Composites Science and Technology 157 (2018) 202–208

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Reinforcement of shape-memory poly(ethylene-*co*-vinyl acetate) by carbon fibre to access robust recovery capability under resistant condition

Hui Xie, Lu Li, Xiao-Ying Deng, Chuan-Ying Cheng, Ke-Ke Yang*, Yu-Zhong Wang

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China

ARTICLE INFO

Article history:
Received 16 September 2017
Received in revised form
27 December 2017
Accepted 17 January 2018
Available online 31 January 2018

Keywords:
Smart materials
Carbon fibres
Polymer-matrix composites
Shape memory polymer

ABSTRACT

Poly (ethylene-*co*-vinyl acetate) (EVA), as one of commercial polymers, has been used early to fabricate shape-memory polymers (SMPs). However, its low recovery stress restricts the potential applications in some tough conditions due to its high flexible feature. Herein, we developed a series of EVA-based composites (cEVA/CF) with remarkably enhanced recovery stress both in free-state and resistant condition by incorporating different amounts of a stiff filler carbon fibre (CF) into the commercial EVA matrix. The observation of morphology showed that CF was well dispersed in EVA matrix, and the thermal properties of cEVA/CF composites were just slightly affected as demonstrated by the DSC analysis. More importantly, the modulus of composites was significantly improved, especially above the melting temperature (T_m). This feature is valuable to improve the recovery stress of cEVA/CF composites as both the shape deformation and recovery occur at $T > T_m$. To investigate the recovery behaviors of the cEVA/CF composites in free-state or with varying external loads, the strategy that combing appropriate clamp operation and well-designed procedures under two DMA modes (DMA Controlled Force and DMA Iso-Strain) was put forward. Compared with pristine cEVA, cEVA/CF composites with 5–30 wt% CF possessed 100–650% increase of recovery stress. Consequently, cEVA/CF composites exhibited a robust shape recovery performance under resistant condition, while the recovery capability of pristine cEVA was totally depressed. Aiming at practical applications, a model of deployable device made of cEVA/CF30 was well-established.

1. Introduction

Due to the capacity of recover its original shape by responding to external stimuli [1–3], shape memory polymers (SMPs) show great potential in real applications involving from simple actuators to complicated biomedical devices [4–8]. As an important class of SMPs, thermally-induced SMPs attract great attention from researchers and engineers since they can be easily designed and actuated just in virtue of the intrinsic thermal characteristics of polymers. In principle, polymers that have a thermal transition (T_{trans}) in the temperature range of interest for certain application can be utilized as switch segment of a SMP. Thus, commercial polymers have distinct advantage in designing SMPs as they are economic and can be simply produced. Up to now, several commercial polymers have been used to design SMPs, such as cross-linked polyethylene (PE) [9], epoxy resin (ER) [10,11], polyurethane (PU) [12,13], polynorbornene (PNB) [14] and poly (ethylene-*co*-vinyl acetate) (EVA) [15,16]. One of the most successful and mature products is the heat-shrink tubing developed from commercial EVA. Because EVA has a broad and suitable melting transition with a adaptable T_m ranging from about 25 to 90 °C [17] and exhibits crystalline-induced elongation (CIE) phenomenon after crosslinking [18], in fact, it possesses versatile functions of one-way shape memory effect (1W SME) and two-way shape memory effect (2W SME), which makes it a good candidate for the SMPs towards multiple practical applications [19–23].

However, as a typical copolymer of ethylene-vinyl acetate with excellent flexibility, EVA (cross-linked or not) is very soft at room temperature with very low stiffness, let alone the situation at high temperature above its T_m ($T > T_m$). From the view of shape memory

* Corresponding author.
E-mail address: kkyangscu@126.com (K.-K. Yang).

https://doi.org/10.1016/j.compscitech.2018.01.031
0266-3538/

process, both deforming and recovering are conducted at $T > T_m$, so the existing shape-memory EVA systems exhibit low recovery stress, which greatly limits their potential applications. Out of the idea shape recovery environment, the actual shape-memory products may need to recover with load or constraint no matter in expected way or not. Hence, it brings a big challenge for researchers to develop SMPs with high recovery stress in the working temperature range and even maintain robust shape memory performance under resistant condition just by employing the commercial polymers, such as EVA.

Taking a full view of previous works, adding stiff reinforcements is considered as a facile and efficient approach to improve the recovery stress of SMPs [24]. VAIA and coworkers demonstrated that adding carbon nanotubes into the thermoplastic elastomer could release up to 50% more recovery stress than the pristine resin [25]. Gall and coworkers incorporated particulate SiC into shape-memory resin, and the bend recovery stress was shown to increase by 50% when adding 20 wt% SiC [26]. They also utilized carbon fibre to reinforce SMPs [27], and similar work was also reported by Leng's group [28]. Just as we mentioned before, programming and recovering of EVA materials are all conducted at $T > T_m$. So, improving the recovery stress mean increasing the stiffness at a specific deformation temperature T_d ($T_d > T_m$). Hence, we think carbon fibre is the best choice to reinforce EVA material due to its high modulus and potential benefit in forming EVA chain entanglements at T_d, which is significant to the enhancement of stiffness and recovery stress.

Besides the enhancement of recovery stress, the shape recovery performance under resistant condition should also be highly concerned as SMPs may function with external resistances. Unfortunately, the researches focused on this aspect are very limited [29–31]. Though the non-ideal recovery has been realized by researchers, systematical and comprehensive study involving recovery stress with or without constraint become a very pressing issue.

To enhance the shape recovery stress of EVA, we developed a series of composites (cEVA/CF) by facilely blending commercial EVA matrix with carbon fibre (CF) first and thermal-crosslinking by the existing of dicumyl peroxide (DCP) thereafter. Generally, a full cycle of one-way shape-memory process includes programing, cooling (fixing) and recovering. For a reasonable comparison of the recovery behavior, most important of all, it is crucial to achieve the same temporary strain [32]. However, as EVA exhibits CIE during cooling which varies with the CF content, it is difficult to achieve the same temporary strain by a conventional programming. In the present work, the strategy that combing appropriate clamp operation and well-designed procedures under two DMA modes (DMA Controlled Force and DMA Iso-Strain) was used to investigate the recovery behaviors of the cEVA/CF composites in free-state or with varying external loads, more importantly, the essential reason for the improvement of recovery stress has been revealed. Finally, a model of deployable device based on cEVA/CF30 was established, and its robust recovery capability under resistant condition makes sense to design more complex devices for real applications.

2. Materials and methods

2.1. Materials

Poly (ethylene-*co*-vinyl acetate) (EVA, 28 wt% vinyl-acetate) was a product from DuPont Packaging & Industrial Polymers, USA. Carbon fibre (CF) with a brand name of T700 was provided by Toray, and the length of CF is about 5 mm. Dicumyl peroxide (DCP) was purchased from Chengdu Kelong Reagent Company, China. All chemicals were used as received.

2.2. Preparation and characterization of cEVA/CF composites

A series of cEVA/CF composites with different mass ratios of CF to EVA (CF wt%) (DCP wt% was 3%) was prepared through two steps, mixing and crosslinking. For synthesis details and basic characterizations, please see in Supporting Information.

2.3. Evaluation of shape-memory effects

2.3.1. General test for SME

The tests were performed on DMA with Controlled Force mode in the followings: a sample was deformed at 100 °C under applied stress, cooled to 0 °C and then released the stress, and finally reheated to 100 °C. The shape fixity ratio (R_f) and the shape recovery ratio (R_r) can be simply calculated by conventional methods [1,33,34].

2.3.2. Investigation of recovery stress

The procedures were conducted as follows: 1) Deforming a cEVA/CF sample at 100 °C by applying stress at a rate of 0.2 MPa/min using DMA Controlled Force mode. When the strain reached 15–17%, the program was manually stopped and the clamp would be locked as preset. 2) Cooling the sample to 0 °C, the strain maintained constant (ε_d) because the tension clamp was locked. 3) Shifting the test mode into DMA Iso-Strain and reheating the sample to 100 °C using a rate of 5 °C/min. The clamp was float and the dynamic strain was set as 0.05%.

2.3.3. Constrained recovery behavior under external stress

The procedures for investigating the constrained recovery performance of cEVA/CF were performed as follows: Steps 1) and 2), the deformation and fixing process, were the same as those mentioned just before. The deformed strain was also labeled as ε_d. 3) Using the DMA Controlled Force mode to apply different external stress on the sample in temporary shape (0 °C), and then reheating to 100 °C using a heating rate of 5 °C/min. The magnitude of recovery strain under each external load was expressed as ε_r. Four typical external stresses (also expressed as Load) were 0, 0.15, 0.40, 0.65 MPa, and the curves of strain *versus* time were recorded. The constrained shape recovery ratio ($R_{r\text{-}L}$) in each case can be calculated by Equation (1).

$$R_{r-L} = \frac{\varepsilon_r}{\varepsilon_d} \times 100\% \quad (1)$$

For better understanding, the test programs for the investigation of recovery stress and constrained shape recovery performance are further illustrated in Fig. 1.

3. Results and discussion

3.1. Preparation and basic characterizations

A series of cEVA/CF composites was prepared by melt blending at 100 °C and subsequently thermal-crosslinking initiated by DCP at 175 °C. Here, 3 wt% DCP was added to each blend to achieve high gel fractions, and CF wt% was adjusted from 0% to 30%. Accordingly, the composites were further coded as cEVA, cEVA/CF5, cEVA/CF10, cEVA/CF15, cEVA/CF20, cEVA/CF25 and cEVA/CF30, respectively. The morphology of cEVA/CF composites and the dispersion of CF in EVA matrix were observed by SEM. The images of three typical samples cEVA/CF5, cEVA/CF15 and cEVA/CF30 revealed that the rod-like CF showed a well dispersion in EVA matrix even its content reached 30% (Fig. 2a). It indicates that melt blending is an effective way to fabricate cEVA/CF composites. Owing to the good dispersion