# Electroactivate shape-memory polymer filled with nanocarbon particles and short carbon fibers

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In addition to the fabrication of shape-memory thermoset polymer nanocomposites filled with conductive nanoparticles and fiber fillers, this paper is focused on factors which would influence the electrical property of this type of material. It is shown that the particulate additives are dispersed homogeneously within the matrix and served as interconnections between the fibers, while the fibrous additives act as long distance charge transporter by forming local conductive paths. The electrical conductivity of the nanocomposite which contains 5 wt % carbon nanoparticles and 2 wt % short carbon fiber is 2.32 S/cm by four-point van der Pauw method, and can be induced by 24 V voltages. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2790497]

Shape-memory polymers (SMPs) have the shape-memory effect as if they can be deformed and fixed into a temporary shape, and then recover their permanent shape by external stimulus. The development in SMP has grown rapidly in recent years, owing to their excellent structural versatility, low manufacturing cost, easy processing, large recoverable deformation, and low recovery temperature.[1] In literature, almost all research has focused on thermoplastic SMP. However, thermoset resin is more useful in the case that higher stiffness and recovery force are required.[2–5] The demand to get rid of external heaters has led to conductive SMPs filled with fillers such as carbon particles, conductive fiber, nickel zinc ferrite ferromagnetic particles, etc.[6,7] In comparison to microsized fillers, nanofillers have greater promise nonlinear improvements in the mechanical and thermal properties.[8–10] The development of electroactivated SMP has already been reported. For example, Cho *et al.*[11] obtained shape-memory polyurethane composites incorporating 5 wt % surface-modified multiwalled carbon nanotubes, and the electrical conductivity of about $10^{-3}$ S cm$^{-1}$ was obtained. Gho *et al.*[12] obtained an electrical conductivity of shape-memory polyurethane filled with 30% carbon black of about $1-10^{-1}$ S cm$^{-1}$. Paik *et al.*[13] obtained shape-memory polyurethane composites incorporating multiwalled carbon nanotubes, and the electrical conductivity was about $2.5 \times 10^{-3}$ S cm$^{-1}$. However, in the above-mentioned research works, either the electrical conductivity of the obtained SMP is poor or the composite is too thin to lose shape-memory effect, unless very high conductive content is used. In this paper, we propose an approach to improve the electrical property of SMP composites by using carbon black (CB) nanoparticle and short carbon fiber (SCF).

The SMP material used in this study was thermoset styrene-based shape-memory resin with a density of 0.90 g/cm$^3$ and cured temperature at 75 °C. Carbon nanoparticle was carbon black with an average particle size of 40 nm and density of 1.81 g/cm$^3$, Brunauer, Emmett, and Teller surface area of 1.21 cm$^2$/g, and electrical volume resistivity of 0.01–0.1 Ω cm at 20 °C. The SCF (T700) was a short fiber with a diameter of 7 $\mu$m, 2–5 mm long, and volume resistivity of $10^{-4}$ Ω cm at 20 °C.

The composites were prepared by hand mixing the styrene-based shape-memory resin with the cross-link agent in a proper proportion at room temperature. Certain amounts of carbon particles and carbon fibers were added in together with an additional solution to reduce the viscosity of the mixture. Mechanical stirring was applied for 15 min, followed by high-energy sonication, 300 W, VCX750 (from Sonics & Materials, inc.) for 1–2 h. A vacuum pump was used for 2–4 h to dispose air bubbles. Subsequently, the mixture was poured into an open mold, and dried at 55–70 °C in oven. Then, the cured composite was cooled at −20 °C for 30–60 min. Finally, the cured composite was taken out of the mold.

Ten types of composites were prepared. Sample A is pure SMP; sample B contains 2 wt % CB; sample C contains 5 wt % CB; sample D contains 6 wt % CB; sample E contains 7 wt % CB; sample F contains 10 wt % CB; sample H contains 15 wt % CB; sample I contains 5 wt % CB and 0.5 wt % SCF; sample J contains 5 wt % CB and 1 wt % SCF; sample K contains 5 wt % CB and 2 wt % SCF.

As shown in Fig. 1, the short fibers disperse randomly. There are many interconnections between fibers. These interconnections form the conductive networks which can be used to explain the excellent electrical conductivity of composites filled with SCF. However, the dispersion of SCF is normally inhomogeneous within composites. As a result, the electrical conductivity of composites filled with SCF only may not be good.

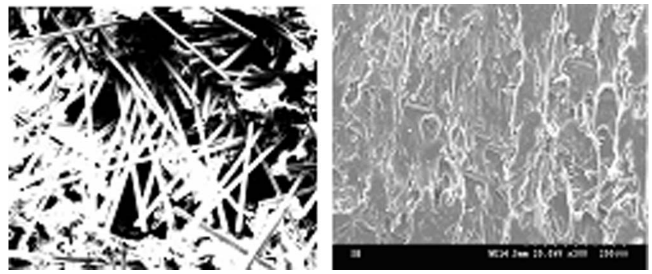

FIG. 1. (Color online) Morphology of short carbon fibers (left) and sectional observation (right).

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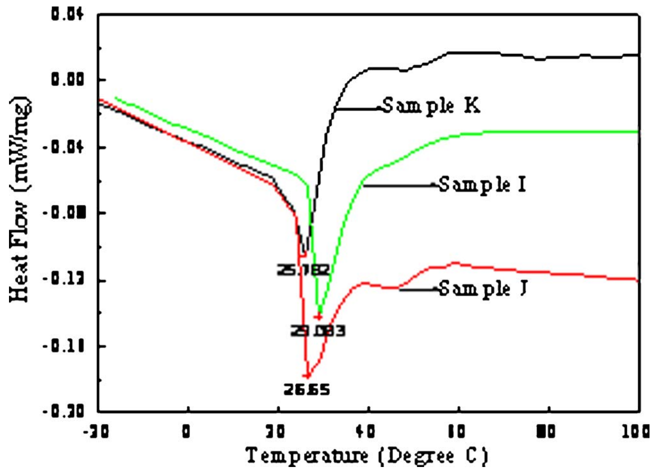


FIG. 2. (Color online) DSC curves of CB/SCF SMP composites.

Differential scanning calorimetry (DSC) tests were performed on samples (3.00–10.00 mg) using an NETZSCH Instrument, DSC 204F1 from 20 to 100 °C at a constant heating rate of 10.0 K/min. The full DSC term curves are plotted in Fig. 2, in which glass transition temperature was determined as 29.083 °C for sample I, 26.65 °C for sample J, and 25.782 °C for sample K. As the glass transition of pure SMP is 45 °C, the conductive fillers cause the drop of the glass transition temperature. Three major possible reasons are behind this drop: nanoparticle filler and moisture will impact the transition temperature and with the increase of filler content, the transition temperature dropped gradually; and the last reason is the solution.[14]

Dynamic mechanical analyzer (DMA) experiments were performed using a NETZSCH DMA 242C to determine the dynamic mechanical properties of sample K. The bend mode result is presented in Fig. 3. All experiments were completed at constant heating rate of 5.0 K/min. The oscillation frequencies were 0.2, 1.0, and 5.0 Hz, respectively. The sample was investigated from −50 to 120 °C. The dimension is $75.0\times 4.73\times 1.10$ mm$^3$.

The experimental results at the above-mentioned frequencies (0.2, 1.0, and 5.0 Hz) were presented, but only the result at the frequency of 1.0 Hz was given out for discussion in this paper. As shown in Fig. 3, the storage modulus reveals the stiffness of the material. The storage modulus of sample K is 2.13 GPa at room temperature of 25 °C at the oscillation frequency of 1.0 Hz. The storage modulus decreases sharply in the glass transition region at approximately 60–90 °C. tan $\delta$ represents the ratio of the loss modulus to storage modulus.

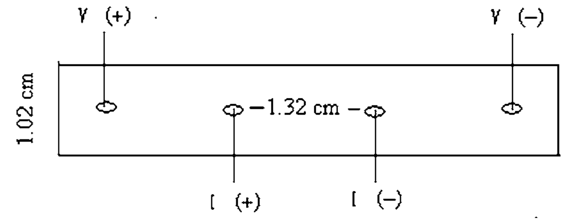


FIG. 4. The measurement of the rectangular sheet.

While either the peak in $E''$ or the peak in tan $\delta$ is often used to define $T_g$, the average temperature of the two peaks is used to determine $T_g$ here. Then, the $T_g$ is found to be 61.03 and 95.44 °C, respectively. Therefore, the $T_g$ is 78.2 °C derived from DMA test.

Two copper electrodes were embedded into the sample for measuring its electrical property. The volume resistance of sample K was investigated using a programmable power supply (PSP-2010 dc apparatus, the maximum voltage is 20 V, and the maximum power is 200 W) by applying directly on it. The volume resistivity was calculated as

$$\sigma = \frac{I}{U}\frac{e}{S}. \tag{1}$$

The current $I$ (0.740 A, at a voltage $U$ of 13 V) through the sample thickness $e$ (0.16 cm) and contact area of electrode and composite $S$ (0.93 cm$^2$) were measured. Its volume resistivity was calculated as $1\times 10^{-2}$ Ω cm. Hence, the electrical conductivity is $1\times 10^{2}$ S/cm$^{-1}$.

The measured electrical conductivity of composites varies depending on the contact area between the electrode and sample. To avoid incidental error in the four-point probe method, van der Pauw four-point method which based on Keithley 2400 and 2000 was introduced.[15] It was employed to measure the volume resistivity of a rectangular sheet ($3.96\times 1.02\times 0.16$ cm$^3$), as shown in Fig. 4. The volume resistance was measured as 56.0 Ω at conditions of a voltage of 24.8 V, electricity intensity of 0.443 A, and temperature of 28.8 °C. The volume resistivity was obtained as 2.32 Ω cm.

The characteristic volume resistivity curves for the samples are plotted in Fig. 5. Both curves of SMP filled with microcarbon powder (MCP) and MCP/SCF serve as references for comparison with the CB and the CB/SCF containing systems. As previously mentioned, a synergy resulting in the MCP/SCF and CB/SCF systems of high conductivity is expected. By comparing the four percolation curves, it can be found that the resistivity of the MCP/SCF and CB/SCF composites with small contents of SCF is lower than that of

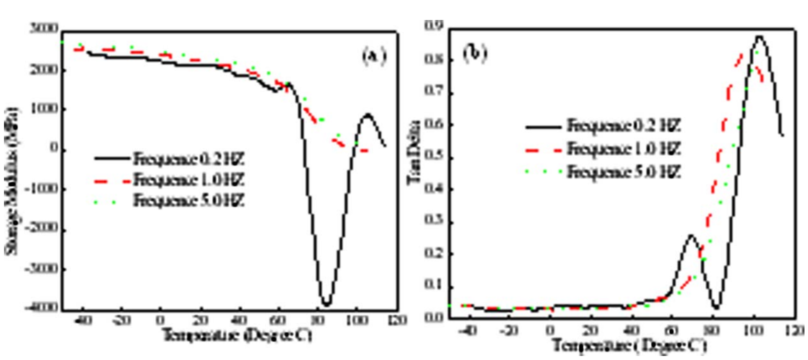


FIG. 3. (Color online) Storage modulus (a) and tan $\delta$ (b) as a function of temperature for sample A at the different oscillation frequencies.

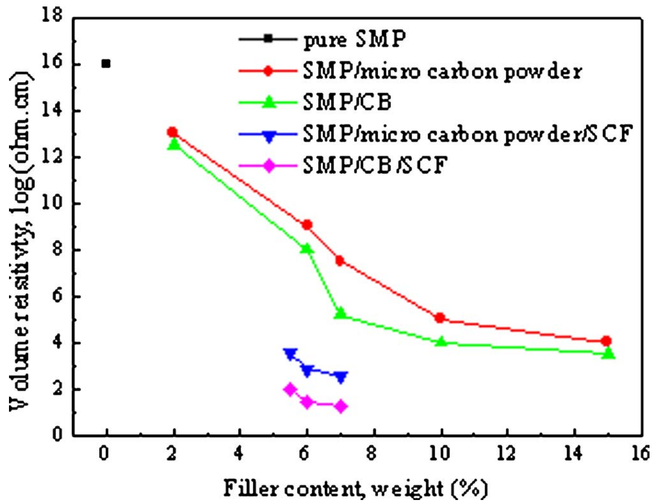


FIG. 5. (Color online) Resistivity of SMP matrix filled with MCP, CB, MCP/SCF, and CB/SCF systems vs filler content.

the composites filled with particle filler only. At the same time, the lower resistivity of the two-filler system may be mainly due to the nanofiller rather than a synergistic effect. That is why the resistivity of the CB/SCF system is still lower than that of the MCP/SCF system.

The CB/SCF composites have excellent electrical property, as short carbon fibers increase the formation of conductive networks. From this study, we may draw the conclusions as follows: (1) The particulate additives are dispersed homogeneously within the matrix and serve as interconnections between the fibers, while the fibrous additives act as long distance charge transporter by forming local conductive networks. (2) The glass transition temperature of the composites is obviously lower than that of the pure SMP. (3) The mechanical properties of the composite are better than those of pure SMP. The storage modulus of the sample increases with SCF filler content increasing, and the glass transition temperature is 78.2 °C from DMA test. (4) The volume resistivity of sample K is 2.32 S/cm as measured by four-point van der Pauw method which is introduced to avoid the incidental errors that arise from four-point probe measurement.

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