obtained.

The obtained three cPEVA films were characterized with respect to their gel content (G) and thermal properties according to the methods described in Ref [9]. G was determined after extraction with toluene for 24 hours at 80 ºC, while differential scanning calorimetry (DSC) experiments were performed with a Netzsch DSC 204 (Selb, Germany) with a constant heating and cooling rate of 10 ºC·min^{-1} to analyze the melting and crystallization temperatures (T_m and T_c).

Programming of the three microstructured cPEVA films was realized by compression in between two smooth Si-wafers at 70 ºC for 20 min and subsequent cooling to 10 °C. For vertical compression two foldback-clips (width 25 mm) were mounted on the ascribed sandwich without lateral displacement of the two Si-wafers, while in case of tilted compression a lateral displacement of ca. 200 to 300 μm was applied before fixing the foldback-clips.

Characterization of shape-memory properties

Atomic force microscopy (AFM) measurements were performed on a MFP-3D-BioTM AFM (Asylum Research, Goleta, USA) equipped with a Cooler/Heater (Asylum Research, Goleta, USA) to control the temperature. The shape recovery process was initiated by step-wise heating the samples from 25 ºC to 100 ºC with a heating rate of 10 ºC·min^{-1}, while AC mode was used to obtain the *in-situ* height images at fixed temperatures. Before scanning, the samples were equilibrated at each temperature for 10 minutes. A cantilever type AC200TS (Olympus, Tokyo, Japan) a with a spring constant of 9.7 N·m^{-1} and a frequency of 150 kHz was applied at a scan rate of 0.5 Hz. For each sample, at least five single micro-cylinders were measured at each temperature in order to calculate a mean value and the respective standard deviation. From the AFM results the changes in micro-cylinder height H and the characteristic angle θ with temperature (illustrated in Figure 1) were analyzed for quantification of the microscopic shape-memory performance. The shape fixity (R_f) and shape recovery ratio (R_r) was calculated according to the following equations, while the characteristic switching temperatures (T_{sw}s) were determined as inflection point of the height-temperature or tilt angle-temperature recovery curve.

$$R_f = \frac{H - H_u}{H_0} \times 100\% \text{ and } R_r = \frac{H - H_u}{H_0 - H_u} \times 100\%$$

Digital microscopy experiments for visualization of the different micro-cylinder arrays before and after programming were carried out with a VHX-100K (Keyence Cor., Osaka, Japan).

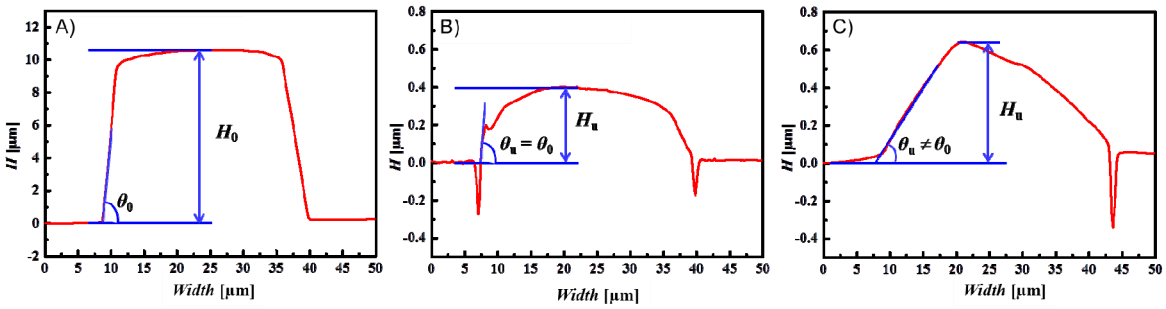

Figure 1. Representative AFM height images of original cPEVA_25 (A) and programmed cPEVA_25 programmed by vertical compression (B) and tilted compression (C), where the height H of the micro-cylinder and the characteristic angle θ are indicated.

RESULTS AND DISCUSSION

The microstructured cPEVA films with different micro-cylinder dimensions were fabricated by soft lithography utilizing a PDMS mold comprising cylindrical micro-wells. The resulting cPEVA films exhibited a high gel content of $G = 93\pm1\%$, indicating an almost complete conversion of the crosslinking reaction. DSC heating curves revealed a broad melting transition related to crystalline polyethylene domains ranging from 25 to 90 ºC with a peak maximum at $T_m = 79\pm1$ ºC, while a crystallization peak was found at $T_c = 59\pm1$ ºC in the cooling curves. The obtained gel content values and the thermal characteristic of the microstructured cPEVA films are in good agreement with previously reported values for cPEVA with an vinyl acetate content of 18 wt% [9].

Based on the DSC results the temperatures applied during programming were chosen to 70 ºC for deformation by compression and 10 ºC for fixation of the temporary shape. Both compression modes (vertical and tilted) resulted in almost flat programmed surfaces as illustrated in Figure 2 showing representative optical microscopy and AFM images of original and programmed micro-cylinder arrays or single micro-cylinders with a diameter of 25 µm (cPEVA_25).

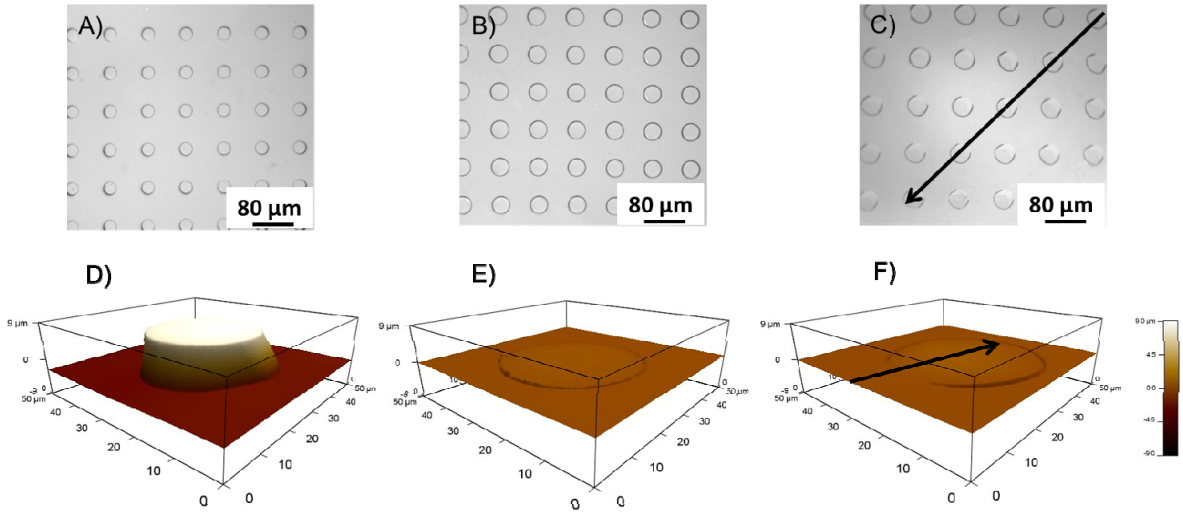

Figure 2. Representative digital microscopy images of micro-cylinder arrays (top) and AFM single micro-cylinder height images (bottom) for cPEVA_25 as processed/original shape (A, D) and in the temporary shape obtained by vertical compression (B, E) or by tilted compression (C, F). The black arrows indicate the displacement direction.

The micro-cylinder height H_0 of the processed microstructured cPEVA films was 9.8±0.1 µm (cPEVA_10), 10.5±0.1 µm (cPEVA_25) and 11.5±0.1 µm for cPEVA_50, while the diameters were found to be identical with that of the utilized PDMS mold. The observed increase in height with increasing micro-cylinder diameter might be related to a higher local

programming stress for microstructures with lower aspect ratio, which may cause an additional local deformation (increase in depth) of the micro-wells in the PDMS mold. The characteristic angle θ_0 was determined to be 78±1° for all original microstructures, which is significantly lower than the theoretically expected value around 90° and can be attribute to the applied AFM measuring technique. After programming almost flat temporary films were obtained where the micro-cylinders are nearly completely compressed into the cPEVA film. For films programmed by vertical compression the micro-cylinder heights H_u were 0.65±0.02 µm (cPEVA_10), 0.40±0.03 µm (cPEVA_25), and 0.48±0.01 µm (cPEVA_50), while the corresponding diameters were 15.9±0.1, 32.2±0.1, and 56.8±0.1 µm and θ_u remained around 78±1°. Films programmed by tilted compression, exhibited a slightly larger height of the temporary shaped micro-cylinders around 0.95±0.01 µm, while θ_u was reduced to values of 3.5±0.5º. Based on these data almost identical high shape fixity ratios of R_f = 93±1% - 96±1% for samples programmed by vertical compression and R_f = 94±1% - 95±1% for films programmed by tilted compression were obtained indicating a high efficiency of the programming procedure (Table 1).

Table 1. Shape-fixity ratio, shape recovery ratio and switching temperature of micro-cylinders with different diameter

Sample ID	vertical compression			tilted compression		
	R_f [%]	R_r [%]	T_{sw} [° C]	R_f [%]	R_r [%]	T_{sw} [° C]
cPEVA_10	93 ± 1	102 ± 1	68 ± 2	95 ± 1	99 ± 1	75 ± 2
cPEVA_25	96 ± 1	99 ± 1	78 ± 2	94 ± 1	97 ± 1	71 ± 2
cPEVA_50	96 ± 1	98 ± 1	75 ± 2	94 ± 1	97 ± 1	75 ± 2

The thermally-induced shape recovery of the microstructures was monitored online by *in situ* AFM experiments, where single micro-cylinders were analyzed at different temperatures during stepwise heating to 100 ºC. From the obtained AFM images (exemplarily shown for cPEVA_25 in Figure 3 B) the changes in H and θ with increasing temperature were extracted. The height profiles measured at temperatures from 20 °C to 100 °C for cPEVA_25 films programmed by vertical or tilted compression are displayed in Figure 3 A and D. Here, a continuous increase in height with increasing temperature becomes obvious and at a temperature of 100 °C the original height of the cPEVA_25 micro-cylinders is fully recovered. While for vertically programmed micro-cylinders the angle θ does not change during shape recovery, θ of tilted programmed

samples increased from 4±1º to 77±1º. Here, it becomes obvious that the way how the programming by compression was conducted is inversely recalled by the temperature dependent microscopic shape change during heating. The related angle vs. temperature data for all three kinds of micro-cylinders are shown in Figure 3 E. A similar behavior is observed for the height vs. temperature graphs displayed in Figure 3 C and F. High shape recovery ratios of $R_f \geq 97\pm1\%$ calculated from the height measured at 100 °C confirm an almost complete recovery for all programmed microstructures. Characteristic switching temperatures (T_{sw}) in the range from 68±2 °C to 78±2 °C were determined as inflection points of the H vs. T data. The determined quantities representing the shape memory performance are summarized in Table 1.

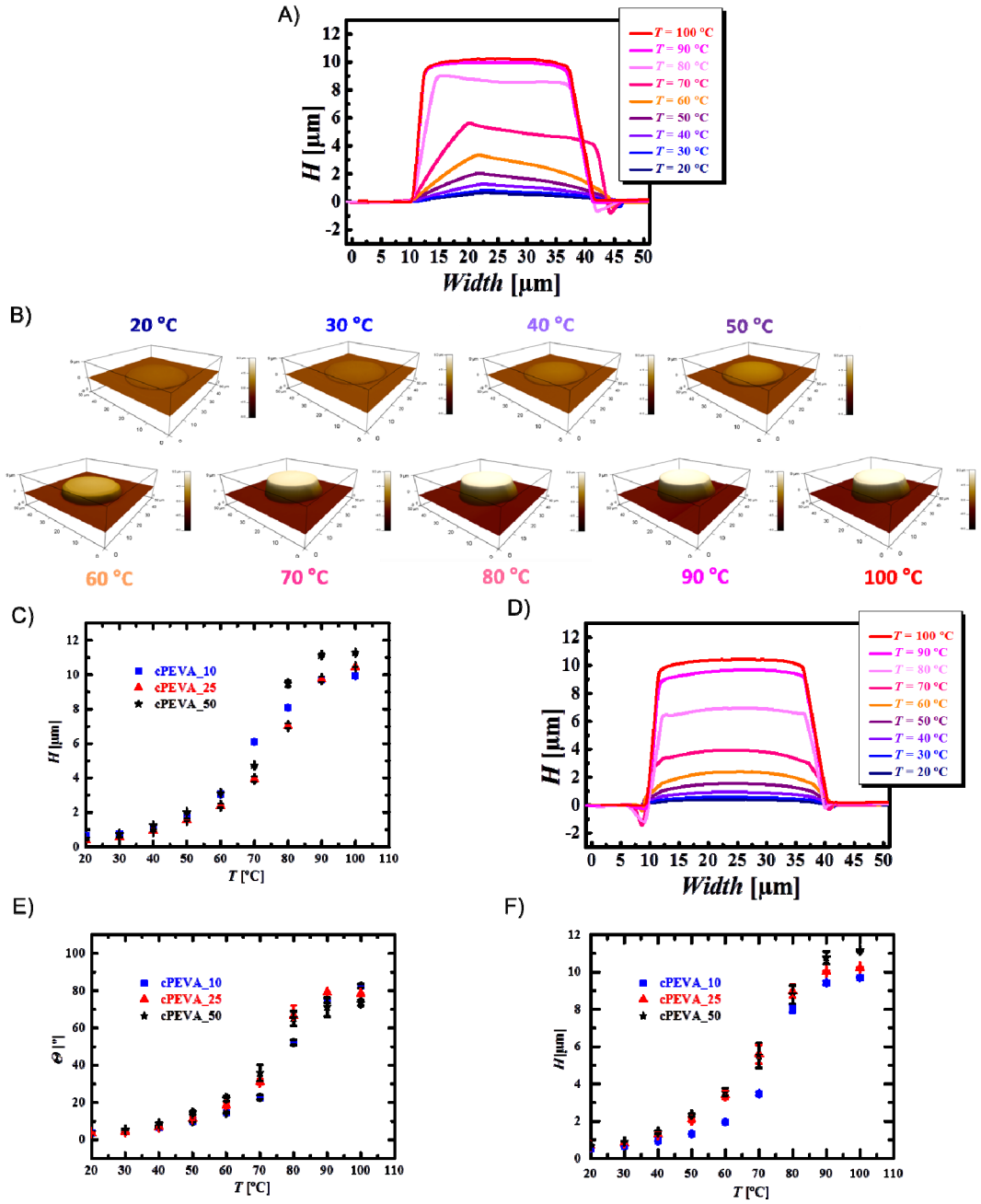

Figure 3. Recovery behavior of differently programmed microstructured cPEVA films either by vertical compression (A-C) or tilted compression (D-F) observed by AFM at different temperatures. A) height profiles and height images B) of cPEVA_25 and C) height vs. recovery temperature graphs for micro-cylinders with different diameters. D) height profiles of cPEVA_25 and height E) as well as θ F) vs. recovery temperature graphs for micro-cylinders with different diameters.

CONCLUSIONS

Microstructured cPEVA films with micro-cylinder arrays were successfully fabricated by a soft lithography approach and programmed by two different deformation modes, vertical and

tilted compression. The temperature driven shape recovery of the microstructures was examined by *in-situ* AFM experiments and visualized by optical microscopy. Excellent shape-memory properties, characterized by R_f values above 92±1% and R_r values ≥ 97±1%, could be achieved independent from the micro-cylinder diameter and the applied compression mode. The obtained switching temperatures were similar to the applied programming temperature of 70 °C. During heating of cPEVA films programmed by tilted compression a continuous increase in θ with temperature was observed, which can be utilized for quantification of the shape recovery. These findings impressively illustrates that microstructures can memorize the way how the programming was conducted by recalling the reverse microscopic shape change during thermally-induced shape recovery. In such a way the generated local recovery forces can be adjusted enabling a controlled micro-manipulation suitable for designing adaptive microfluidic devices.

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