



Short communication

Dual-responsive triple-shape memory polyolefin elastomer/stearic acid composite



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ABSTRACT

Triple-shape memory polymers (triple-SMPs) have one permanent and two temporary shapes, which enable more complex actuation than traditional dual-SMPs. This work reports a novel polyolefin elastomer (POE)/stearic acid (SA) composite with excellent triple-shape memory and dual-responsive properties. SA displays two well-separated thermal transitions when melt-blending with POE, and is capable of memorizing two temporary shapes under different temperatures. It is found that the robust “house of cards” structure formed by the flake-like SA crystals in the composite is the key player behind the unique behavior. In addition, the actuation of the POE/SA composite can also be triggered upon exposing the material to the appropriate chemical vapor at room temperature. The triple-shape memory and dual-responsive ability atop the simple preparation process dramatically widen the applications of this fantastic material.

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1. Introduction

Shape memory polymers (SMPs) are the smart materials that are able to adopt various temporary shapes and recover to the original shapes upon an external stimulus, like heat, UV light, electric or magnetic field, or moisture [1–5]. This unique shape change ability makes SMPs a highly desirable class of materials for numerous applications, such as intelligent packaging, aerospace, sensors, actuators, and smart fabrics [6–8]. The thermally-induced SMPs usually use crystalline polymers [9–13] or crystallizable segments [14–17] as the switching phase to fix the temporary shapes. Exposing such a SMP to heat, causes the switching phase to exist above its transition temperature (T_{trans}) (the melting temperature) and in a highly deformable state. Subsequent deformation with an applied force and cooling below the T_{trans} freezes the temporary shape through crystallization of the switching phase. By heating the material above T_{trans} again, it will recover to its original shape by the entropic force [18].

Recently, small molecular crystals (SMC), such as paraffins or fatty acids, are discovered to be promising candidates for the switching phase of SMPs. Compared to the crystalline polymers with low melting point, paraffins and fatty acids are substantially cheaper and only need very low supercooling to trigger crystallization, and thus attract increasing interest. Weiss et al. made SMPs with high fixity and recovery ratios by adding fatty acids or fatty acid salts to elastomeric ionomers [19–22]. Feng et al. reported making shape memory elastomers through solution blending and precipitation of paraffins and poly(styrene-*b*-(ethylene-*ran*-butene)-*b*-styrene) (SEBS) or olefin block copolymer (OBC) [23,24]. Cavicchi et al. obtained a robust SMP by swelling cross-linked natural rubber with stearic acid (SA) [25]. So far, the reported stimulus for SMC-based shape memory polymers is heating, however, for some specific applications where large temperature fluctuations are undesirable, non-thermal stimuli might be required, for example, chemo-sensors for detecting volatile gases. On the other side, the dual-shape memory effect only enables one directed movement in a shape recovery cycle. The capability to perform two or more independent shape changes, known as triple-shape or multi-shape effects [26–32], will allow complex actuation and tremendously broaden the field of potential applications.

In this work, the crystalline small molecule SA is selected to melt-blend with POE, which is a thermoplastic elastomer with

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good elastic recovery, by twin-screw extruder. No organic solvents are involved in the extrusion process and the final material is directly obtained without other treatment. The POE/SA composite shows good capability to fix two temporary shapes, recover sequentially from one shape to the other, and eventually regain the permanent shape in a single shape memory cycle. In addition, POEs are non-polar materials with saturated molecular chains, providing excellent chemical stability at room temperature, while SA is a kind of small molecular fatty acid, which is easily soluble in ether, tetrahydrofuran (THF), etc. Thus, the POE/SA composites are good candidates for chemo-responsive (solvent-driven) SMPs. A nearly full shape recovery is achieved when the composite is exposed to THF or ether vapor at room temperature. The present study provides an efficient and scalable strategy to generate triple-SMPs with dual-responsive properties.

2. Experimental section

2.1. Specimen preparation

The SA with a melting temperature $T_m = 69\text{--}70\text{ }^\circ\text{C}$ was purchased from Sinopharm Chemical Reagent Company (Shanghai, China). POE (8450) was purchased from the Dow Chemical Company. The SA and POE were dried at $50\text{ }^\circ\text{C}$ for 12 h prior to extrusion.

The POE/SA composites were prepared using a Micro 27 GL-40D (Leistritz, Nuremberg, Germany) twin-screw extruder and a temperature profile of 100, 120, 130, 140, 150, 175, 200, 175, and $150\text{ }^\circ\text{C}$, from the main feeder to die, was used to optimize blending quality. The SA content in the composites was 10, 30, and 50 wt%.

2.2. Characterization

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the POE/SA composites with different SA content were obtained using Thermofisher Nicolet IS5 in the ATR mode. Pure POE and SA were also measured for reference. The thermal properties of the POE/SA composites were evaluated by a Mettler DSC-821e apparatus (Mettler Toledo, Switzerland) in nitrogen atmosphere. The tensile testing was conducted on a SANS CMT6503 universal testing machine (Shenzhen, China) with a crosshead speed of 50 mm/min. The as-extruded POE/SA composites were fractured in liquid nitrogen and the cross sections were observed by a field emission scanning electron microscopy (FESEM) (Magellan 400, FEI Co. Ltd.) at 10.0 kV. The polarized optical microscopy (POM) observations were carried out using Olympus (BX51) optical microscope and Olympus (C-5050ZOOM) camera. A Linkam (350) hot stage was used to control the sample temperature.

2.3. Shape memory testing

The triple-shape memory testing was carried out by the following procedure. An as-extruded strip specimen with a size of $40\text{ mm} \times 2\text{ mm}$ (length \times diameter) was immersed into a water bath under a controlled constant temperature of $80\text{ }^\circ\text{C}$ for 2 min and was bent into an "L" shape ($\theta_1 = 90^\circ$). The L-shaped specimen was transferred into a water bath at $50\text{ }^\circ\text{C}$ while holding the applied force constantly for 2 min. After the applied force was released, a small amount of recovery occurred and the bending angle was recorded as $\theta_{\text{fix}1}$. The specimen was further bent to a "U" shape ($\theta_2 = 180^\circ$) at $50\text{ }^\circ\text{C}$ and then transferred into a water bath at $25\text{ }^\circ\text{C}$ while holding the applied force constantly for 2 min. After the applied force was released, a small amount of recovery occurred and the bending angle was recorded as $\theta_{\text{fix}2}$. For shape recovery, the specimen with fixed shapes was immersed into the water bath of $60\text{ }^\circ\text{C}$ and $80\text{ }^\circ\text{C}$ in sequence and the resultant bending angles were

recorded as $\theta_{\text{rec}1}$ and $\theta_{\text{rec}2}$ respectively. The same specimen was tested for five times. The shape fixity ratio (R_{f1} and R_{f2}) and the shape recovery ratio (R_{r1} and R_{r2}) were calculated according to the following equations.

$$R_{fi} = \frac{\theta_{\text{fix}i}}{\theta_i} \times 100\%$$

$$R_{r1} = \frac{\theta_{\text{fix}2} - \theta_{\text{rec}1}}{\theta_{\text{fix}2} - \theta_{\text{fix}1}}$$

$$R_{r2} = \frac{\theta_{\text{rec}1} - \theta_{\text{rec}2}}{\theta_{\text{rec}1}}$$

3. Results and discussion

The FTIR-ATR spectra of POE, SA and POE/SA composites are shown in Fig. S1. The peaks between 2840 and 2920 cm^{-1} are attributed to the stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ groups in both POE and SA. The characteristic peak at 1700 cm^{-1} is assigned to the stretching vibration of the $\text{C}=\text{O}$ group in SA. The characteristic peaks at 1295 and 935 cm^{-1} indicate the in-plane bending vibration and the out-of-plane bending vibration of the $-\text{OH}$ group in SA, respectively. The spectra of the POE/SA composites include all the peaks of the POE and SA. The results show that there is no chemical interaction between the two components and the SA content in the composites is as expected. The thermal properties essential for triggering SMP were investigated by differential scanning calorimetry (DSC), as shown in Fig. 1a. The melting peak around $100\text{ }^\circ\text{C}$ (T_{m1}) is attributed to the crystalline ethylene segments of POE, which form a physical network within POE, prevent chain relaxation, and consequently provide the driving force for shape recovery. This intrinsically physical cross-linking leads to an important advantage that the permanent shape of the material can be changed when the temperature is raised above T_{m1} . On the other hand, the fixity of temporary shapes is determined by SA. The melting point of pure SA is at $73\text{ }^\circ\text{C}$, while it splits into two peaks upon incorporation with POE. For the POE/SA (50/50) composite, the two distinct melting points are at $72\text{ }^\circ\text{C}$ (T_{m2}) and $50\text{ }^\circ\text{C}$ (T_{m3}) respectively, which provides the feasibility of generating good triple-SME. The two well-separated thermal transitions of SA can sequentially fix two temporary shapes through crystallization with temperature decreasing, and the fixed shapes can be released in the reverse order upon heating. The three cycles of heating and cooling thermograms of the POE/SA (50/50) composite are shown in Fig. S2. For the POE/SA (70/30) composite, the lower melting temperature T_{m3} shifts to $45\text{ }^\circ\text{C}$, approaching the body temperature range. This is potentially useful for medical applications, since it enables shape recovery at mild conditions [33,34].

The tensile stress-strain behavior of the materials was investigated, as shown in Fig. 1b. The POE/SA (90/10) composite retains the ductility of POE and displays a typical elastomeric behavior with no yield point. The elongation at break is higher than 1000% and the tensile strength is around 15 MPa. A yield point appears when the content of SA increases to 30 wt%. The elongation at break and the tensile stress at large stain exhibit a decreasing tendency with the SA content. However, for the POE/SA (50/50) composite, the elongation at break is still close to 600% and the tensile strength is around 7 MPa, which indicates the material maintains the tenacity and deformation ability, which is important for the shape memory performance.

The structures of the POE/SA (50/50) composite were studied by

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