Synergic effect of carbon black and short carbon fiber on shape memory polymer actuation by electricity

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This paper presents a study on the effect of carbon black (CB) and short carbon fibers (SCFs) on shape memory polymer (SMP) actuation by applying electric current. The coexistence of CB and SCF electrically conductive networks, supporting each other, resulting in significant improvement of electrical properties, was supported by optical microscopy, while the roles of particulate and fibrous fillers were distinguished by scanning electron microscopy. In sequence, the volume resistivity curves of one filler systems and two fillers systems were figured out and compared. Moreover, experimental results substantiated that the actuation voltage of two-filler SMP composites' shape recovery was prominently lower in comparison with that of one-filler systems at the same filler content. Additional, the response of glass transition temperature (T_g) and thermomechanical properties to filler content and two fillers' synergic effect were characterized and illuminated experimentally. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3026724]

I. INTRODUCTION

Investigation of shape memory polymer (SMP) has become an interesting topic in recent years, owing to their many novel properties and great potential.[1] Same as other shape memory materials, SMPs have the typical shape memory effect (SME); however, the recovery can be triggered by various external stimuli, not only heat such as in shape memory alloys (SMAs), but also light,[2,3] solution,[4–6] etc. Among them, the thermoresponsive SMPs have been the major focus under investigation in the past. Although SMPs have found a few applications, they have not fully reached their technological potential, largely due to the fact that the actuation of thermal-responsive SMPs is normally only driven by external heating.

So far, the development of electroactivate SMP has been documented in literature.[7–11] In these papers, it is found that the electrical conductivity of 10^{-3}, 2.5×10^{-3}, and 1×10^{-1} S cm^{-1} was obtained, when shape-memory polyurethane composites incorporating of 5 wt % surface-modified multiwalled carbon nanotubes, 5 wt % untreated multiwalled carbon nanotube, and 30 wt % carbon black (CB), respectively. As mentioned above, researches on electroresponsive SMP suggested that either the composite is too thin to lose SME or the electrical conductivity is poor, unless very high filler content is used.[12]

In this paper, we propose a novel approach to make shape recovery be induced conveniently by passing an electrical current. The aim of this paper is to investigate the electrical and thermomechanical properties of styrene-based SMP composites (SMPCs) containing CB nanoparticle and short carbon fiber (SCF) and to qualitatively analyze the effect of particulate and fibrous fillers on these corresponding physical properties.

II. EXPERIMENTAL PART

The SMP material used in this study was a thermosetting styrene-based shape-memory resin with a density of 0.92 g/cm^3 and curing temperature of 75 °C (Cornerstone Research Group Inc., OH). CB (AX-010) particles were purchased from GuangZhou Sunny Plaza Trading Co., LTD. 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 particles had a electrical volume resistivity of 5×10^{-2} Ω m at 20 °C. The density was in the range of 1.80–1.85 g cm^{-3}. The SCF cut from carbon fiber (T700) was of 0.5–3 mm length short fiber with a diameter of 7 μm, stress strength of 4900 MPa, and volume resistivity of 1.5×10^{-4} Ω m at 20 °C.

SMP composites were fabricated through the following steps. The CBs were suspended in the ethanol solvent by ultrasonication (VCX750, Sonics & Materials, Inc.). The suspension went through a vacuum filtering process to get rid of the solvent. The SCFs were dried in oven at a temperature of 200 °C to dispose of the moisture and the resin coated on the SCFs' surface. Second, a crosslink agent was mixed with styrene-based SMP resin and stirred well. After that, a certain amount of ultrasonicated CB was added into the mixture, followed by mechanical stirring for 30 min at a constant of 600 rad/min. Then the dried fibrous filler was added into system and mixed by mechanical stirring at a constant of 300 rad/min. Subsequently, the mixture must undergo vacuum treatment. In sequence, the mixture was transferred into a

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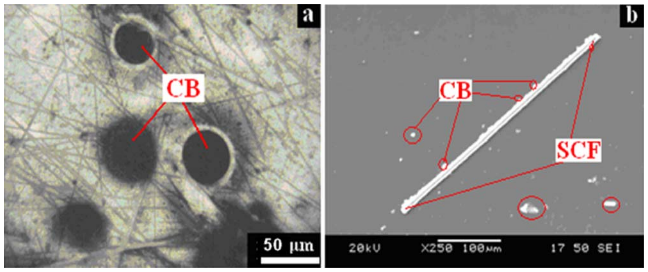

FIG. 1. (Color online) The morphologies of SMP matrix with 2 wt % CB and 0.1 wt % SCF by optical microscopy and scanning electron microscopy observation.

close mold made of glass sheet and rubber tube and kept in an oven for 24 h at a constant temperature of 75 °C for solidification.

In this study, *x*CB denotes the SMPCs with *x*% of weight fraction of CB, and the same as *y*SCF which denotes the composites with *y*% of weight fraction of short carbon fiber. Hence, SMP/*x*CB/*y*SCF presents the SMP composite filled with *x*% of weight fraction of CB and *y*% of weight fraction of short carbon fiber. 13 samples were prepared to investigate the effect (including synergic effect) of CB and SCF on the physical properties of SMP. More importantly, these samples were used to obtain the electrical properties of one-filler and two-filler systems, and then compared to the experimental results.

III. RESULTS AND DISCUSSIONS

Two microstructure images in Fig. 1 show the formation of cosupporting conductive networks. Such conductive networks could improve the electrical properties of polymeric composites and result in them with reduced percolation filler content.[13–16] The dispersion of particles and short fibers in SMPC systems were studied in Ref. 16. However, in this study, the cosupporting of electrically conductive networks were imaged by a ZEISS optical microscope, while the roles of particulate and fibrous fillers played in conductive networks were distinguished and analyzed by scanning electron microscopy (JEOL SEM, JSM-5600LV) image. Figures 1(a) and 1(b) show the morphology comparison of two fillers' distinct roles playing in influencing on polymer.

From the two images in Fig. 1(a), it is found that there is a distinct difference between fibrous and particulate fillers in influencing the electrical conductivity of the composites. SCFs (darkish lines) may be considered to provide the conductive pathways and promote relatively long distance charge transfers, leading to easy formation of continuous conductive networks, resulting in a significant drop in electrical resistance. Normally, these SCFs play a more prominent role in comparison with the particles aggregates in a single-particle-filler system. The continuous conductive pathways characterizations are carried out using a ZIESS optical microscope combined with a Sony charge-coupled device camera and an "Analyses" soft imaging system, while particles and their aggregates act as the nodes among the fibers by forming local conductive pathways, which improves orientation of short fiber.

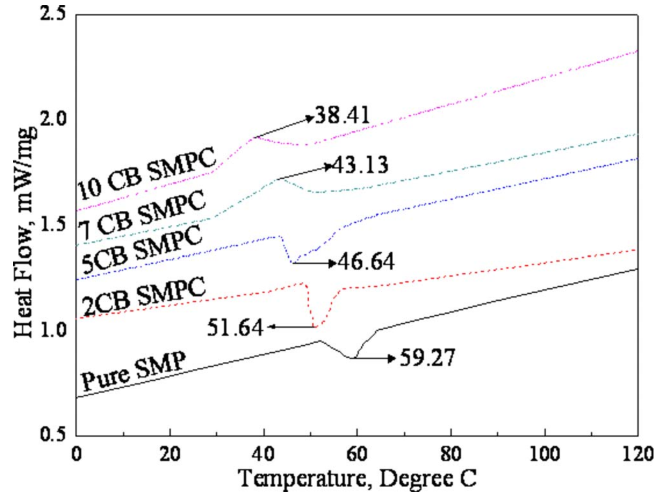

FIG. 2. (Color online) The T_g of pure SMP and its composites filled with CB.

The white dots and white line, representing the particulate and fibrous filler, respectively, can be observed by following Fig. 1(b). Interestingly, the significantly important role of two-filler system plays in influencing the electrically and thermally conductive property of insulating polymer. There are many particles and their aggregates that are adsorbed on the surface of SCF. These enlarge the area of conductive fillers and homogeneously improve the electrical and thermal conductivity of polymer. As a result, the cosupporting two-filler system is expected to enhance conductivity and therefore synergistic effects are expected.

Differential scanning calorimetry (DSC) experiments were performed on a Netzsch (Selb, Germany) DSC 204F1. All experiments were performed with a constant heating and cooling rate of 10 K min^{-1}. The samples were investigated in the temperature range from 0 to 120 °C. The sample was heated from 20 to 120 °C, then cooled down to 0 °C, and again warmed up to 120 °C. Whenever a maximum or minimum temperature in the testing program was reached, this temperature was kept constant for 2 min. The T_g was determined from the second heating run. As in Refs. 16 and 17, the nanoparticles have effect on the T_g, and with the increase of filler content, the depression of T_g is obvious. On the other hand, the T_g of carbon fiber reinforced SMP composite is higher than that of pure SMP.[18] However, there are few studies that investigate the effect of SCF and hybrid two-filler system on the T_g of polymeric composite. In this section, the effect of CB, SCF, and the hybrid two-filler system on the T_g of SMP is presented.

The soft segment formed the reversible phase of SMP and its thermal transition was of crucial importance for shape-memory performance. The T_g was determined by DSC and it was found that the transition temperature of composite is lower than that of the pure SMP. The change of T_g as function of filler content is presented in Figs. 2 and 3. T_g is determined as 59.27, 51.64, 46.64, 43.13, and 38.41 °C for pure SMP, 2CB SMPC, 5CB SMPC, 7CB SMPC, and 10CB SMPC, respectively, as shown in Fig. 2. As we can see, the glass transition occurs within a temperature range from 35 to 60 °C. Furthermore, the result reveals that particle filler has

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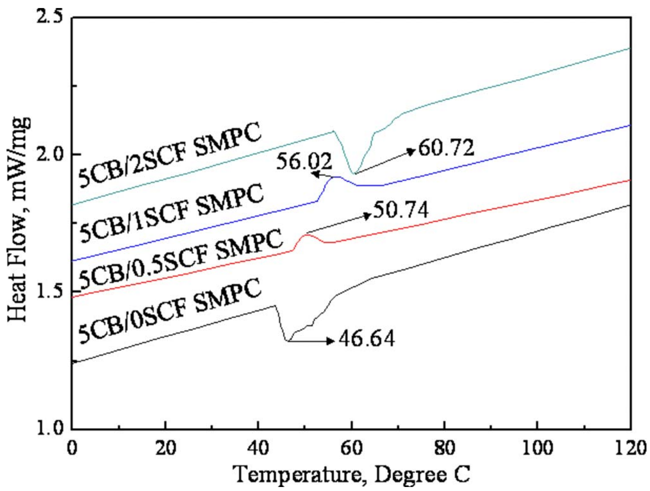

FIG. 3. (Color online) The T_g of SMP filled with 5CB and different contents of SCF.

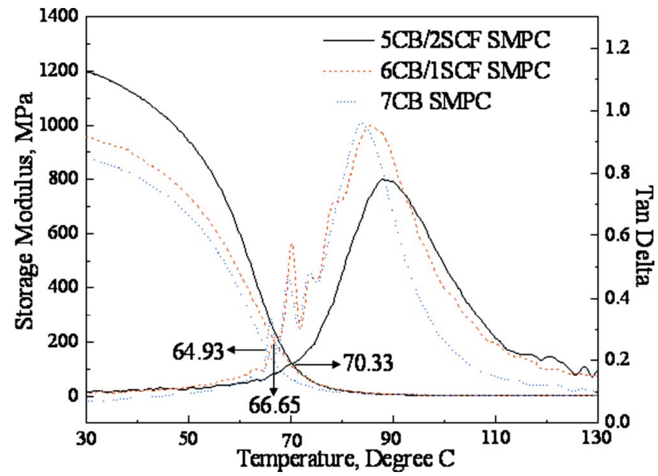

FIG. 4. (Color online) Tangent delta curves of samples at the oscillation frequency of 1 Hz.

a negative effect on the transition temperature and with increase of CB filler content, the transition temperature dropped gradually. The obvious drop can be gained from the curves of SMP/7CB and SMP/10CB composites.

T_g curves in Fig. 3 are plotted to investigate the effect of SCF on the soft segment and T_g of composites that filled with the same filler content of CB. The T_g are 46.64, 50.74, 56.02, and 60.72 °C for SMP/5CB/0SCF, SMP/5CB/0.5SCF, SMP5CB/1SCF, and SMP5CB/2SCF composites, respectively. In comparison, the T_g of SMP/CB systems reduced substantially in the presence of carbon fiber shown in Fig. 2 irrespective of the filler content. As mentioned in the experimental part, the CB particles with characteristic size of 18–20 nm, which were of the same order as the size of typical segment ~10 nm, which may have prevented close packing of the chains. Thus, the more dramatic decrease in T_g in the presence of CB can be attributed to the particle's size and geometry effect. Note that the typical size of SCFs of ~7 μm was about two orders of magnitude higher than the size of segments of which the thermal properties were caused only marginal influence by SCF. However, the thermal behavior of segments was blocked by the interactive friction between macromolecular chains of ~1 μm.

The determination of the dynamic mechanical properties was performed on a Netzsch DMA 242C (Netzsch, Germany). The influence of filler content on the thermal and thermomechanical properties was investigated at varied temperature. All experiments were performed in the three-point bending mode at a constant heating rate of 10.0 K min^{-1}. The oscillation frequency was 1.0 Hz, and samples were investigated in the temperature interval from 30 to 130 °C.

In the dynamic mechanical thermal analysis measurements of composites filled with total 7 wt % conductive filler, the storage modulus and tangent delta were recorded against the temperature. The storage modulus is the modulus of elastic portion of material while the loss modulus is the modulus of viscous portion. Tangent delta that is defined as the ratio of the loss modulus over the storage modulus indicates the damping capability of a material. As shown in Fig. 4, the T_g is defined as the point of intersection between storage modulus and tangent delta curves. Thus, the results of composites containing 5CB/2SCF, 6CB/1SCF, and 7CB were 70.33, 66.65, and 64.93 °C, respectively. It reveals that the T_g reaches its critical values at lower temperature with the particulate filler content increase and the fibrous filler content decrease, while the total filler content is the same. So, the fibrous filler plays a more positive effect on the thermomechanical properties compared to particulate filler, e.g., T_g and the damping and thermodynamic capability of materials. However, the particulate filler plays a contrary role to fibrous filler. This can be attributed to the fact that the obvious enhancement of mechanical properties originated from the effect of SCF on composites.

Electrical resistivity of the SMP composites was measured by a Van De Pawn four-point probe method Keithley 2400 resistivity tester and a Keithley 2000 picoammeter/voltage source. There are four electrodes that were embedded into samples. The schematic presentation of discal sample preparation for resistance measurements of was plotted in Fig. 5.

The volume electrical resistivity as function of filler weight fraction of SMP composites measured at room temperature is presented in Fig. 6. It is seen that electrical percolation occurred at low filler content of 4 wt %, while the volume resistivity of $10^{5.28}$ Ω cm, in composites of single CB prepared in the chaotic system. Based on our previous experience and on literature results, to obtain a synergistic effect, the content of filler should be above its percolation threshold. The characteristic volume resistivity curves for the single CB samples indicate that at 5 wt % the composites have turned conductive. This curve also serves as references

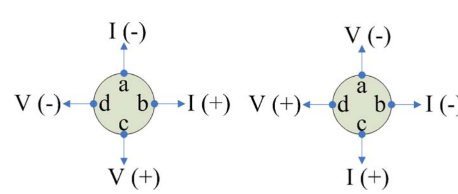

FIG. 5. (Color online) The schematic mechanism of measurement of Van De Pawn.

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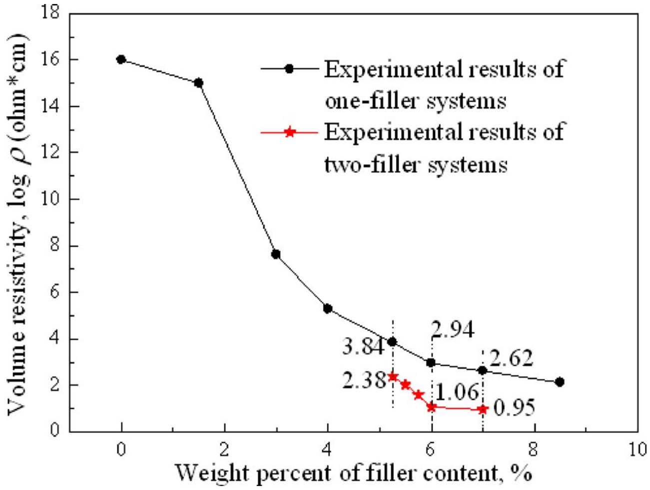

FIG. 6. (Color online) Resistivity of SMP matrix filled with CB and CB/SCF vs filler content.

for comparison with hybrid two-filler containing systems. Samples consisting of SMP, 5 wt % CB and varying contents of SCF were prepared and their volume resistivities are depicted in Fig. 6. As previously mentioned, a synergic effect resulting in reduction of composites of high conductivity is expected. However, preliminary analysis of the resistivity results is not conclusive. Comparison of the two curves shows that even with the lower quantity of fibers that is necessary to make all composites conductive at 5 wt % CB, the resistivity of the SMP/CB/SCF systems is still lower than that of the corresponding systems filled by CB only. In comparison, the volume resistivity of the SMP/5.25CB, SMP/6CB, and SMP/7CB is $10^{3.84}$, $10^{2.94}$, and $10^{2.62}$ Ω cm, respectively, which is nearly 100 times higher than that of the two-filler composites with $10^{2.38}$, $10^{1.06}$, and $10^{0.95}$ Ω cm at the corresponding filler content. This can be attributed to the fact that the inherent fibrillar form of SCF has a higher aspect ratio and orientation to form a three-dimensional network in the composites, ensuring better electrical response than that of particulate fillers. Moreover, from the curves, it is indicated that if the SMP is filled with appropriate content of CB and SCF, the composites will own perfectly electrical properties and behave like a conductor.

The electrically induced SME is exemplarily demonstrated for composite filled with 5CB/2SCF in Fig. 7, where a change in shape from temporary shape to permanent shape occurring within 50 s is shown. The used specimen was about 112 mm × 23.2 nm × 4 nm. After heating the sample

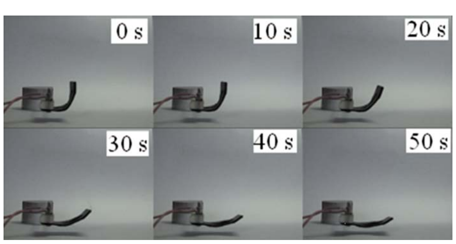

FIG. 7. (Color online) Series of photographs showing the macroscopic SME of SMP/5CB/2SCF composite. The permanent shape is a plane stripe of composite material, and the temporary shape is deformed as right-angled shape.

to 65 °C, it was deformed to a right-angled shape and cooled to fix this temporary shape by the formation of soft-segment crystallites. After this programing process, the sample kept the temporary shape in the absence of external forces as can be seen in Fig. 7 (0 s). The shape transition in the dc field of 25 V was documented with a digital camera. After 20 s, the starting conversion of the flexural shape was observed, taking another 30 s to be completed. The final shape was close to the original plane shape with some remaining flexion due to friction between the soft polymer and the glass plate. The rate of shape recovery was strongly dependent on the magnitude of the applied voltage and the electrical resistivity of composite.

IV. CONCLUSIONS

This paper presents a systematic study on the conducting SMPCs and the influence of CB and SCF on their physical properties. Especially, this type of composites show excellent electrical property, as fibrous filler cooperates with particulate filler enhancing the formation of conductive networks. From this study, the following conclusions can be drawn. (1) The conductive network of electroresponsive SMP composite containing CB and SCF is virtually formed resulting in a sharp insulator-conductor transition, and it can be heated efficiently by passing an electric current, so it presents a novel approach to realize shape recovery induced by electricity. (2) As DMA test showed, the thermomechanical properties of composite are influenced by the conductive fillers. Sometimes, fibrous fillers enhance the mechanical properties of composites more obvious than particulate fillers.

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