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Synergistic effect of siloxane modified aluminum nanopowders and carbon fiber on electrothermal efficiency of polymeric shape memory nanocomposite

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ABSTRACT

The present study reports an effective approach of significantly enhancing electrothermal efficiency and shape recovery performance of shape memory polymer (SMP) nanocomposite, of which shape recovery was induced by electrically resistive heating. Metallic aluminum (Al) nanopowders synthesized from Al^{3+} solution were chemically grafted onto carbon fiber. Siloxane groups were grafted onto surfaces of the Al nanopowders to enhance the interfacial bonding between the carbon fiber and SMP matrix via van der Waals force and covalent bond, respectively. The siloxane modified Al surfaces could improve both the electrically induced shape recovery performance and electrothermal efficiency through facilitating the electrically resistive heating from carbon fiber into the SMP matrix. Effectiveness of the synergistic effect between siloxane modified Al surface and carbon fiber was demonstrated to achieve the electrical actuation for SMP nanocomposites at a low electrical voltage below 4.0 V.

1. Introduction

As one representative of the intelligent shape memory materials, shape memory polymers (SMPs) gained significant interest in recent years [1–3]. With a specially designed structure, SMPs are able to change their deformed shapes and adapt to the conditions of their surrounding environment [4–7]. In addition to the macroscopic changes, SMPs also show a stimuli-responsiveness on the level of single molecule [8–10]. For instance, macromolecules adopt different configurations and conformation depending on the environmental conditions [11]. Here the shape memory effect (SME) in the SMPs is originated from the change in entropy function [12]. Generally, the SMPs are incorporated with at least two different "phases", i.e., a stable network and a switching transition, which could be triggered by the external stimulus. The former phase plays an essential role in stabilizing the whole polymer network and retaining its original shape. On the other hand, the second phase temporarily fixes the shape by a glass transition or a melting transition [13–15]. This is the classic dual SME in the SMPs, i.e. one temporary shape is transformed into the permanent shape [16,17]. In contrast, triple and multiple SMPs feature two or more than two temporary states besides their permanent one. There are two principal strategies for the design of triple and multiple SMPs, i.e., a very broad thermal transition or multiphase design [18–20].

Currently, SMPs are investigated extensively in the research fields of smart materials and structures due to their unique SME and tailorable properties [21–23]. Tremendous progress in synthesis, characterization, modeling and simulation of the SMPs has been made in the last two decades [24–28]. Thermally stimuli-responsive SME in SMPs have also been achieved using photo-active, magnetic-active, water (or solvent)-active and electro-active approaches [22,29–32]. Utilization of electrically resistive heating to trigger the SME in the SMPs is desirable and convenient to apply in a number of practical applications, especially where directly thermal heating is not easily achieved [33–37]. A variety of conductive ingredients have been added into the insulating SMP

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matrix to enable remote actuation of shape recovery via the electrically resistive heating [38–40]. Among these conductive ingredients, nanopaper, made from an aggregate of carbon nanotubes (nanofibers or graphene), has triggered enormous interest due to its superior electrical properties [41–43]. It was found that the electrical resistivity of the nanopaper enabled SMP nanocomposite is approximately 0.1 Ω cm [44]. However, the interfaces between the nanopaper and SMP matrix could be a critical issue due to a large dissimilarity in their electrically and thermally conductive properties [37–41]. Consequently, the efficiency of heat transfer from the nanopaper to the SMP matrix is seriously limited [45,46]. Aluminum (Al) nanopowders have good electrical and thermal conductivities. And it would be beneficial to combine Al nanopowders with organically reactive groups for carbon fiber and SMP matrix to enhance the electro-actuation efficiency. A synergistic effect of siloxane modified aluminum (Al) surface and carbon fiber is introduced in this study. A layer of metallic Al nanopowders with a variety of thickness was grafted onto the carbon fibers to improve the thermal conductivity perpendicular to the fiber mat. Siloxane groups were then employed to modify the Al surface, and thus the interfacial bonding between the SMP matrix and carbon fiber was significantly improved via van der Waals force and covalent bond, respectively. There are three aims in this study via introducing modified Al power coated on carbon fiber, one is to enhance thermal conductivity, the second is enhance electrical conductivity and the last is bonding. The combination of siloxane modified Al surface and carbon fibers was consequently used to achieve an efficiently electrical actuation and improve electrically induced recovery performance of the SMP composites at low voltages of 4.0 V, 5.0 V and 6.0 V.

2. Experimental details

The vinyltriethoxysilane (VTES) solvent was purchased from Aladdin Chemistry Corporation and the silane hydrolysate was prepared into a water and ethanol mixture. 1 ml VTES solvent was initially added into the mixture that was incorporated of 1.5 ml distilled water and 22.5 ml ethanol. The volume ratio of VTES: distilled water: ethanol was 4:6:90, where the pH value was ranged from 6 to 7. The mixture was subsequently mechanically stirred for 2 h and then was kept for 3 days to enable a sufficient number of active SiOH groups generated, as illustrated in Fig. 1.

The metallic Al nanopowders were grafted onto the carbon fiber mat via a sputtering approach in a vacuum. The Al layers with different thicknesses of 300 nm, 600 nm, 1000 nm, 1500 nm and 1800 nm were deposited onto the carbon fiber mat. The carbon fiber mat grafted with Al nanopowders were then soaked in a silane hydrolysate at 25 °C for 100 s and then cured at 120 °C for 20 min to modify the Al surface by siloxane groups. A schematic illustration of the modification process of the Al surface by siloxane groups is shown in Fig. 2.

The SMP used in this study is an epoxy-based fully formable thermoset SMP resin. After being cured, the glass transition temperature of the SMP is approximately 110 °C. Resin transfer molding technique was used to fabricate the SMP nanocomposites. The carbon fiber mat incorporated with siloxane modified Al surface was placed onto the bottom of the mold. After filling in, the mixture was cured at a ramp of approximately 1 C/min from 25 °C to 80 °C and kept for 3 h before being ramped to 100 °C at 1 °C/min and this was also maintained for 3 h. Finally, the sample was ramped to 150 °C at 1 C/min and kept at this temperature for 5 h to produce the final SMP nanocomposites.

Scanning electron microscopy (SEM) was used to study the morphology and structure of carbon fibers grafted with Al nanopowders and siloxane modified Al surface. The structural determination of the siloxane groups surface modified Al nanopowders was performed on the Fourier transform infrared (FTIR) spectroscopy (Nicolet AVATAR 360) in a transmittance mode from 4000 to 400 cm^{-1}. The electrical resistivity of the SMP nanocomposite incorporated with the carbon fiber grafted with siloxane modified Al layer was determined with a van der Pauw four-point probe apparatus, which has four probes with an adjustable inter-probe spacing.

3. Results and discussion

3.1. Morphology of siloxane modified Al surface

Surface morphology and microstructure of carbon fibers grafted with Al nanopowders and siloxane modified Al surface obtained from SEM are shown in Fig. 3. The morphology and structure of Al nanopowders are visible along the axial direction of the carbon fibers, as shown in Fig. 3(a) and (b). It is shown that the Al nanopowders are attached and homogeneously cover the entire surface of carbon fiber and stick to the carbon fibers due to their large specific surface areas. On the other hand, the morphology and structure of the Al surface decorated by the siloxane groups are presented in Fig. 3(c) and (d) at a scale of 10 μm and 5 μm, respectively. The siloxane modified Al nanopowders have a diameter ranging from 300 to 800 nm. There is an oxidation reaction to remove the metallic particles, resulting in the increase of roughness of Al aggregates. This could increase the interfacial bonding between the carbon fiber and SMP matrix via increased mechanical friction, together with adding the reactive organic siloxane groups.

3.2. Fourier transform infrared (FTIR) spectroscopy

FTIR measurement results are shown in Fig. 4. Two major peaks can be observed at 1729 cm^{-1} for C–O band and 1004 cm^{-1} for the Si–O–C band. The frequencies around 1729 cm^{-1} and 1004 cm^{-1} are linked to the Al surface modified by the siloxane. The siloxane groups are surface grafted onto the Al nanopowders that are expected to react with the polymeric SMP macromolecules to improve the interfacial bonding with the carbon fiber via the plasticizing effect. There is another actively unsaturated groups of -Si-CH=CH_2 on the Al surface to react with the epoxy-based polymer matrix via chemical copolymerization interaction. On the other hand, the Al nanopowders were grafted onto the carbon fiber mat via a sputtering approach. There is a large van der Waals force between Al nanopowders and carbon fiber due to their high

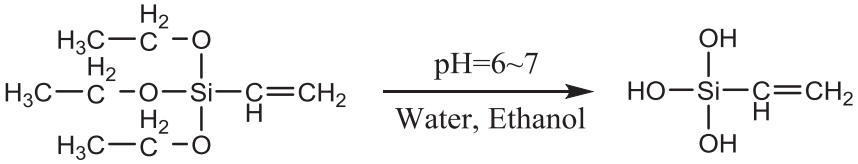

Fig. 1. The hydrolytic process of VTES.