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Synergistic effects of carboxylic acid-functionalized carbon nanotube and nafion/silica nanofiber on electrical actuation efficiency of shape memory polymer nanocomposite

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ABSTRACT

Synergistic effects of self-assembled carboxylic acid-functionalized carbon nanotube (CNT) and nafion/silica nanofiber on the electro-activated shape recovery behavior of shape memory polymer (SMP) nanocomposite were investigated. Carboxylic acid-functionalized CNTs were self-assembled onto the carbon fiber mat to enhance their bonding reliability and achieve efficient electrical actuation for SMP matrix. Nafion/silica nanofibers were electrospun onto surfaces of the carbon fiber mat to prevent electrically resistive heat dissipation. The combination of electrically/thermally conductive CNTs and thermally resistive nafion/silica nanofibers results in improvement for both electrically induced shape recovery and actuation efficiency in the SMP nanocomposite.

1. Introduction

Shape memory polymers (SMPs) are one of the fascinating shape memory materials featured with the shape memory effect (SME), high elastic strain, tailorable transition temperature as well as a wide ranges of mechanical and physical properties [1–5], and they have attracted significant academic and industrial attentions due to their potential applications in biomedicine, aeronautics, astronautics and textile [6–12]. In the last three decades, tremendous progress in chemical synthesis, characterization, composite science and technology, design of actuation approach, modeling and simulation of shape recovery behavior results in a rapid development and applications of SMP materials [13–18]. The electrical actuation of the SMPs is desirable in a number of engineering applications, especially in where direct heating is not conveniently achievable [19–21].

Most pristine SMPs are inert to electrical current, thus preventing the SME from being directly induced via electrically resistive heating. A variety of electrically conductive nanoparticles, such as carbon nanotubes (CNTs) [22], carbon black [23], carbon nanofibers (CNFs) [24,25], graphene, Au nanorods [26] etc., have been introduced into SMP nanocomposites. However, it is generally difficult for dispersion control of the nanoparticles to achieve a continuously and steadily conductive path or network in polymer matrix, thus resulting in a large electrical resistivity [27,28]. Consequently, CNT, CNF or graphene is scaled up into alignment, mat or nanopaper forms to provide a continuously and steadily conductive path to significantly reduce the electrical resistivity, and achieve efficient electrical actuation at a low electric voltage [29–34]. However, the interface bonding between the SMP matrix and nanopaper is weak due to their large dissimilarity in electrically and thermally conductive properties, causing limited applied electric current and slow recovery speed [35]. Recently, a synergistic hybrid of nanoparticles and nanopaper (or surface modified nanopaper) was employed to improve both the thermally and electrically conductive properties of SMP matrix and increase the recovery speed [32]. It should be noted that the electrical actuation efficiency, of which is a measure of the conversion rate transformation from electric energy into electrically resistive heat

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energy, has not been systematically investigated in the previous studies [32,35,36]. Effective ratio used to calculate the efficiency of the energy transformation from electricity into resistive heat that is used to trigger the shape recovery of SMP matrix. Furthermore, the resistive heat is not completely utilized to transfer to the SMP matrix due to the energy dissipation in the air in practical. Therefore, high actuation efficiency is critical for the sustainable development and practical application of SMP activated by electricity. In this study, synergistic effects of electrically/thermally conductive carbon nanotube (CNT) and thermally resistive nafion/silica nanofiber on the electrical actuation efficiency and electro-activated recovery behavior of SMP nanocomposite were explored and studied. Carboxylic acid-functionalized CNTs were self-assembled to enhance their bonding reliability and achieve electrical actuation of SMP matrix. Nafion/silica nanofibers were electrospun onto surfaces of the carbon fiber mat to prevent electrically resistive heat dissipation. A schematic illustration of the working mechanism and synergistic effect of CNT and nafion/silica nanofiber on the electrical actuation of SMP nanocomposite is presented in Fig. 1.

2. Experimental details

The carboxylic acid-functionalized CNT (as-received powder), was supplied by Shenzhen Nanometer Gang Co., Ltd., China. Its diameter ranges from 10 to 20 nm and the length is from 1 to 15 μm. CNT of 0.08 g was mixed with 80 mL distilled water to form a suspension. Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) of 1 mL was used as surfactant and was dropped into the CNT solution to aid the dispersion. The CNT suspension was ultrasonically treated for 20 min, and then, the homogeneous suspension was filtrated through a carbon fiber mat under a high pressure to deposit the CNTs. To strengthen the connection force of CNTs with the carbon fiber mat, 2 mL polyvinyl alcohol (PVA) was introduced after filtration. Finally, the carbon fiber mat grafted with CNTs and PVA was dried at 30 °C for 24 h.

The thermally resistive nafion/silica nanofibers (with the thermal conductivity as low as 0.2 W/cm·K) were able for electrospinning and prepared via the roller electrostatic spinning apparatus (Nanospider, Elmarco Company, Czech Republic). Commercial nafion polymer was purchased from DuPont, USA. Polyethylene oxide (PEO) was obtained from Changchun Jinghua Company, China. Tetraethyl orthosilicate (TEOS-98%) was supplied from Sigma-Aldrich Chemical Co., China. HCl (36.38%) solution and ethanol (99.7%) were purchased from Beijing Chemical Company, China. In the process of electrospinning, the applied electric voltage between collector and electrode was kept at 30 kV. The electrode-to-collector distance was 15 cm, and the electrode rotation rate was 3 rpm. The weight ratio of nafion nanofiber and silica nanofiber in the electrospun nafion/silica composite was 40: 60.

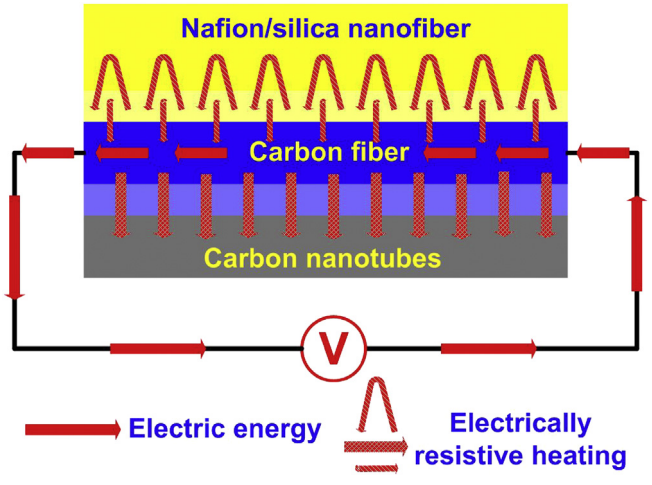

Fig. 1. A schematic illustration of working mechanism and synergistic effect of CNT and nafion/silica nanofiber on the electrical actuation of SMP nanocomposite.

The SMP used in this study was an epoxy-based fully formable thermoset SMP resin. After curing, it is featured with the thermo-responsive SME with a glass transition temperature of 100 °C. Carbon fiber mat (0.12 g) with nafion/silica nanofiber (0.08 g) and different weight concentrations of CNTs (0 g, 0.08 g, 0.10 g, 0.12 g, 0.14 g) were prepared for SMP nanocomposites. Preparation of SMP composites involves multi-steps: (1). Carboxylic acid-functionalized CNTs were deposited onto the carbon fiber. (2). Nafion/silica nanofibers were deposited onto the carbon fiber mat on the opposite surface to the CNTs. (3). Carbon fiber mats were initially placed on a polytetrafluoroethylene (PTFE) mold. (4). Resin transfer molding technique was used to make the SMP composite. After filling the mold, the resin (12.0 g) was cured at a ramp of 1 °C/min from room temperature to 80 °C and kept for 3 h before being ramped down to 100 °C at 1 °C/min and was kept for 3 h. Finally, it was ramped to 150 °C at 1 °C/min and kept for 5 h to produce the final SMP nanocomposites (with a weight of 4.0 g). A schematic illustration of the carbon fiber mat grafted with carboxylic acid-functionalized CNTs via van der Waals force is shown in Fig. 2(A), and a schematic synthesis route of nafion/silica coated nanofiber mat via electrospinning approach is presented in Fig. 2(B).

Scanning electron microscope (SEM, VEGA3 TESCAN) was used to characterize the surface and cross-section morphologies of CNTs and nafion/silica nanofiber. The electrical resistivity of SMP nanocomposites was characterized with a four-point probe method. The apparatus has four probes. A constant current passes through two probes and an output voltage is measured across the other probes with the voltmeter. To reduce experimental errors in the tests, the SMP nanocomposite is prepared with a symmetrical square shape (30×30 mm^2). An average of twenty measurements is used to determine the electrical resistivity.

3. Results and discussion

3.1. Morphology of CNT and nafion/silica nanofiber assemblies

Fig. 3(A) is an SEM image of the typical surface view of the raw CNT assembly at an accelerating voltage of 10.00 keV. It is revealed that the CNTs have diameters ranging from 10 to 50 nm and are entangled with each other. No apparent aggregate of nanotubes and multi-scale porous structures were found. The porous structure has an average size of 10–100 nm. A network structure was formed through mechanical interlocking between individual nanotubes. Such a continuous network made of individual CNT is able to provide conductive paths for electrons under an electric current in the SMP nanocomposite, resulting in an excellent electrical conductivity. Fig. 3(B) reveals that nafion/silica nanofiber has a belt structure and is uniformly dispersed at a scale of 50 μm. The nafion/silica nanofiber was entangled with each other. Here, the assembly of nafion/silica nanofiber is expected to prevent the heat transfer and exchange from the underlying carbon fiber to the atmosphere due to their thermally resistivity.

3.2. Electrical resistivity measurement

The electrical resistivity of the nanocomposites with various weight concentrations of CNTs is plotted in Fig. 4. The error bar represents a standard deviation to present the variability of the tested results. As the weight of CNTs is increased from 0, 0.08, 0.10,