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Synergistic effect of self-assembled carboxylic acid-functionalized carbon nanotubes and carbon fiber for improved electro-activated polymeric shape-memory nanocomposite

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Synergistic effect of self-assembled carboxylic acid-functionalized carbon nanotubes and carbon fiber for improved electro-activated polymeric shape-memory nanocomposite

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The present work studies the synergistic effect of self-assembled carboxylic acid-functionalized carbon nanotube (CNT) and carbon fiber on the electrical property and electro-activated recovery behavior of shape memory polymer (SMP) nanocomposites. The combination of CNT and carbon fiber results in improved electrical conductivity in the SMP nanocomposites. Carboxylic acid-functionalized CNTs are grafted onto the carbon fibers and then self-assembled by deposition to significantly enhance the reliability of the bonding between carbon fiber and SMP via van der Waals and covalent crosslink. Furthermore, the self-assembled carboxylic acid-functionalized CNTs and carbon fibers enable the SMP nanocomposites for Joule heating triggered shape recovery. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4811134]

Polymeric materials that demonstrate the ability to return their original shape when subjected to an appropriate stimulus are referred to as shape-memory polymers (SMPs). This phenomenon is defined as the shape-memory effect (SME). In fact, depending on the exact working conditions, SMP may have the viscous-elastic behavior or the SME, which is made possible via phase/state change resulting from molecular rearrangement. A change in the structure and/or morphology above the transformation temperature induces the thermally responsive shape recovery. In thermally responsive SMPs, glass transition or melting transition is required to initiate this phase and/or state change. In recent years, as a smart material, SMPs have attracted increased attention from the scientific community due to their abundant advantages over their metallic counterpart, namely shape memory alloys (SMAs). Low cost, light weight, a broad range of transformation temperature, high durability, and high recoverable strain (up to 200% in many SMPs) are some of the important advantages among others, which enable SMPs to be used in numerous applications, ranging from aerospace engineering to biomedical engineering. With the application domain of SMPs growing rapidly, there are still some challenges that SMPs must overcome before their full potential can be explored. In addition to lower recovery stress and longer response time as compared with SMAs, poor thermal, electrical, and magnetic properties imply that electromagnetic responsive SME is most likely not applicable for SMPs.

With regard to these above challenges, SMP composites and nanocomposites become desirable due to their tailorability after reinforcement. Extensive research works have been done on electrically conductive SMP composites by means of blending with electrically conductive fillers, such as carbon fiber, carbon nanotubes (CNTs), conductive hybrid fibers, nickel powder, carbon black, and carbon nanofibers (CNFs). However, this approach always requires a higher loading level of conductive fillers to achieve lower electrical resistivity. With a higher loading level of filler, a higher viscosity in the SMP mixture is resulted by the strong interaction between SMP resin and conductive filler, which prevents the efficient transfer of properties of the filler to the matrix. Recently, CNF mat and nanopaper have been explored for electrically conductive SMP nanocomposites. However, the interface between the nanopaper and SMP composite may be damaged even upon purely thermal cycling due to large dissimilarity in their thermo-mechanical properties. Consequently, the efficiency of heat transfer from the nanopaper to the SMP is limited. The synergistic effect of self-assembled carboxylic acid-functionalized CNTs and carbon fiber on the electrical properties and electro-activated recovery behavior of SMP nanocomposites is studied in this paper. The combination of CNT and carbon fiber aims to improve the electrical and thermal conductivities of the SMP nanocomposites. Carbon fiber is employed to achieve the SME in SMP nanocomposites induced by electricity. Carboxylic acid-functionalized CNTs are grafted onto the carbon fiber and, self-assembled by deposition, in order to significantly enhance the reliability in bonding between the carbon fiber and the SMP via van der Waals and covalent crosslink. A schematic illustration of the carbon fiber grafted with carboxylic acid-functionalized CNTs via van der Waals force is shown in Fig. 1(a), while a schematic illustration of the joining between carbon fiber and SMP via covalent crosslink is presented in Fig. 1(b).

The carboxylic acid-functionalized CNTs were received in powder form, which were synthesized by chemical vapor deposition (CVD) and have a purity of 97%. The nanotube has an outer diameter of 50–100 nm and a length of 5–15 μm. The non-ionic surfactant (Triton X-100, C14H22O(C2H4O)n), has a hydrophilic polyethylene oxide group and a hydrophobic...
The Triton X-100 has 9.5 ethylene oxide units on average. The hydrophobic group of the surfactant backbone is in close contact with the CNTs, resulting in the modified CNTs having a hydrophilic polyethylene oxide group. This non-ionic surfactant improves the dispersion of CNTs in an aqueous solution. The CNT suspension was sonicated with a high-intensity sonicator (VCX Sonicator 750, Sonics & Materials, Inc., Newtown, CT, USA) at room temperature (about 22°C) for 40 min at an ultrasound power level of 300 W. Two duty cycles were applied for the dispersion of CNTs. After an initial 15 min sonication, both CNT suspension and probe were cooled back to room temperature. The sonication was carried out again for another 15 min under the same condition. The CNT suspension was then membrane filtrated under a positive pressure of the resin transfer molding was kept at approximately 6 bars. After filling the mold, the mixture was cured at a ramp of approximately 1°C/min from room temperature to 100°C and kept for 5 h before being ramped to 120°C at 20°C per 180 min. Finally, it was ramped to 150°C at 30°C per 120 min to produce the final SMP nanocomposites.

The morphological structure of the carbon fiber grafted with carboxylic acid-functionalized CNTs were characterized using field emission scanning electron microscopy (FESEM). Figures 2(a) and 2(b) show the surface morphology of the carbon fiber with the grafted CNTs at an accelerating voltage of 20.00 keV. The bright lines correspond to individual nanotubes and the dark areas correspond to the bare carbon fiber. The CNTs stick to the carbon fiber surface along the outer edges of the grooves with different angles due to high specific surface area of the individual nanotube. These images confirm that CNTs are grafted onto the carbon fiber via the membrane filtrated process, and there are a large amount of CNTs grafted onto the fiber. On the other hand, the morphology and structure of the CNT arrays were characterized with the SEM technique as shown in Fig. 2(c). The CNT array was made up of well-dispersed individual nanotubes with very little aggregate due to the influence of the solvent. It is concluded that no large aggregate of CNTs was
found and individual nanotubes were closely packed within the network structure. Therefore, the bonding between CNT and carbon fiber will be significantly improved owing to higher surface area of CNTs than their aggregates.

Electrical resistivity of SMP nanocomposites was characterized by the four-point probe technique in the van de Pauw mode using a Keithley 2400 resistivity tester and a Keithley 2000 picoammeter/voltage source. Four electrodes were embedded into the sample. Figure 3 shows a schematic illustration of the setup. When a Kelvin connection is used, the electrical current is supplied with a pair of force connections. The current is a positive DC current injected into contact “1” and taken out of contact “2” and is measured in amperes (A). The voltage is a DC voltage measured between contacts “3” and “4” with no externally applied magnetic field, measured in volts (V), as shown in mode I in Fig. 3(a).

For the other mode (II), the current is a positive DC current injected into contact “1” and taken out of contact “3” and is measured in amperes (A). The voltage is a DC voltage measured between contacts “2” and “4” with no externally applied magnetic field, measured in volts (V), as shown in the Fig. 3(b). The electrical resistances of two modes are, therefore, used to calculate the electrical resistivity of the tested sample according to the van de Pauw equation, as follows:

\[
\exp\left(-\frac{\pi d}{\rho} \cdot R_1\right) + \exp\left(-\frac{\pi d}{\rho} \cdot R_2\right) = 1, \tag{1}
\]

where \(d\) is the thickness, \(\rho\) is the electrical resistivity, \(R_1\) is the electrical resistance of mode I, and \(R_2\) is the electrical resistance of mode II. To improve the sufficient degree of accuracy, it should be checked the repeatability of measurements. And the resistivity values are also compared after switching polarities of modes I and II.

Figure 4 compares the resistivity of different composites. The weight concentration ratios of the CNTs to the SMP are 1:12, 3:40, 1:15, 7:12, 1:20, 1:24, and 1:30, respectively, and the weight concentration ratio of the carbon fiber to the SMP is always 1:16. With more CNTs grafted onto the carbon fiber, the electrical resistivity of the SMP nanocomposite gradually decreases. As we can see, the average electrical resistivity of nanocomposite decreases from 0.093 to 0.086 \(\Omega\) cm, as the weight of carboxylic acid-functionalized CNTs grafted onto the carbon fiber increases from 0.08 to 0.20 g. This is lower than most previously reported conductive SMPs (e.g., the 8.91 \(\Omega\) cm in a polystyrene SMP filled with hybrid filler,\(^{14}\) 12.18 \(\Omega\) cm in a polyurethane SMP filled with nickel powders,\(^{15}\) 1.7 \(\Omega\) cm in a polystyrene SMP coated with CNF mat,\(^{18}\) 1000 \(\Omega\) cm in a polyurethane SMP filled with multi-walled CNTs,\(^{21}\) and 10 \(\Omega\) cm in a polyurethane SMP filled with nickel powder and carbon black\(^{22}\)). The results show that the electrical resistivities of the SMP nanocomposites are significantly improved by the synergistic effect of carbon fiber and carboxylic acid-functionalized CNT.

The synergistic effect of carbon fiber (0.6 g in weight) and carboxylic acid-functionalized CNT (0.08 g in weight) on the actuation of the SMP nanocomposites (10.3 g in weight) was studied on a “Q” shaped composite sample under a DC power supply. Digital images were taken with a video camera. A snapshot of shape recovery sequence of SMP nanocomposite specimen incorporated with carbon fiber grafted with carboxylic acid-functionalized CNTs is shown in Fig. 5. The flat (permanent shape) nanocomposite specimen with a dimension of 40 \(\times\) 4 \(\times\) 3 mm\(^3\) was bent into “U” shape (temporary shape) at 110°C. This temporary shape was maintained until the specimen was cooled down to room temperature. No apparent shape recovery was observed after the deformed specimen was kept in the air for 30 min. A constant 12 V DC voltage and 0.5 W power was

FIG. 3. Schematic illustration of van de Pawn method for measuring electrical resistivity. (a) Measurement model I. (b) Measurement model II.

FIG. 4. Electrical resistivity of SMP nanocomposites incorporated with different weight concentrations of carbon fiber grafted with carboxylic acid-functionalized CNT. Each type of test was repeated 20 times.

FIG. 5. Snapshot of Joule heating-induced SME of SMP nanocomposites with carbon fiber (0.6 g in weight) grafted with carboxylic acid-functionalized CNTs (0.08 g in weight), with the weight of the SMP part being 0.96 g.
applied to the SMP nanocomposite. After 25 s, dramatic shape change started. About 100% recovery was achieved in about 45 s of heating.

We demonstrate a simple way to produce electrically activated SMP nanocomposites by application of deposition of carboxylic acid-functionalized CNTs. The electrical properties of the SMP matrix were improved by incorporating with carboxylic acid-functionalized CNTs and carbon fibers. These carboxylic acid-functionalized CNTs were self-assembled and grafted onto the carbon fiber to significantly enhance the reliability in bonding between carbon fiber and SMP via van der Waals and covalent crosslink and Joule heating was possible at a low electrical voltage.

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