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

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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 programmed 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 (CNFs) [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 (C14H22O(C2H4, O)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 filtered under a high pressure and a nanopaper was self-assembled.
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 T_g 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. 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].

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.
3.3 Thermomechanical property analysis

Differential scanning calorimetry (DSC) experiments were performed with DSC 204F1, Netzsch, Germany. All experiments were conducted with a constant heating and cooling rate of 10 °C min⁻¹. The samples were investigated in the temperature range from 25 to 120 °C. They were heated from 25 to 150 °C, then cooled down to 25 °C. Whenever a maximum or minimum temperature in the testing program was reached, this temperature was kept constant for 2 min. The samples were cooled to 25 °C. In the polyurethane SMP, the Tg is responsible for the SME. Exceeding it activates the polymer segments and thereby allowing the material to regain its permanent (or original) form. Therefore, the Tg is a critical parameter and is necessary for characterizing the shape recovery performance of SMPs. The change in Tg as function of the temperature for the SMP nanocomposites incorporated with different number of layers is presented in Fig. 3(a and b). Tg is determined by the heating run as 50.02, 51.68, 50.69, and 52.92 °C for the SMP nanocomposite with one-, two-, three- and four-layered nanopaper, respectively. While the Tg is determined by the cooling run as 50.01, 51.67, 62.23, and 62.45 °C for the SMP nanocomposite with two-, three- and four-layered nanopaper, respectively. It can be seen that the glass transition occurs within a temperature range from 50 to 65 °C. The experimental results could be attained from the multi-layered nanopaper that enhances the bonding strength between carbon fiber and the SMP matrix, resulting in improved thermomechanical properties. However, with an increase in weight content above a certain value, the thermomechanical properties of the SMP matrix would be decreased due to an increase in separation distance among the macromolecules.

3.4 Electrically triggered shape recovery and temperature distribution

The tested SMP nanocomposite was incorporated with a four-layered nanopaper and originally had a flat shape. After the sample was heated above its Tg, it could be deformed into a desirable shape upon application of an external force. Cooling back to room temperature, the SMP nanocomposite with a temporary (deformed) shape was subsequently fixed. The electrical actuation was studied on a “P” shaped SMP nanocomposites sample. The flat sample with a dimension of 80 × 10 × 4 mm³ was bent into a “U” shape at 80 °C. Images were taken with a digital camera at a constant frame rate of 30 Hz, and with an appropriate visual range to detect the sample’s curvature. Snapshots of the shape recovery sequence of the SMP nanocomposite sample is shown in Fig. 4. A constant 30 V DC voltage was applied to the SMP nanocomposite. It took 80 s to complete the shape recovery. It showed very little recovery ratio during the first 10 s, but then exhibited a faster recovery behavior until 60 s. Finally, the SMP nanocomposite sample regained its original (permanent) shape. Therefore, the function and effectiveness of the four-layered nanopaper in the actuation of SMP nanocomposite by resistive Joule heating were experimentally demonstrated and characterized.

Simultaneously, an infrared video camera (FLIR Infrared Camera) was used to record and monitor the shape recovery behavior and temperature distribution. Nine snap-shots of the tested SMP
A nanocomposite sample were presented in Fig. 5. Furthermore, the temperature distribution along the tested sample (100 selection points were set) was plotted in Fig. 6. High temperatures were found where internal strains were higher than the local resistivity. With electricity being applied, the resistive Joule heating resulted in the gradually increased in temperature. At 80 s, the maximum temperature of the sample reached approximately 102.5 °C, and the external electricity was turned off to avoid thermal degradation of the polymer. Consequently, the temperature on the tested sample lowered to room temperature. In this manner, the temperature distribution and shape recovery process were well recorded and monitored for the electrical actuation of the SMP nanocomposite.

To further characterize the effect of multi-layered nanopaper on the electrical actuation of SMP nanocomposites, a comparison of the electric power of the SMP nanocomposites incorporated with one-, two-, three- and four-layered nanopaper was carried out to

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identify the improvement in the performance at the electric voltage of 30 V, as shown in Fig. 7. The experimental results indicate that the SMP nanocomposite incorporated with a four-layered nanopaper had the highest electric power of 15 W due to its lowest electrical resistivity, while that of the SMP nanocomposite incorporated with one-, two- and three-layered nanopaper is 3.9 W, 6.9 W and 11.7 W, respectively. Therefore, it can be seen that the multi-layered nanopaper improve the electrical actuation of the SMPS.

4. Conclusion

A series of experiments were conducted to study the multi-layered nanopaper enabled SMP nanocomposites, of which the shape recovery was achieved by the electrically resistive Joule heating. The multi-layered nanopaper was to improve the interfacial bonding and enhance the reliability in bonding, and helped to transfer the resistive Joule heating from the nanopaper to the SMP matrix. Both Tg and electrical property of the nanocomposite were improved by the multi-layered nanopaper. The electrically driven recovery behavior was characterized at an electric voltage of 30 V. Furthermore, the temperature distribution of the SMP nanocomposite incorporated with four-layered nanopaper was recorded and monitored in the recovery process by electricity. We demonstrated a simple way to produce the electro-activated SMP nanocomposites by using multi-layered nanopaper in which Joule heating was possible at a low electrical voltage.

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