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Self-assembled multi-layered carbon nanofiber nanopaper for significantly improving electrical actuation of shape memory polymer nanocomposite

Haibao Lu [a,*], Fei Liang [b], Yongtao Yao [a], Jihua Gou [b,*], David Hui [c]

[a] Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin 150080, China
[b] Composite Materials and Structures Laboratory, Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, USA
[c] Composite Material Research Laboratory, Department of Mechanical Engineering, University of New Orleans, LA 70148, USA

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ABSTRACT

This study presents an effective approach to significantly improve the electrical properties of shape memory polymer (SMP) nanocomposites that show Joule heating triggered shape recovery. Carbon nanofibers (CNFs) were self-assembled to form multi-layered nanopaper to enhance the bonding and shape recovery behavior of SMP, respectively. It was found that both glass transition temperature (*Tg*) and electrical properties of the SMP nanocomposites have been improved by incorporating multi-layers of self-assembled nanopapers. The electrically actuated shape recovery behavior and the temperature profile during the actuation were monitored and characterized at a voltage of 30 V.

1. Introduction

Shape memory effect (SME) of polymers is the ability to store a programmed shape indefinitely and fully recover to an original shape in response to an environmental stimulus, such as heat, light, electricity, magnetism, and water [1,2]. Unlike shape memory alloys (SMAs), the SME of shape memory polymers (SMPs) is predominantly an entropic phenomenon [3,4]. More appropriate terms for the two structural requirements for the SME are switch segment and netpoint [5]. This dual-state system is essential to enabling the SME in these polymers [6,7]. For amorphous networks, shape memory behavior is realized by programming around the glass transition temperature (*Tg*). In a typical shape memory cycle, the material is heated above *Tg*, deformed to the desired shape, then cooled rapidly below the *Tg* to fix the programed shape for indefinite storage. The SMPs are attractive for great research interest and a number of potential applications due to their advantages, such as their light weight, ease in manufacturing and the ability for tailored properties to precisely meet the needs of a particular application [8–10]. Moreover, they can store and recover large deformation, which is desirable for deployable and morphing structures [11]. Despite tremendous progress in synthesis, analysis, characterization, actuation methods and modeling enables us to develop SMPs through a knowledge based approach [12–14]. Fundamental research aims to other stimuli different than heat (e.g. light, electric current or alternating magnetic fields) and enabling more desirable requirements on demand [15–19]. Among these approaches, the utilization of electrically Joule resistive heating to trigger the shape recovery of SMPs is desirable for practical applications where it would not be possible to use heat. Some previous efforts used electrically conductive SMP composites with carbon nanotubes (CNTs) [20], short carbon fibers [21], carbon black [22], carbon fiber [23], carbon nanofibers (CNFs) [24], nanopaper [25], graphene [26], *etc.* The nanopaper was used with some degree of success owing to significant improvement in electrical conductivity [27]. In this study, multi-layers of the nanopaper were incorporated into the SMP to enhance the bonding between the nanopaper and the SMP matrix. The multi-layers of the nanopaper also improved the electrical properties to achieve a fast actuation at a low electric voltage for the SMP nanocomposites.

2. Experimental

CNFs are available with diameters ranging from 20 to 150 nm and lengths of 5–15 μm. Distilled water was used as a solvent. The raw CNFs of 0.6 g were mixed with 600 ml of distilled water to form a suspension. The surfactant Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) of 2 ml was introduced to aid the dispersion of the CNFs. The CNF suspension was then sonicated with an ultrasound power level of 1200 W for 20 min. After which, the suspension was filtrated under a high pressure and a nanopaper was self-assembled

* Corresponding authors. Tel.: +86 45186412259 (H. Lu).
E-mail addresses: luhb@hit.edu.cn (H. Lu), Jihua.Gou@ucf.edu (J. Gou).

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on the hydrophilic polycarbonate membrane. The CNF nanopaper was further dried in an oven at 120 °C for 2 h to remove the residual water and surfactant.

The polymer matrix is a polyurethane-based fully formable thermosetting SMP resin. The cured resin is engineered with a *Tg* of 50 °C. The resin transfer molding process was used to fabricate the SMP nanocomposites. One, two, three and four layers of the nanopaper were placed on the bottom of the metallic mold. The SMP resin was then injected into and filled into the mold. The relative pressure of the resin transfer molding was kept at approximately 6 bars. After filling the mold, the mixture was cured at room temperature for 24 h to produce the final SMP nanocomposites.

3. Results and discussion

3.1. Morphology and structure of multi-layered SMP nanocomposite

Scanning electron microscopy (SEM) was used to study the surface morphology and structure of multi-layered nanopaper enabled SMP nanocomposite. Fig. 1(a) shows the typical surface view of the CNF nanopaper at an accelerating voltage of 10.00 keV. The CNFs have a diameter ranging from 20 to 150 nm, and are entangled with each other. No large aggregates of nanofibers were observed. The self-assembled and multi-layered CNF nanopaper confirms a continuously conductive network. Fig. 1(b) illustrates macroscopic structure variations of the SMP nanocomposite with two layers of nanopaper. In this two-layered nanopaper enabled SMP nanocomposite, there are four interfaces between the nanopaper and the SMP matrix. Therefore, it is expected to improve the interface bonding of SMP nanocomposite through the multiple layers of the nanopaper. Fig. 1(c and d) reveal the morphology and structure of the interface bonding between the multi-layered nanopaper and SMP matrix. The interfacial bonding between the matrix and multi-layered nanopaper is expected to improve the mechanical properties and performance of the polymer composites [28,29]. Furthermore, it also will facilitate in transferring the Joule heat from the nanopaper to the SMP matrix.

3.2. Electrical resistivity measurement

The electrical resistivity was determined with a four-point probe apparatus (QUAD PRO-SIGNATONE, computerized four point resistivity system). This approach is an electrical impedance measuring technique that uses separate pairs of current-carrying and voltage-sensing electrodes to make more accurate measurements than the traditional two-terminal sensing method. In order to reduce experimental errors from many previous measurements, it is preferable that the tested sample is symmetrical. Fig. 2(a) shows a schematic illustration of the setup. The apparatus has four probes with an adjustable inter-probe spacing. A constant current passed through two outer probes and an output voltage was measured across the inner probes with a voltmeter. The electrical resistances of thirteen modes are used to calculate the electrical resistivity of the tested samples according to the van der Pauw expression. The electrical resistivity of the nanopapers with a different layer number was plotted in Fig. 2(b). The electrical resistivities of the nanopapers were plotted against different locations. Thirteen locations were chosen to determine the electrical resistivity for the tested nanopapers. Each data point denotes the resistivity at a particular zone. In the experiments, it was found that the average values of electrical resistivity are 6.41 Ω cm, 3.22 Ω cm, 2.12 Ω cm and 1.67 Ω cm, as the SMP nanocomposite incorporated with one-layer, two-layer, three-layer and four-layer CNF nanopaper, respectively, as shown in the curve of Fig. 2(c). The electrical resistivity of SMP nanocomposite is improved with an increase in the layer number of nanopaper. It is expected that the more CNFs in the nanopaper, the more conductive paths are formed in the continuous network. Given more conductive paths, more electrons are involved in an electrical circuit. Therefore, the amplitude of electric current and current carrying capability both increase. Additionally, more conductive paths will increase the probability of forming relatively shorter distances for a reduced electrical resistance to the electric current [30].

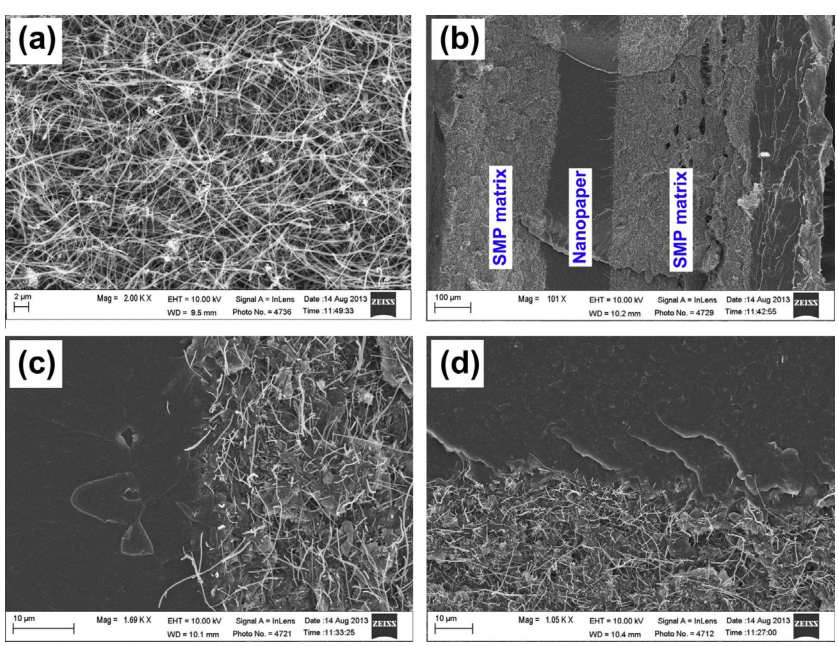

Fig. 1. The morphology and structure of multi-layered nanopaper and the SMP nanocomposite at an accelerating voltage of 10.00 keV. (a) Morphology of multi-layered nanopaper. (b) Structure of multi-layered nanopaper enabled SMP nanocomposite. (c) and (d) Morphology and structure of the interface between the multi-layered nanopaper and the SMP matrix.