Composites Part A 110 (2018) 70–75

Contents lists available at ScienceDirect

Composites Part A

journal homepage: www.elsevier.com/locate/compositesa

Light-actuated reversible shape memory effect of a polymer composite

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ARTICLE INFO

Keywords:
Shape memory
Light-induced
Reversible actuator

ABSTRACT

In the current study, a novel polymer composite with excellent light-actuated two-way shape memory effect (2W-SME) was fabricated using poly (ethylene-co-vinyl acetate) (EVA) as matrix and *p*-aminodiphenylimide (*p*-AP) as both light-absorber and heat source (EVA/*p*-AP). Unlike traditional thermally-driven two-way reversible shape memory polymers, in our concept, the EVA/*p*-AP featured remotely controlled and light-manipulatable reversible two-way shape memory behaviors. Utilizing the distinct light-responsive behavior of *p*-AP in the irradiation of 365 nm ultraviolet (UV) light, the EVA/*p*-AP composite exhibited excellent light-actuated reversible 2W-SME by a light-manipulated procedure. The results from this study indicated that the composite material could have greatly potential applications in soft reversible drivers.

1. Introduction

Traditional shape memory polymers (SMPs) are an exciting class of intelligent materials that can be deformed into a provisional shape and return to the initial shape under suitable stimulus [1–13]. This ability has two distinct advantages: first, traditional SMPs can exhibit a series of complex shape transformations (spiral, petal, origami and so on) in response to an external stimulus; second, the original shape can be deformed and reprogrammed multiple times. Due to these unique properties, traditional SMPs have greatly potential applications in various fields, such as aerospace field [14], biomedical devices [15], optoelectronic field [16,17], self-healing materials [18,19] and information carriers [20–22]. However, the so-called traditional SMPs with non-reversible one-way shape memory effect (1W-SME) show disadvantages when used in some fields where reversible bidirectional SME is needed.

Most recently, semi-crystalline polymers have been reported to exhibit reversible two-way SME (2W-SME), as their synthesis is easier and cheaper than liquid crystalline elastomers or other polymers [23–27]. Two strategies have been used to realize this feature. That is, under persistent external mechanical forces [28] or stress free conditions [29], the 2W-SMPs exhibit invertible changes between two shapes upon temperature variations. The actuating mechanism of 2W-SME under constant forces is that the polymer segments crystallize and elongate along the direction of constant forces below the crystallization temperature, and melting leads to segments shrinkage above the melting temperature [30]. The behavior of 2W-SME under stress free conditions results from the correlated interplay between a network formed by chemically cross-linking and a crystalline scaffold, each having the ability of encoding a unique shape. The relaxation of elongated segments upon heating is reversed by polymer crystallization along the original pathway on cooling [31]. Currently, the known reversible shape switching of 2W-SMPs is generally observed by outer direct heating and cooling cycles, and the cooling temperatures are low [26,29]. However, this characteristic of 2W-SMPs restricts their applications in some fields, such as aerospace, textile, biomedicine, and so on. To circumvent this situation, a remotely controlled and reversible 2W-SME with relatively high cooling temperature is highly desired.

Accordingly, in this study, we report reversible 2W-SME in chemically cross-linked poly (ethylene-co-vinyl acetate) (EVA) using dicumyl peroxide (DCP) as thermal initiator with *p*-aminodiphenylimide (*p*-AP) as a light-responsive source (EVA/*p*-AP) capable of transformation between two different shapes under cyclic UV light stimulation. Herein, mainly three samples with different weight ratios of *p*-AP and EVA have been fabricated to understand the light-manipulatable 2W-SME. Excitedly, the EVA/*p*-AP composite with 0.5 wt% *p*-AP exhibits excellent 2W-SME by a light-manipulated procedure. Therefore, this developed reversible 2W-SMP can be used as remotely controlled smart devices like light-manipulated self-sufficient grippers, artificial muscles, shape-switching drug delivery carriers, and so on.

2. Experimental section

2.1. Materials

Poly (ethylene-co-vinyl acetate) (EVA, 18 wt% vinyl-acetate) was

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https://doi.org/10.1016/j.compositesa.2018.04.019
Received 29 January 2018; Received in revised form 28 March 2018; Accepted 16 April 2018

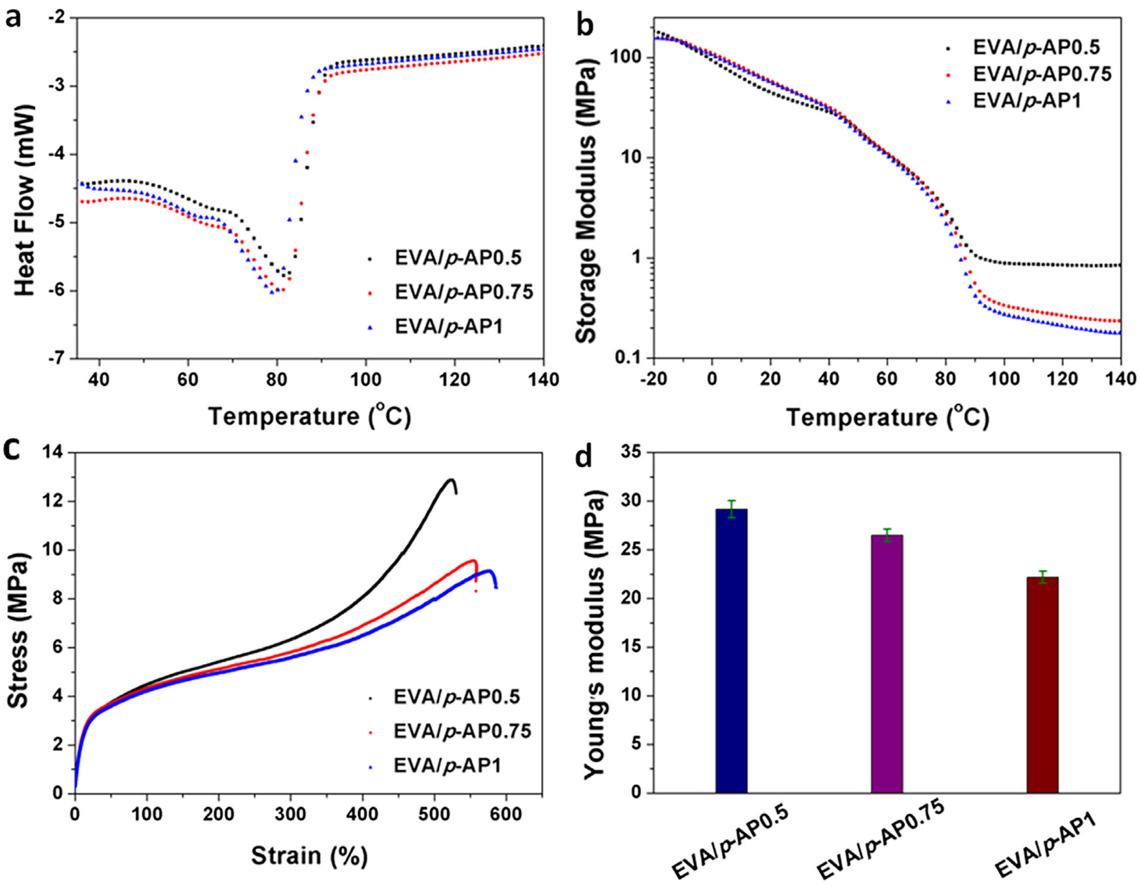

Fig. 1. (a) Representative heating DSC thermograms of the EVA/*p*-AP composites, (b) DMA curves of storage modulus, (c) tensile results at room temperature, and (d) Young's modulus values from the tensile test of the EVA/*p*-AP composites with *p*-AP: EVA weight ratios of 0.5: 100, 0.75: 100 and 1: 100. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

purchased from DuPont Company. Dicumyl peroxide (DCP, 98%) and toluene (99.8%) were purchased from Sigma-Aldrich. The *p*-aminodiphenylimide (*p*-AP) was obtained from Aladdin. All chemical reagents were used without any further purification or modification.

2.2. Preparation

The EVA/*p*-AP polymer composite was synthesized as follows. Firstly, *p*-AP and EVA with the weight ratios of 0.5: 100, 0.75: 100 and 1: 100 were dissolved in toluene, respectively. DCP with the weight of 4% EVA was dissolved in toluene and poured into the EVA & *p*-AP mixed solutions under a high speed stirring. Secondly, the mixed solutions were volatilized in an aerator by stirring. When the mixed solutions became viscous, they were further dried in vacuum for one day at ambient temperature. After drying, the polymer mixture was thermally embossed at 130 °C for 45 min in a stainless steel mold at 3 MPa. Finally, stripping the material from the mold, the EVA/*p*-AP sheet with thickness of about 1 mm was obtained.

2.3. Characterization

Differential scanning calorimetry (DSC 1, Mettler-Toledo, Switzerland) was used to characterize the thermal properties of the polymers. Prior to the actual tests, all samples were raised to 130 °C and maintained for several minutes in order to delete any unknown thermal history. The heating rate was 10 °C min^{-1}. Dynamic mechanical analysis (DMA, Q800, TA Instruments, USA) measurements were conducted in tension mode from −30 to 150 °C. The heating rate was 3 °C min^{-1}, and the frequency was 1 Hz.

The room-temperature mechanical properties of the specimens were measured using a materials testing machine (Z010, Zwick/Roell, Germany) according to the ASTM D638 test method. The crosshead speed was 5 mm min^{-1}. Three specimens were tested.

2.4. Shape memory evaluation

DMA Q800 in a tension and controlled force mode was used to evaluate the shape memory behaviors. The rate was 5 °C min^{-1} during heating and cooling processes.

For 1 W-SME characterizations, shape fixity ratio (R_f) and shape recovery ratio (R_r) were calculated by:

$$R_f = \frac{\varepsilon}{\varepsilon_{load}} \times 100\% \tag{1}$$

$$R_r = \frac{\varepsilon - \varepsilon_{rec}}{\varepsilon} \times 100\% \tag{2}$$

ε_{load} denotes the highest strain under constraint, ε is the strain fixed after cooling and unloading, ε_{rec} is the strain which is unrecovered.

In a 2W-SME test under a constant load condition, the sample was heated at a high temperature, then a load was added. This load was kept constant in the whole testing process. The temperature was adjusted down and up between a low temperature and a high temperature at a rate of 5 °C min^{-1}.

In a 2W-SME test without stress, the samples were heated to a high temperature and kept for 5 min. Then a constant force was applied, followed by cooling the sample. When the temperature reached 0 °C, the stress was removed. Finally, shape deformation-recovery cycles were performed with repeated heating (below melting temperature) and cooling.