Contents lists available at ScienceDirect

Materials Letters

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

Novel vapor-grown carbon nanofiber/epoxy shape memory nanocomposites prepared via latex technology

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ARTICLE INFO

Article history: Received 27 September 2013 Accepted 14 June 2014 Available online 21 June 2014

Keywords: Shape memory materials Polymeric composites Epoxy Carbon nanofiber Latex technology

A B S T R A C T

In this study, novel vapor-grown carbon nanofiber (VGCNF)/epoxy shape memory (SM) nanocomposites were prepared via latex technology. The prepared nanocomposites showed excellent SM functionality. The mechanical and SM properties of the nanocomposites were significantly improved by adding VGCNF. © 2014 Elsevier B.V. All rights reserved.

1. Introduction

Shape memory polymers (SMPs), which have attracted considerable attention in recent years because of their scientific and technological significance, are a new class of stimuliresponsive materials that can maintain a temporary shape and subsequently recover their original shape by external stimuli, such as heat, light, magnetic field, and chemicals [1–4]. As novel smart materials, SMP composites can be potentially applied in microelectromechanical systems, biomedical engineering, and space deployable structures [5].

Epoxies, which are widely used in many non-SM applications, such as coatings, adhesives, construction, and manufacturing, exhibit high strength, good thermal stability, and chemical resistance. Many recent studies have proven the good SM properties of epoxies [6–8]. The shape recovery ratio and elastic modulus of epoxies range from 98% to 100% and from 2 GPa to 4.5 GPa, respectively [1]. Unfortunately, the processes of epoxies are very environmentally unfriendly, complex, expensive, and the breakage elongation of epoxies are usually very low.

In the current study, latex technology was used to prepare VGCNF/epoxy SM nanocomposites. The mechanical and SM properties of the prepared nanocomposites were also valuated. The

http://dx.doi.org/10.1016/j.matlet.2014.06.084 0167-577X/© 2014 Elsevier B.V. All rights reserved. advantages of this technique include simplicity, versatility, reproducibility, and reliability. This study is the first to prepare VGCNF/ epoxy SM nanocomposites from water-borne epoxy resin using latex technology.

2. Material and methods

Preparation of VGCNF/epoxy SM nanocomposites: A three-step procedure was used to prepare VGCNF/epoxy SM nanocomposites, as shown in Fig. 1. First, VGCNFs (VGNF[®], Showa Denko K.K., Japan) were added to water-borne epoxy resin (synthesized by phase-inversion technique in our previous research [8,9]) with particles ranging from 50 nm to 300 nm and dispersed to homogeneity using an intensive mixer in a beaker at room temperature. A curing agent (AB-HGA[®], Zhejiang Anbang New Material Development Co., Ltd., China) was then added to the mixture. The weight ratio of the water-borne epoxy resin to the curing agent was 4:1. Second, the mixture was frozen in liquid nitrogen for 5 min and the aqueous solvent was removed using a Labconco Free Zone freeze-dryer operated at 0.1 mbar and -20 °C for 48 h. The resulting composite powder was compressed into films at 120 °C for 2 h between polypropylene sheets under a pressure of 10 MPa.

Experimental procedure: The images of the water-borne epoxy resin and VGCNFs were examined under a transmission electron microscope (JEM-2100F, JEOL, Japan) operated at 200 kV. The morphology of the nanocomposites was conducted under a field





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Fig. 1. Schematic of the three-step process for preparing of VGCNF/epoxy nanocomposites via latex technology. (A) TEM micrograph of the water-borne epoxy resin particles; (B) TEM image of pristine VGCNFs; and (C) SEM image of the fracture surfaces of the VGCNF/epoxy nanocomposites (fractured under liquid nitrogen). The inset of Fig. 1(C) is a sample of the VGCNF/epoxy nanocomposites. The VGCNF concentration is 1.0 wt%.



Fig. 2. (A) Recovery procedure of 1.0 wt% VGCNF/epoxy nanocomposites by pouring hot water (65 °C) in a Petri dish; and (B) storage moduli and tan delta values of the pristine epoxy resin, and 1.0 wt% VGCNF epoxy nanocomposites obtained from DMA testing.

emission scanning electron microscope (Ultra 55, Zeiss, Germany) operated at voltage of 3 kV. The storage modulus and tan delta of the nanocomposites were determined via a dynamic mechanical analysis (DMA) Q800 (TA Instrument, America) at a frequency of 1 Hz; the temperature was increased from 0 °C to 100 °C at a rate of 5 °C/min. The static tensile test of the pristine epoxy resin and the 1.0 wt% VGCNF/epoxy nanocomposites were carried out via a testing machine (INSTRON 3367) at a crosshead speed of 5 mm/ min using dumbbell-shape specimens at room temperature. At least five effective specimens were tested. The shape memory properties of the pristine epoxy resin and the developed nano-composites were examined by the fold-deploy shape memory test

[7]. The dumbbell-shape specimens with a square base (approximately $150 \times 10 \text{ mm}^2$) and a thickness of 3.5 mm were heated to 65 °C above glass transition temperature (T_g) in the oven, and then bent into a "U" shape circling a central axis with a diameter of 54 mm. The specimens were cooled to 25 °C below T_g at 25 °C in the air and held with a constant external force for 10 min. The specimens were unloaded at 25 °C, completing the shape fixity process. The specimens were heated from 25 °C to 65 °C under no load to examine their shape recovery capacity. Shape fixity and recovery ratios are important parameters for evaluating SMP characteristics [7,10]. These parameters are defined in Eq. (1) [7]. The maximum bending angle, bending angle, and bending angle at

each temperature were recorded as θ_{max} , θ_{fixed} , and θ_i , respectively.

$$R_f = \frac{\theta_{\text{fixed}}}{\theta_{\text{max}}} \times 100\%, \text{ and } R_r = \frac{\theta_{\text{max}} - \theta_i}{\theta_{\text{max}}} \times 100\%$$
 (1)

3. Results and discussion

As shown in Fig. 2(A) a sample with a thickness of 0.55 mm and a width of 32 mm was rolled after heating to 65 °C and then stored during cooling to room temperature. The shape recovery test was carried out by pouring hot water (65 °C) in a Petri dish. The nanocomposites with 1.0 wt% VGCNF shows fast recovery rate as soon as it comes in contact with water; it shows full recovery of its



Fig. 3. Stress-strain behavior of the pristine epoxy resin and the 1.0 wt% VGCNF/ epoxy nanocomposites at 25 $^\circ\text{C}.$

original shape within 5 s. The storage moduli and tan delta values of neat epoxy and its composite observed from the DMA test are shown in Fig. 2(B). Both samples underwent glass transition and exhibited similar temperature-dependent viscoelastic properties. The storage modulus observed at temperatures far below the T_{σ} was two orders of magnitude larger than that observed at temperatures above the T_g . For example, 1.0 wt% VGCNF/epoxy nanocomposites exhibited storage moduli of 3322.6 MPa at 15 °C and 8.7 MPa at 80 °C. These results suggest that the VGCNF/epoxy nanocomposites are excellent SM materials. With addition of VGCNF, the T_{g} of the composites was improved compared with the pristine epoxy. Good VGCNF dispersion and interfacial properties (an non-covalent functionalization between the surfactant of water-borne epoxy resin and VGCNFs caused by absorption of groups onto the VGCNF surface by π - π stacking effects, as proven in our previous research employing Raman spectroscopy [9]) between filler and matrix restricts the segmental motion of epoxy molecules, leading to increased T_g .

Fig. 3 shows the stress–strain behavior of the pristine epoxy resin and the VGCNF/epoxy nanocomposites. After the addition of VGCNF, the ultimate strength and yield strength of the VGCNF/ epoxy nanocomposites are higher than those of the pristine epoxy resin. This finding can be attributed to the reinforcing effect of VGCNFs: (1) superior tensile modulus and strength; (2) welldispersed and well-incorporated in the matrix. The surfactant of the water-borne epoxy resin, an non-covalent surfactant and mentioned in the above paragraph, can effectively improve VGCNF dispersion without damaging the VGCNFs by non-covalent functionalization [9,10]. The non-covalently attached molecules can help form a better interface between the VGCNFs and the epoxy, potentially improving the adhesion between the VGCNF and the surrounding epoxy matrix. As a result, an improvement in



Fig. 4. (A) Curves of recovery ratio with time in the first cycle of the shape recovery tests; (B) curves of fixity ratio with time at 25 °C; (C) schematic of shape recovery performance test; and (D) shape recovery behavior of the 1.0 wt% VGCNF/epoxy nanocomposites in an oven with an observation window at 65 °C.

mechanical properties was achieved. Interestingly, the ultimate strength of the pristine epoxy resin is lower than that of the common epoxy resin, whereas the ultimate elongation of pristine epoxy resin is much higher than that of the common epoxy resin [7]. This finding may be attributed to the addition of emulsifiers acting as a plasticizer in the preparation of the water-borne epoxy resin. However, the yield strength of the pristine epoxy resin is twice as higher as that of SM polyurethanes at 25 °C [11,12].

The SM properties of the pristine epoxy resin and developed nanocomposites are shown in Fig. 4. As shown in Fig. 4(A), the shape recovery ratios for both pristine epoxy resin and VGCNF/ epoxy nanocomposites are very high (approximately 100%). Moreover, the shape recovery rate of the nanocomposites is lower than that of the pristine epoxy resin. Furthermore, the advanced nanocomposites show excellent shape fixity (approximately 98%) even after 120 h at 25 °C, as shown in Fig. 4(B). The phenomena can be attributed to the high T_g composite with a high storage modulus, which required a higher deforming energy at the same temperature resulting in lower recovery rate, especially at low temperature. A high storage modulus also leads to a lower tendency of the composite to return to its original shape resulting in higher fixity ratio [13]. In addition, VGCNF particles will not only increase the fixity ratio but also keep the shape recovery ratio similar to the pristine bulk. Therefore, an extremely high shape fixity and recovery ratios, and excellence mechanical properties indicate the good SM functionality of the VGCNF/epoxy composites prepared via latex technology.

4. Conclusions

Novel VGCNF/epoxy SM nanocomposites were prepared via latex technology. With the addition of 1.0 wt% VGCNF, the yield strength and Young's modulus of the pristine epoxy resin are significantly increased. In addition, the SM properties are significantly improved. Notably, the shape recovery ratios of the VGCNF/epoxy nanocomposites are as high as 100%. The mechanical property of the pristine epoxy resin is more outstanding than that of SM polyurethanes, and the breakage elongation is much higher than that of the common epoxy resin at room temperature. Our proposed method is applicable to various host polymers and does not require organic solvents. Thus, the current simple and environmental friendly approach may be used to synthesize SM nanocomposites as temperature sensor materials. Future work will focus on the SM properties and electrical conductive behaviors of the novel nanocomposites.

Acknowledgments

The authors gratefully acknowledge the Instrumental Analysis Center of Zhejiang Sci-Tech University for their testing assistance during testing.

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