Carbon nanotube chains in a shape memory polymer/carbon black composite: To significantly reduce the electrical resistivity

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Instead of individually aligned along the external electric field, the carbon nanotubes (CNTs) were electrically induced into aligned chains in a shape memory polymer (SMP)/carbon black (CB) composite, which would serve as long-distance conductive channels to bridge the CB aggregations. Compared with SMP composites with randomly filled CNTs, the electrical resistivity in those with chained CNTs was reduced for more than 100 times. The fabricated conductive SMP composites could be actuated by a low electrical power. © *2011 American Institute of Physics*. [doi:10.1063/1.3556621]

As an emerging class of smart polymer that has dual-shape capability, shape memory polymers (SMPs) can be fixed into a temporary shape, and then recover their permanent shapes in the presence of an external stimulus,[1–3] such as electricity,[4,5] light,[6] magnetic fields,[7] and solvents.[8,9] Among all the actuation approaches, electrical induction has been received more research interest due to its easy procedure. The SMPs could be actuated through resistive Joule heating by simply applying an electrical current, getting rid of external heaters, inconvenient devices or bulk system to generate the actuating environment. To render the SMPs into electrically conductive, carbon nanotubes (CNTs) are selected as fillers in this paper due to their superb properties.[10] Compared with other conductive fillers (powder,[11] continuous fibers,[12–14] etc.), CNTs will not only offer strong mechanical reinforcement effect on the material but also influence little on the recoverable strain of SMPs.

It is generally accepted that aligned CNT films would offer many advantages compared to bulk samples with randomly distributed CNTs, and the electrical alignment is considered as a most convenient and efficient approach. Under an electric field, single CNT could be electronic polarized, and aligned along the direction of the electric field if the movement is not restricted by its environment. By dispersing CNTs in ethanol, Chen *et al.*[15] and Bubke *et al.*,[16] respectively, demonstrated the feasibility of CNTs alignment under electric field. Martin *et al.*[17] reported the multiwalled CNT networks in epoxy system induced by electric field. Park *et al.*[18] reported the single-walled CNT short clusters in a light-cured polymer but individual CNT morphology in the clusters was not referred. In all the current investigations, the spatial dimensions between two electrodes are in micrometer or even nanometer ranges. In our study, SMP specimens were prepared in a centimeter range for the actuation experiment. In such an electrode distance, the CNTs tend to assemble into conductive chains, rather than individually align along the external electric field.

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Here, three types of specimen with different amount of carbon black (CB) were fabricated, namely, SMP/CB/CNT (chained), SMP/CB/CNT (random), and SMP/CB. The CB content varies from 10 to 15 wt % in each specimen type, and the CNT content is always 1 wt %. The composite matrix was made from styrene-based thermosetting shape memory resin (Cornerstone Research Group Inc., Ohio State), with a density of 0.92 g/cm^3. The CB (AX-010) particles were purchased from GuangZhou Sunny Plaza Trading Limited Co. The mean aggregate size was 4 μm, the mean domain size (x-ray diffraction) was 18–20 nm, and the domain content was 65 wt %. The multiwalled CNTs were purchased from Shenzhen Nanometer Gang Limited Co., with an average length of 1 μm and an average diameter of 50 nm.

Under the external electric field, the dipole moment of CNTs strongly depends on the viscosity of the liquid polymer.[19,20] Due to the high viscosity of the shape memory resin (12 Pa s), a dimethylformamide (DMF) solution (50 vol %) was added to significantly reduce the viscosity of the liquid blend. During the curing interaction, the DMF solution will be vaporized. The alternating current (ac) electric field was selected to minimize the electrophoretic migration effect.

The SMP/CB/CNT (chained) specimen was prepared in the following steps. First, the styrene resin was mixed with the dibenzoyl peroxide hardener at a weight ratio of 24:1. CB and CNTs (1 wt %) were mixed with the blend and well stirred. Second, the suspension was placed in a sonicator (SONICS-44349N) at an output amplitude of 60% for a total of 40 min, in intervals of 10 min. 50 vol % DMF solution was then mixed into the blend. Third, the mixture was poured into the space between two aluminum electrodes. The distance between the electrodes was 3 cm, and the applied electric voltage was 500 V (50 Hz). An ampere meter was series connected into the setup. When the electric current increased to a constant value, the external electric voltage was turn down to avoid generating excessive heat. Forth, the whole setup was placed in an air-tightened box and kept in an oven for 24 h at 80 °C for solidification. After the volatilization of DMF, a specimen embedded with CNT chains

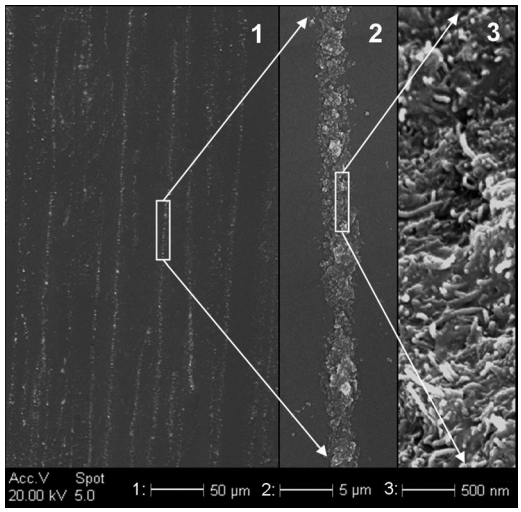

FIG. 1. SEM image of SMP/CB/CNT (chained) with 10 wt % CB. Insets: zoom-in views of one CNT chain.

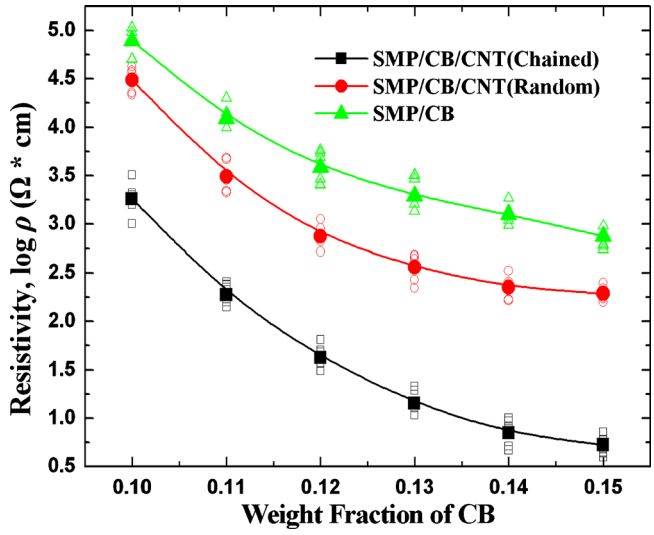

FIG. 3. (Color online) Curves of resistivity vs weight fraction of CB.

inside was obtained. The cured specimen was about 1 mm thick. SMP/CB/CNT (random) and SMP/CB specimen were prepared in a similar way but without the electric field.

The morphology of the CNT chains in the SMP composite was observed by a scanning electron microscope (SEM). As is shown in Fig. 1 (left), many parallel CNT chains are observed with a magnification magnitude of 1000. To demonstrate that the applied CB does not possess such an electroinduced chaining effect in the investigated SMP composite, SMP specimen embedded with 10 wt % CB was prepared under the same electric filed as mentioned above, and its SEM image is presented in Fig. 2. It is observed that the CB is aggregated under the electric field, rather than formed into chains. The mechanism of CNT chains' forming can be described as followings: initially, each CNT is electronically polarized into nanosized dipole by the external electric field. However, due to the small distance between two CNT and the strong Coulombic force between oppositely charged ends, the attraction force dominates the local force field, and hence, the CNTs will attract each other to assemble, rather than individually aligns along the external electric field. When the assembled CNTs, which can be treated as diploes in big sizes, grow to a certain critical size, the average distance between them is significantly increased, and hence the aligning force induced by external electric field surpasses the local Coulombic force. Then, the aligning movement is started and with enough time passed, the CNT chains are formed in the SMP matrix.

Subsequently, samples with dimensions of $1 \times 10 \times 20$ mm^3 were cut from each fabricated specimen and connected to aluminum electrodes to test the electrical resistivity. The resistance was measured by a digital multimeter (DT9205A), and the corresponding electrical resistivity was calculated according to the sample dimension. Versusing the CB content, Fig. 3 shows the curves of electrical resistivity for SMP/CB/CNT (chained), SMP/CB/CNT (random) and SMP/CB. Each data on the curves are calculated by taking the average value of six readings from six different pieces of the same sample. From the figure, the randomly distributed CNTs slightly reduce the electrical resistivity of the composites. However, if well chained, the same amount of CNTs reduces the electrical resistivity by over 100 times. The remarkable reduction in electrical resistivity allows the electrical actuation of SMPs in low power consumption.

To demonstrate the electroinduced shape recovery, three samples with the same dimensions (Fig. 4, right) were cut out from each SMP composite with 15 wt % CB concentrated. The samples were pre-bent at 80 °C, and then cooled back to 19 °C. Then, a 25 V direct current electric voltage

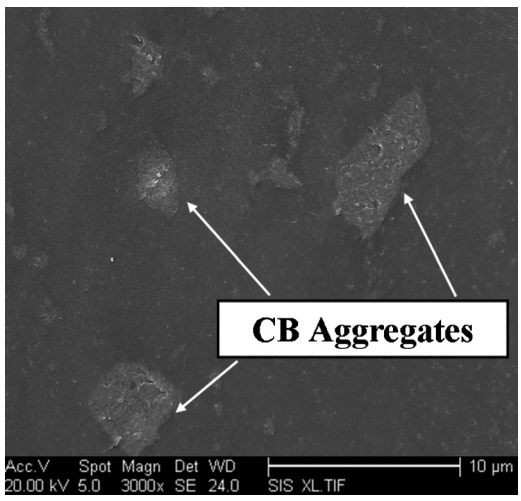

FIG. 2. SEM image of SMP composite filled with 10 wt % CB prepared under electric field.

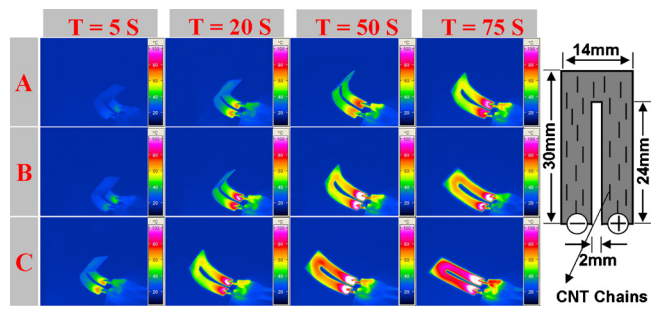

FIG. 4. (Color online) Snap shots of shape recovery and temperature distributions. Sample A: SMP/CB, Sample B: SMP/CB/CNT (random), Sample C: SMP/CB/CNT (chained). Right figure shows the sample dimension and experimental setup for Sample C.

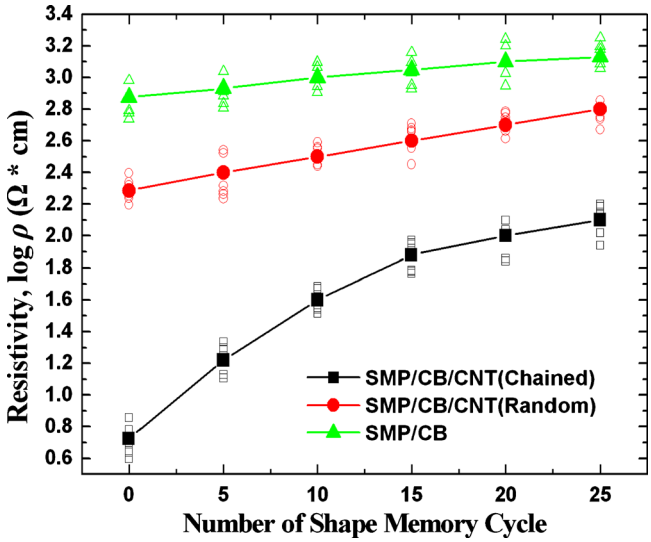

FIG. 5. (Color online) Degradation of electrical conductivity upon shape memory cycles.

was applied, and an infrared video camera (AGEMA, Thermovision 900) was used to monitor the temperature distribution and shape recovery simultaneously. The four snap shots of each sample were shown in Fig. 4 (left). Due to the reduction in electrical resistivity, the heating efficiency of SMPs composite with chained CNTs is improved significantly. Within 75 s, sample with CNT chains was heated above 95 °C, and a full shape recovery was achieved. In terms of power consumption, it is about 1.45 W in sample SMP/CB/CNT (chained). For comparison, SMP with random distributed CNT reached a temperature about 68 °C, and SMP without CNT reached 60 °C. Both of them did not fully recover to the permanent shape. The heating efficiency of SMP/CB/CNT (random) was improved slightly in comparison with SMP/CB.

Additionally, to investigate the conductivity degradation performance of the SMP composites, the electrical resistivity of the three samples (Samples A, B, and C) were retested after 25 shape recovery cycles (prestretched for 20% at the temperature of 90 °C, and then cool down to 19 °C). As shown in Fig. 5, the degradation degree of electrical conductivity in sample SMP/CB/CNT (chained) is relatively higher than the other two samples. This is because that the shape recovery ratio in a SMP is normally not 100%. More conductive paths in the SMP composite with CNT chains may be destroyed after certain shape recovery capabilities, and hence the conductivity was degraded upon thermomechanical cycles.

In summary, CNTs (1 wt %) were aligned into conductive chains in SMP/CB composites by applying an ac electric field. Compared with the samples without CNTs or with randomly distributed CNTs, the electrical resistivity is reduced by over 100 times. We also demonstrated that a piece of composite ($1 \times 14 \times 30$ mm^3) blended with 15 wt % of CB and 1 wt % of chained CNT has a electroactive shape recovery behavior in response to 25 V electrical voltage. The proposed approach is a convenient and efficient way to significantly reduce the electrical resistivity of SMP composites.

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