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Conductive Shape Memory Polymer Composite Incorporated with Hybrid Fillers: Electrical, Mechanical, and Shape Memory Properties

KAI YU,[1] YANJU LIU[2] AND JINSONG LENG[1,*]

[1]*Science Park of Harbin Institute of Technology (HIT), Centre for Composite Materials, No. 2 YiKuang Street, P.O. Box 3011, Harbin, P.R. China*

[2]*Department of Aerospace Science and Mechanics, Harbin Institute of Technology (HIT), No. 92 West dazhi Street, P.O. Box 301, Harbin, P.R. China*

ABSTRACT: In this article, separated carbon nanotubes (CNTs) aggregations were bridged by short carbon fibers in the conductive polymer composites, where a styrene-based shape memory polymer (SMP) was selected as the matrix resin. Due to the synergistic effect of hybrid fillers, the electrical resistivity of the SMP composites was significantly decreased in comparison with those with only CNTs embedded. Benefits offered by the hybrid fillers to the electrical, mechanical, and shape memory properties of the developed conductive SMP composites were experimentally demonstrated in detail. The additionally acquired shape memory capability could expand the application scope of traditional conductive polymer composites.

Key Words: carbon nanotubes, short carbon fibers, shape memory polymer, conductive polymer composites.

INTRODUCTION

COMPARED with conventional metallic conductors, conductive polymer composites exhibit unique properties that are appreciated in many practical applications, such as easy processing, lightweight, low cost, corrosion resistance, etc. Besides, after doping various amounts of conductive fillers, the range of electrical conductivity of the polymer composites could be controllable. Thus, conductive polymer composites have been widely applied in forms of conductive paints, coatings, caulks, sealants, adhesives, sheets, tubes and structural components, etc. Generally, three classes of polymer resins are utilized as the composite matrices, namely thermoplastic polymers (rigid, meltable, e.g., polyethylene), elastomers (stretchable, e.g., rubber), and thermoset polymers (rigid, not-meltable, e.g., epoxy).

As an emerging class of thermoset polymers, shape memory polymers (SMPs) additionally possess a dual-shape capability, referring to the shape recovery from a temporary shape to the permanent shape after SMPs are exposed to external stimulus, such as electricity (Leng et al., 2007, 2008a, b, 2009; Liu et al., 2009), light (Lendlein et al., 2005), magnetic fields (Buckley et al., 2006; Mohr et al., 2006; Schmid, 2006), and solvents (Huang et al., 2005; Leng et al., 2008c; Lv et al., 2008, 2009). Recently, electric-induced SMP composites have gained extensive research interests due to their convenient and efficient actuation method. The SMP composites could be actuated through Joule heat by simply passing an electric current, just like that of NiTi shape memory alloys (Triantafyllou and Psarras, 2010), getting rid of external heaters, inconvenient devices, or bulk system to generate the actuating environment. Primary art to achieve the electrical actuation of SMPs is doping conductive fillers, for example, conductive powder, nanowires, nanotubes, and continuous fibers (Gall et al., 2000; Zhang et al., 2007; Zhang et al., 2010) to render the insulating polymers into electrically conductive. In this way, SMP composites can not only serve as traditional conductive polymer composites to transport electrons, but also provide considerable actuating forces during the shape recovery process. Their application scopes could also be subsequently expanded due to the additionally acquired shape-memory capability.

The actuating forces in conductive SMP composites increase along with the improvement of mechanical properties. Among all the conductive fillers, continuous fibers (e.g., carbon fiber) can significantly enhance the stiffness and strength of polymers (Stankovich et al., 2006), but the recoverable strain (up to 400% in pure SMPs) in the conductive SMP composites is seriously

*Author to whom correspondence should be addressed.
E-mail: lengjs@hit.edu.cn
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decreased due to the relatively low deformation ability of continuous fibers (Kimura et al., 2002; Ni et al., 2007). On the other hand, the conductive powder (e.g., carbon black) seems to have little influence on the deformation performance of SMPs, but it also has little mechanical reinforcement effect on the material. Hence, conductive nanowires or nanotubes are more desirable for the application.

In this article, styrene-based shape memory resin was selected as the matrix and carbon nanotubes (CNTs) were recruited as one type of conductive filler in the investigated SMP composites due to their superb electrical, mechanical, and thermal properties (Saito et al., 1998). The embedded CNTs were expected to significantly improve the overall performance of the composite material. However, our previous investigations indicated that even though the mechanical properties and electrical conductivity of SMPs increased remarkably along with the addition of CNTs, excessive amount of CNTs (around 4.5 wt%) would increasingly inhibit the polymerizing reaction of the styrene-based shape memory resin, which would subsequently lead to decreased elastic modulus and stretch of the materials. In this case, the allowable CNT content in the conductive SMP composites is limited in practical applications where high strength or stiffness of the conductive polymer composites is required. Meaning while, the electrical resistivity of the SMP composites will also stand at the semiconductor level which is not suitable for the electrical actuation of SMP composites in a low electric power.

In view of these, we selected short carbon fibers (SCFs) as the second conductive filler to bridge CNT aggregations in the conductive SMP composites. In the hybrid conductive fillers system, SCFs would serve as conductive channels in relatively long distances, while CNTs played a role of local conductive pathways. The synergic effect of hybrid fillers helped to significantly reduce the electrical resistivity of the conductive SMP composites. Besides, due to the small length of SCFs, the recoverable strain of the conductive SMP composites was not expected to decrease too much in comparison with pure SMPs. Benefits to the electrical, mechanical, and shape memory properties of the developed conductive SMP composites were experimentally demonstrated in the article. The improved conductivity also permitted electrical actuation of conductive SMP composites in a low electric power.

INVESTIGATED MATERIAL AND FILLERS

In our study, the styrene-based shape memory resin (Veriflex® S VF 62) with a density of 0.92 g/cm^3 was purchased from Cornerstone Research Group, Inc., Dayton, Ohio, USA, which is a two-part, fully formable thermoset SMP resin system. Some mechanical and thermal properties of the pure SMP are presented in Table 1.

The applied SCFs were chopped from continuous carbon fiber (T700) with an average length of 2 mm, an average diameter of 7 μm, tensile strength of 4900 MPa, and volume resistivity of 1.5×10^{-4} Ωm at room temperature. The multi-walled CNTs were purchased from Shenzhen Nanometer Gang Co., Ltd., with an average length of 1 um and diameter of 50 nm. To present a clear comparison between the electrical resistivity of conductive SMP composites embedded with CNTs only and hybrid fillers, two groups of composite specimens were prepared, in which the weight fractions of conductive fillers varied within the same range, namely SMP composites with 2.5 wt%, 3 wt%, 3.5 wt%,and 4 wt% CNTs, and SMP composites with 1 wt% CNTs/1.5 wt%, SCFs, 1.5 wt% CNTs/1.5 wt%, SCFs, 2 wt% CNTs/1.5 wt% SCFs and 2.5 wt% CNTs/1.5 wt% SCFs.

The conductive SMP composites with specified SCFs or CNTs concentrations were prepared in the following steps: First, the shape memory resin was mixed with crosslink agent at a weight ratio of 24:1. Second, CNTs were mixed with the blend and well stirred. The suspension was then placed in a high-energy sonicator (SONICS-44349N) at an output amplitude of 60% for a total of 40 min, in intervals of 10 min. Third, for the conductive SMP composites with hybrid fillers, SCFs were doped into the mixture, and followed by a high shear mixing. Forth, the mixture was placed in an air-tightened box to completely remove the air bubble, and then transferred into a close mold. Fifth, the resin

Table 1. Mechanical and thermal properties of thermosetting styrene-based SMP.

Mechanical properties	*Value*	*Method*
Tensile strength	22.96 MPa	ASTM D638
Tensile modulus	1241.1 MPa	ASTM D638
Tensile elongation to break	3.90%	ASTM D638
Flexural strength	31.72 MPa	ASTM D790
Flexural modulus	1241.1 MPa	ASTM D790
Thermal properties		
Glass transition temperature	143° F/62°C	
Thermal conductivity at 18.9°C	0.17 W/m//K	

mixture was cured with a ramp of approximately 1°C/min from room temperature to 75°C. The specimen was then held at 75°C for 3 h before being ramped to 90°C at 15°C/180 min. Finally, it was ramped to 110°C at 20°C/120 min.

ELECTRICAL PROPERTIES

Morphology Observations by Scanning Electronic Microscope

Generally, the electrical conductivity of a polymer composite is resulted from the competitions among three conducting mechanisms: conductive channels/networks effect, tunnel effect, and filed emission effect. With a low concentration of conductive fillers and low magnitude of external electric field, tunnel effect plays a dominated role for electrons transportation due to the low probability to form conductive channels or networks in the polymer composites. When the external electric field is increased to a certain level, filed emission resulted electron transportation is prominent. Under a specified magnitude of external electric field and higher content of conductive fillers, the conductive channels or networks would be easily formed and begin to dominate the electron transportation mechanism in the polymer composites. Since the developed conductive SMP composites are expected to possess a low electrical resistivity, the conductive channels/networks would be the main reason for the electrical conductivity. However, it is also noted that SCFs and CNTs are interconnected with each other by the SMP resin. Thus, the tunnel effect resulted electrons transportation also exists in the local conductive channels or networks.

The microcosmic morphology of the hybrid fillers in the conductive SMP composites was observed by a scanning electronic microscope (SEM), Camscan, MX2600. And the details of micro/nanopatterns of the SMP composites incorporated with 1.5 wt% SCFs and 2.5 wt% CNTs are shown in Figure 1. When a voltage is applied on the SMP composite, SCFs are expected to efficiently transport electrons among the CNT aggregations due to their excellent electrical conductivity. Continuous conductive pathways could be easily formed between the electrodes. The bridging effect of SCFs on the CNT aggregations in relatively long distance is considered as the main reason for the significant drop of electrical resistivity in the SMP composites. The SEM observation in Figure 1(a) reveals that SCFs are interconnected with each other in the conductive SMP composite, which expands separated conductive channels into networks, further improving the electrical conductivity. Meaning while, these SCFs also play a considerable role of mechanical reinforcement for the SMP composites. Figure 1(b) shows the morphology of CNTs distribution in the SMP matrix. Even though CNTs were dispersed by ultrasound energy before the curing reaction of SMP composites, most of them congregated again after a curing cycle (24 h). As the figure shows, CNTs aggregate as clusters instead of absolutely separating from each other. In this way, the CNTs aggregations will act as conductive nodes among the SCFs, and form local conductive pathways in the composite. Due to the large amount of conductive channels and stable networks formed in the composite, the electrical resistivity can be reduced remarkably in comparison with those with CNTs embedded only.

Electrical Resistivity of the Conductive SMP Composites

In this section, specimens with dimensions of $2 \times 5 \times 25\,mm^3$ were cut out from each fabricated conductive SMP composite and connected to aluminum electrodes to test the electrical resistivity. Through our previous research works, it is found that testing results of electrical properties for conductive SMP composites are different with varying contact positions between the electrodes and specimen. To avoid incidental error, the Van De Pawn four-point probe method was used in this study (as is shown in the inset view of Figure 2). Each data were measured by taking the average value of six readings from six different pieces of the same specimen. The corresponding electrical resistivity was calculated according to the specimen dimension.

The electrical resistivity curves of the prepared SMP/CNT and SMP/CNT/SCF specimens were plotted in Figure 2. We also referred electrical resistivity curves of SMP composites filled with microcarbon powder (MCP)/SCF and carbon black (CB)/SCF (Leng et al., 2008b) for comparison with the CNT and the CNT/SCF containing systems. It can be found that for the SMP/CNT specimens, even though their electrical resistivities decrease from $10^{6.078}$ $10^{4.276}\,\Omega m$ by increasing the CNT content from 2.5 to 4.0 wt%, the conductivity of the SMP composites still stands at the semiconductor level. But after doping 1.5 wt% SCFs and keeping the weight fractions of conductive fillers at the same range, an average of 1000 times decrease in the electrical resistivity is observed in the SMP/CNT/SCF composites, which could be treated as electrical conductors. The significantly improved electrical conductivity is attributed to the synergistic effect between SCFs and CNTs, as is indicated in the SEM observations. At the same time, it is observed that with 1.5 wt% SCFs and 2.5 wt% CNTs, the electrical resistivity of the SMP composite is decreased to $10^{0.904}\,\Omega m$, indicating that the developed SMP/CNT/SCF composites reach a higher electrical conductivity level with lower weight fraction of conductive fillers in comparison with those that contain CB/SCF and MCP/SCF system. The lower resistivity of the CNT/SCF system is mainly

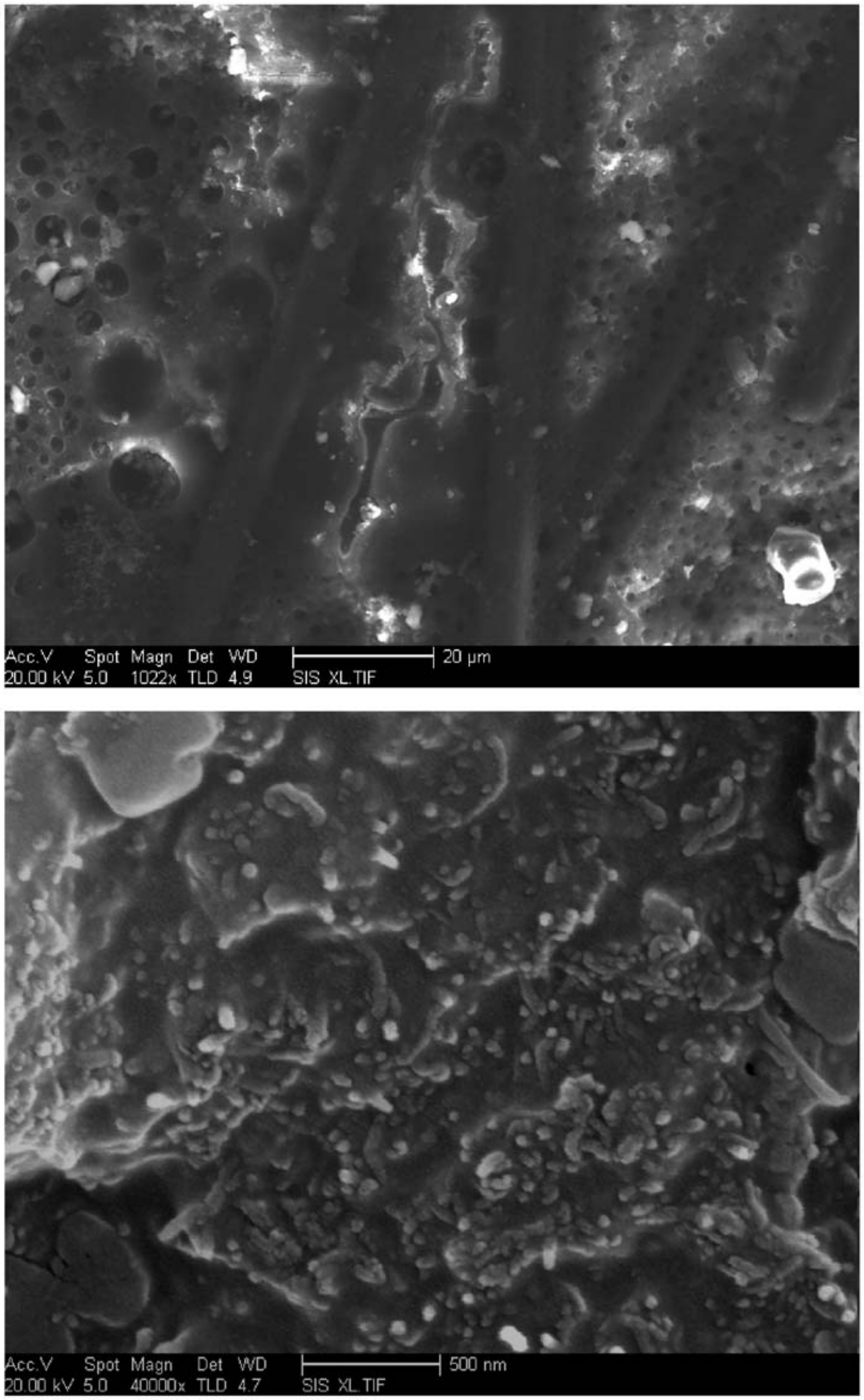
(a)
(b)


Figure 1. *Morphologies of the conductive SMP composite incorporated with 1.5 wt% SCFs and 2.5 wt% CNTs observed by SEM. (a) Morphology of SCFs; (b) Morphology of CNTs.*

due to the excellent electrical conductivity of CNTs. Another advantage to be noted is that in CB/SCF and MCP/SCF system, the CB and MCP only play a role in the local conductive pathways formation, without mechanical reinforcement effect. But in the CNT/SCF system, the mechanical properties of the conductive SMP composite could be enhanced simultaneously because of the superb mechanical properties of CNTs. The dual reinforcement effect of the CNT/SCF system on the mechanical properties of conductive SMP composites is beneficial for their applications as stress-bearing components or structures.

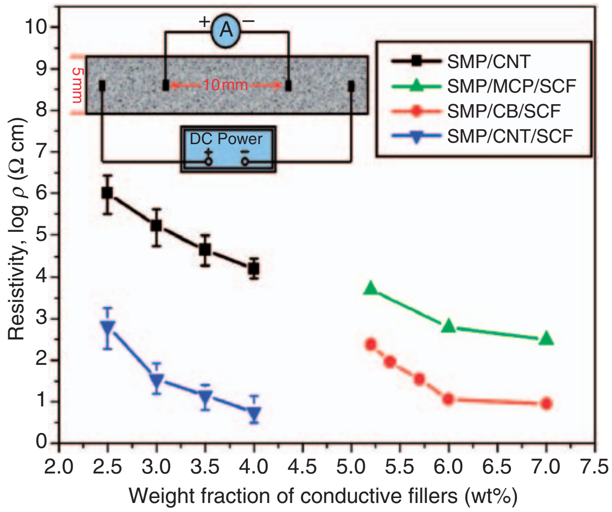


Figure 2. *Resistivity of SMP composites filled with CNT, CNT/SCF, CNT/MCP, and CNT/CB (Inset view: Experimental setup for the resistivity measurement).*

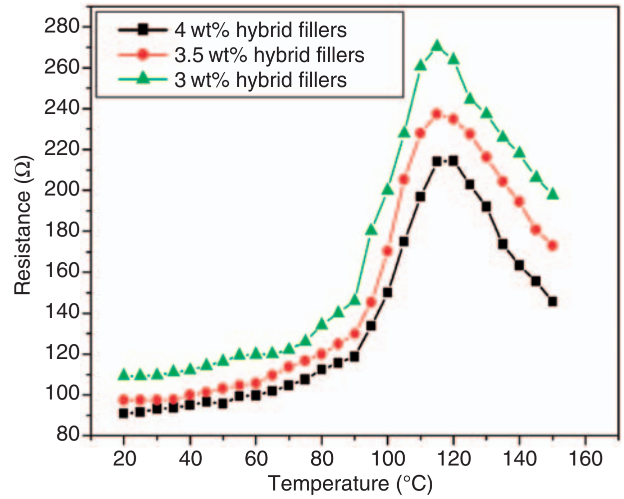


Figure 3. *Curves of resistance vs temperature in the conductive SMP composites with various weight fractions of hybrid fillers.*

Temperature Sensitivity of the Electrical Resistivity

One of the thermo-sensitive effects in conductive polymer composites is the resistance changing with increasing temperature in a certain temperature range, namely the positive temperature coefficient (PTC) effect or negative temperature coefficient (NTC) effect. The PTC or NTC effect for conducting polymer composites depends remarkably on the properties of polymer matrices and conducting fillers. In this work, the dependence of the resistance on the temperature within the range from 20°C to 150°C is investigated with a constant heating rate of $1.0^{\circ}C{\cdot}min^{-1}$. Meanwhile, resistance of three specimens ($2 \times 5 \times 20\,mm^3$) with 3 wt% hybrid fillers (1.5 wt% SCFs/1.5 wt% CNTs), 3.5 wt% hybrid fillers (1.5 wt% SCFs/2 wt% CNTs) and 4 wt% hybrid fillers (1.5 wt% SCFs/2.5 wt% CNTs) were meausred simultaneiously for comparasion.

As is shown in Figure 3, the volume resistance decreases along with the addition of hybird fillers. From 20°C to about 80°C, the resistance of each specified specimen increases slowly with temperature increasing. Then after 80°C, its resistance increases dramatically with increasing temperature, showing a classic PTC effect. The PTC effect in the developed conductive SMP composites resulted from the discordant thermal expansion coefficients between the matrix resin and conductive fillers. In a relatively low temperature, a stable conductive network is formed in the conductive SMP composites. With the increase of surrounding temperature, the matrix SMP expands faster due to its higher thermal expansion coefficient in comparison with the hybrid fillers, which leads to the average distance among the hybrid fillers increasing. Some conductive pathways may be disconnected and the electrical resistivity of the conductive SMP composites is subsequently elevated. On the other hand, molecule vibration degree increases along with elevation of temperature, which would block the electrons movement and further increase the electrical resistivity of the conductive SMP composites.

With temperature increasing above 110°C, the volume resistance falls down obviously. All the three specimens begin to show a classical NTC effect. This is because that when the surrounding temperature is increased to a critical level, the viscosity of the SMP matrix decreases and the flowability of the polymer segments increases. Meaning while, the electron movement degree is significantly intensified. These three factors cause the electrical resistivity of the conductive SMP composites decreases at this stage. The revealed temperature sensitive capability offer opportunities to apply the developed conductive SMP composites as temperature sensors.

Strain Sensitivity of the Electrical Resistivity

In the following test, the resistance of the conductive SMP composites changes with the strain altering. The dependence of the resistance on the tensile strain in the range from 0% to 1.5% was investigated with a constant rate. Similar with the former study, all the three specimens with different weight fractions of hybird fillers were also tested for comparison.

Figure 4 shows curves of resistance values versus stain in the conductive SMP composites. At the same strain rate, specimen with higher weight fraction of hybird fillers exhibits a lower resistance due to the increased continuous conductive channels. The volume resistance is also observed to increase with the tensile strain, and the slope of each curve increases continuously.

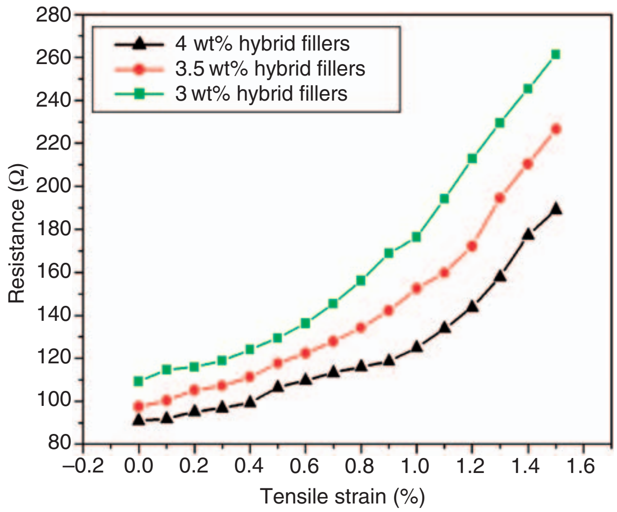


Figure 4. *Curves of resistance vs tensile strain in the conductive SMP composites with various weight fractions of hybrid fillers.*

The detailed resistance variation trend for each specimen can be expressed as follows: at the beginning, with the increase of tensile strain, the average distance among CNTs in their aggregations, average distance between local CNTs aggregations and SCFs fillers increases gradually. The contact situation between CNTs and SCFs is also influenced. Thus, electrons transportation over a small distance is destroyed under the outer tensile forces. However, new conductive paths are constructed consequently, which can somewhat compensate for conductivity losses resulted from increased distances between conductive fillers. With a further increase in the tensile strain, the CNTs and their aggregations begin to break away from SCF fillers, and eletron transportation over large distances is destroyed. In this case, resistance increases drastically. In general, accompanied by outer loading or shape changing, the phenomena of strain-dependent resistance in the conductive SMP composites will occur, and the stain sensitive capability of the developed conductive SMP composites could directly or indirectly reveal the outer forces focued on them.

MECHANICAL PROPERTIES

Isothermal Static Tensile Properties

Based on micro and macro mechanics, many mechanical property prediction models of composites reinforced by randomly distributed fillers have been developed during the past few decades. Some empirical relationships are also available to be used in the determination of approximate properties of random SCFs or CNTs reinforced composites.

Typically, the modified Halpin–Tsai (Christensen, 1997) equation can be expressed as following:

$$E_c = \frac{3}{8}E_1 + \frac{5}{8}E_2 \tag{1}$$

Where $E_1 = E_m(1 + \xi\eta_1 v_f/1 - \eta_1 v_f)$, $E_2 = E_m(1+ \xi\eta_2 v_f/1 - \eta_2 v_f)$, $\eta_1 = ((E_f/E_m) - 1)/(E_f/E_m) + 2(l/d)$ and $\eta_2 = (E_f/E_m) - 1/(E_f/E_m) + 2$

In this relationship, the E_c, E_m, and E_f are the Young's modulus of composite, matrix, and reinforcement fillers respectively. l donates the average fillers length and d is the average diameter of fillers. Halpin suggests that $\xi = 2(l/d)$ gives good predictions in the relationship. Besides the Halpin–Tsai equation, we also selected Rom, Clyne, and Cox equations to theoretically predict the tensile modulus of the developed conductive SMP composites with various weight fractions of hybrid fillers.

To deliver a detailed study on the tensile properties of the developed conductive SMP composites, isothermal static tensile tests were also conducted to experimentally demonstrate the mechanical properties. The tests were operated on a Zwick/Roell servo-mechanical testing frame where an Instron^R clip-on extensometer and self-contained extension sensor were utilized simultaneously. The static tensile tests were performed at a loading speed of 1 mm/min within the chamber. In the integrated testing software, the output ports were selected as load and displacement, and the corresponding engineering stress and strain were calculated according to the specimen dimensions. Four specimens ($2 \times 15 \times 80\,mm^3$ with 2.5 wt% hybird fillers (1.5 wt% SCFs/1 wt% CNTs), 3 wt% hybird fillers (1.5 wt% SCFs/1.5 wt% CNTs), 3.5 wt% hybird fillers (1.5 wt% SCFs/2 wt% CNTs) and 4 wt% hybird fillers (1.5 wt% SCFs/2.5 wt% CNTs) were cut out from each prepared conductive SMP composite.

Figure 5 shows a comparison between the experimental results and theoretical predictions in the tensile property analysis of the conductive SMP composites. In this figure, the four experimental data of tensile modulus were obtained by calculating the slope of linear part in the strain-stress curves of the isothermal static tensile tests. And the breaking elongations of each specimen were also marked. It is found that the tensile modulus is greatly enhanced by adding the hybrid fillers. Compared with pure SMP, the tensile modulus is increased from 1.24 to 3.64 GPa by doping 1.5 wt% SCFs and 2.5 wt% CNTs. The significant reinforcement effect is attributed to the higher modulus of SCFs (240 GPa) and CNTs (over 1 TPa). Meanwhile, it is also observed that the calculation results in Rom, Cox, and Clyne models are relatively deviated with the experimental values. But predictions in Halpin–Tsai model show a similar slope and a closer prediction with the

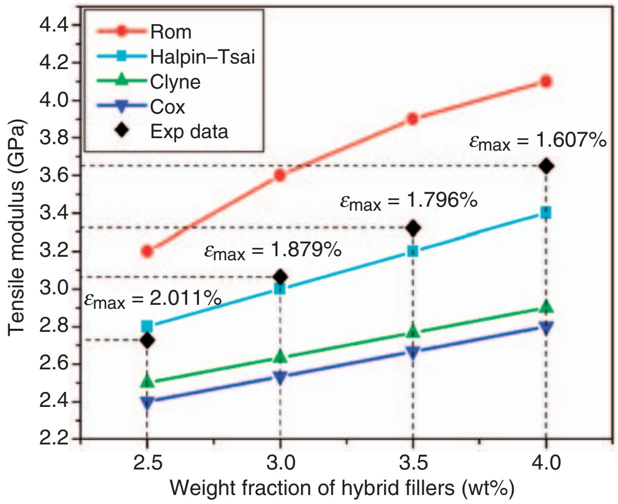


Figure 5. *Curves of tensile modulus vs weight fraction of hybrid fillers.*

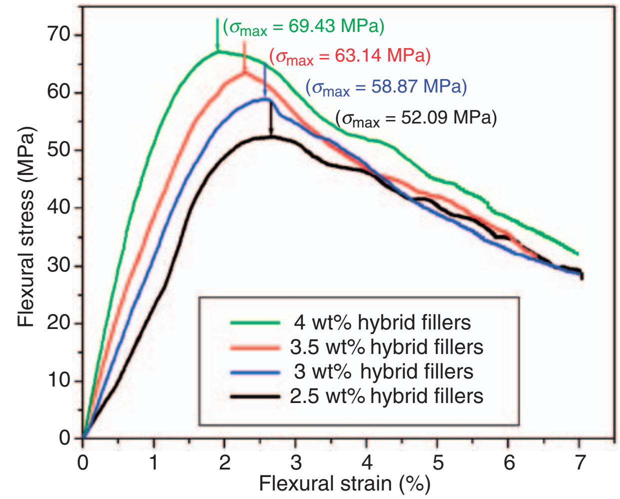


Figure 6. *Curves of flexural stress vs flexural strain with various weight fractions of hybrid fillers.*

experimental results, indicating that with the addition of hybrid fillers, the Halpin–Tsai model can provide a more precise prediction during the mechanical analysis of the conductive SMP composites.

Besides, the breaking elongation of each specimen decreases along with the addition of hybrid fillers. This is because that the debonding between the hybrid fillers and matrix resin is considered to be the major failure characterization in the specimens. With the occurrence and propagation of cracks at the boundary of matrix and fillers, the tensile modulus of the specimen decreases gradually and finally the specimen is ruptured. The ultimate tensile strength and breaking elongation are strongly influenced by the randomicity of hybrid fillers distribution.

Isothermal Static Flexural Properties

The isothermal static flexural behavior of SMP bulk and SMP-based composites is always studied to determine their shape memory behavior such as recovery time, recovery ratio, and bending recoverability. In this section, the flexural modulus, flexural strength, and maximum flexural stain of the developed conductive SMP composites were measured using three-point bending test on a Zwick/Roell servo-mechanical test frame. The static flexural test was performed at a loading speed of 2 mm/min and a testing temperature of 25°C. Four rectangular specimens were cut out from the prepared conductive SMP composites. The specimen dimensions and weight fractions of hybrid fillers were the same as those in the static tensile tests. In the integrated testing software, the output ports were selected as load and displacement, and the corresponding flexural stretch, flexural stress, and flexural strain were calculated according to GB/T 1449-2005 stand.

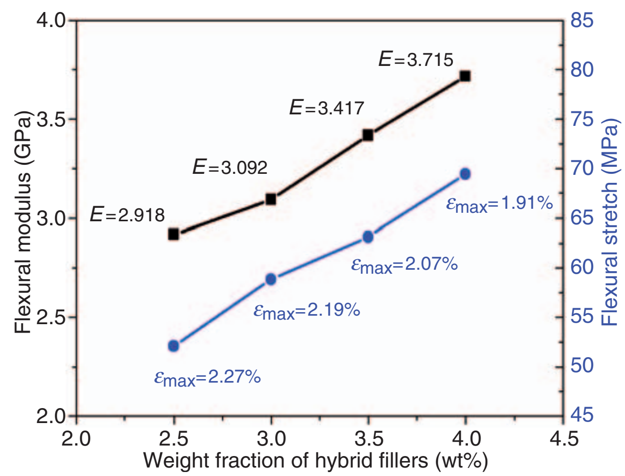


Figure 7. *Relations between flexural modulus and flexural stretch vs weight fraction of hybrid fillers.*

Figure 6 reveals the relations between flexural stress and strain in the developed conductive SMP composite. For a convenient comparison, we also summarized the flexural modulus, flexural stretch, and maximum flexural strain of each specimen in Figure 7. As shown in Figure 6, the flexural stress increases proportionally to the hybrid filler fractions. The flexural stretch of specimens with 2.5 wt%, 3 wt%, 3.5 wt%, and 4 wt% hybrid fillers are 52.09 MPa, 58.87 MPa, 63.14 MPa and 69.43 MPa, respectively. Compared with the flexural stretch of pure SMP (31.72 MPa), an obvious increment of the flexural strength is observed in the developed SMP composites. This phenomenon may be mainly attributed to the native mechanical properties of the hybrid fillers.

Furthermore, in Figure 7, the maximum flexural strain is observed to decrease along with the addition of hybrid fillers, and the flexural modulus of the conductive SMP composites increases from 2.92 to 3.712 GPa. Compared with that of pure SMP (1.24 GPa), the enhanced flexural modulus indicates that the bending recovery force and the flexural load-bearing ability of the conductive SMP composites could be improved simultaneously.

SHAPE MEMORY PROPERTIES

Thermoechanical Properties

The storage modulus of SMP composites measures the stored energy in the viscoelastic state, representing the elastic portion of material. The data could be used to calculate the shape recovery stress under various loading conditions. Here, the thermomechanical properties of the conductive SMP composites were determined on a Netzsch DMA 242C (Netzsch, Germany) equipment. All the specimens, with the same dimensions of $70 \times 12 \times 2\,\text{mm}^3$, were tested in the three-point bending mode at a constant heating rate of $10^\circ\text{C min}^{-1}$, an oscillation frequency of 1 Hz, and an examined temperature range of 20 to 140°C. They were initially locked into a deformation of 0 % with zero initial force. The temperature-dependent storage modulus of the conductive SMP composites with 2.5 wt% hybrid fillers (1.5 wt% SCFs/1 wt% CNTs), 3 wt% hybrid fillers (1.5 wt% SCFs/1.5 wt% CNTs), 3.5 wt% hybrid fillers (1.5 wt% SCFs/2 wt% CNTs) and 4 wt% hybrid fillers (1.5 wt% SCFs/2.5 wt% CNTs) is summarized in Figure 8.

The data shows that for a conductive SMP composite with a specified amount of hybrid fillers, the storage modulus far below T_g is about two orders of magnitude larger than that above T_g. For instance, the conductive SMP composite with 1.5 wt% SCFs and 2.5 wt% CNTs exhibits a storage modulus of 3069.3 MPa at 25°C, while it is just 220.37 MPa at 100°C. The thermomechanical properties of the conductive SMP composites are expected to improve due to the reinforcement of the hybrid fillers. Additionally, because the typical size of CNTs is of the same order as the size of segments in polymer network, they could be well bonded with the SMP matrix and play a more prominent role in the thermomechanical property reinforcement. The friction interactions among CNTs and macromolecule segments help SMP composites to resist external loading. It should also be noted that with the increase of temperature, storage modulus of SMP composites with 2.5 wt% CNTs decreases more quickly than those of the other three. This is because the glass transition temperature (T_g) of SMP composite would decrease along with the addition of CNTs content. At the same temperature above corresponding T_g, the glass transition degree is higher in SMP composite with more CNTs concentrated. Under the synergistic effect of the hybrid fillers, the storage modulus of the SMP composite is reinforced, indicating that more shape recovery stress would be generated during the glass transition reaction.

As calculation samples, the temperature-dependent shape recovery forces and shape recovery moments of the developed conductive SMP composites were calculated under tensile and bending deformations. In the above-mentioned investigations, the maximum tensile elongation and maximum flexural strain of the composites at the temperature of 20°C were 1.61% and

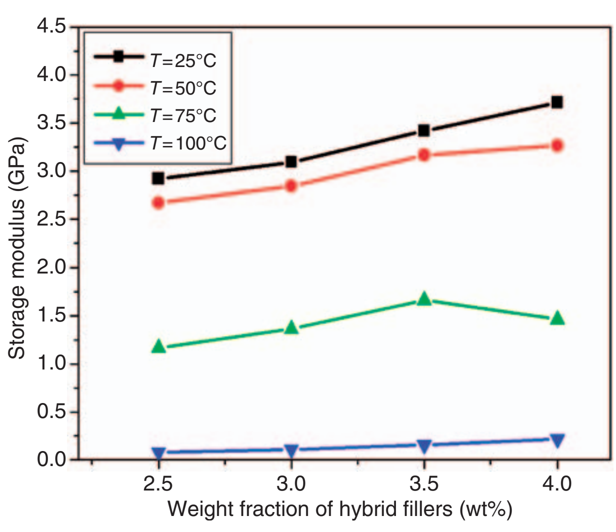


Figure 8. *Curves of storage modulus under various temperature vs weight fractions of hybrid fillers.*

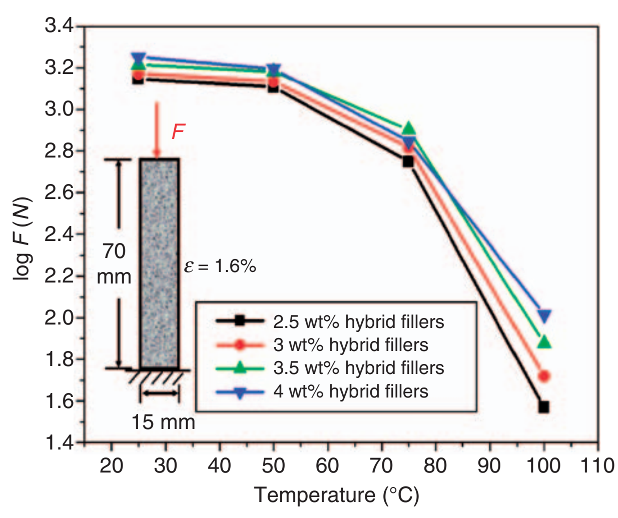


Figure 9. *Tensile shape recovery forces of the conductive SMP composites under various temperatures.*

1.91%, respectively. Thus, the tensile strain and flexural strain in the calculation samples were respectively supposed to be 1.6% and 1.9%, and the dimensions of the SMP composite was supposed to be $70 \times 15 \times 2\,\mathrm{mm}^3$. Based on the classic material mechanics, the shape recovery forces under the tensile deformation could be calculated by the following equation:

$$F = A \times E(t) \times \varepsilon \qquad (2)$$

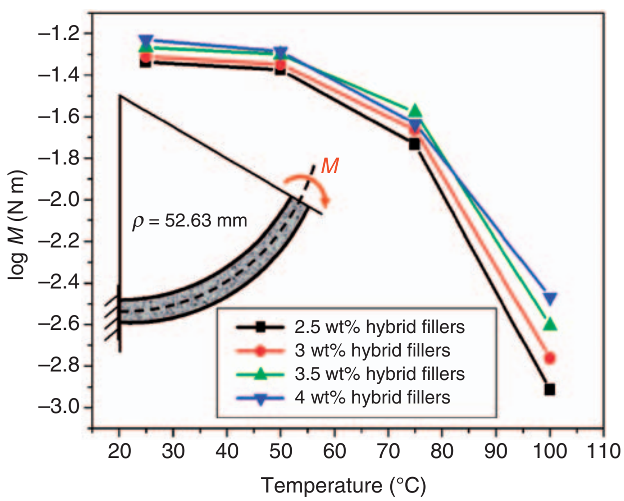


Figure 10. *Bending shape recovery moment of the conductive SMP composites under various temperatures.*

where A is the cross section area of the conductive SMP composites, $E(t)$ is the temperature-dependent storage modulus, and ε is the tensile strain (equals 1.6%).

Meaning while, the shape recovery moments under the bending deformation could also be calculated by the following equation:

$$M = \frac{E(t) \times I_z}{\rho} \qquad (3)$$

where $E(t)$ is the temperature-dependent storage modulus, I_Z is moment of inertia, and ρ is the corresponding curvature radius.

The temperature-dependent tensile shape recovery forces and bending shape recovery moments of the conductive SMP composites were calculated and summarized in Figures 9 and 10. As is shown in the figures, for each specimen, the recovery force and moment decrease slowly at the beginning, and then a sharp decrease is observed after the temperature of 50°C. The variation trend could be explained as followings: initially, the molecular chains are frozen in the SMP composites when the temperature is relatively low, and the shape recovery effect can not be fully expressed at this stage. At this stage, the elastic modulus of the SMP composites is relatively high and more stress will be generated per unit of strain. In other words, if the material is fixed and in exposure to external forces, more resistance stress will be generated inside the materials.

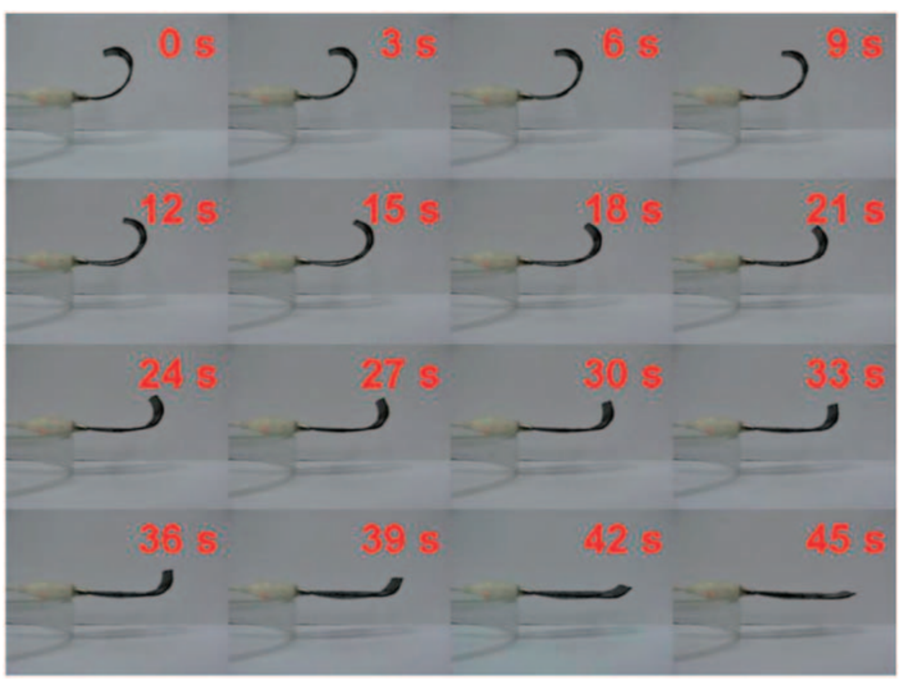


Figure 11. *Series of photographs showing the macroscopic shape recovery process of the conductive SMP composite.*

With the temperature increase, the molecular chains in the materials begin to defrost and the locomotory units start to move, resulting in the elastic modulus decreasing. Even though the conductive SMP composites start to show their shape memory effect, the tensile shape recovery forces and bending shape recovery moments decrease drastically since the materials begin to show viscoelasticity.

Moreover, under the same glass transition degree, the tensile shape recovery forces and bending shape recovery moments are expected to considerably increase with the addition of hybrid fillers, indicating that the hybrid fillers can reinforce the conductive SMP composites in a positive way, not only for its mechanical properties, but also the actuating capability. The calculation results could provide meaningful guidance for further design and manufacture of smart actuators based on the proposed SMP composites.

Shape Memory Behavior Driven by Electricity

As SEM observations show, the 3D conductive network was formed in the SMP composites. The electric resistivity was significantly decreased with a slight amount of SCFs (1.5 wt%). When a certain level of electrical conductivity of the SMP composites is reached, electrical resistive heating would be yielded from applied electric energy. As the internal temperature being raised to the switch transition temperature of SMP composites, shape recovery would be triggered by the inductive Joule heating. Because of the low electric resistivity in the developed SMP composite, electrical actuation in a low power could be therefore realized.

The shape recovery behavior of conductive SMP composites being driven by electric current was carried out and monitored by video camera, as shown in Figure 11. The demonstrated specimen was cut out from the prepared SMP composite with 2.5 wt% CNTs and 1.5 wt% SCFs incorporated, with dimension of $75 \times 40 \times 2\,\mathrm{mm}^3$. The specimen was then cut into a 'n' shape to form macro conductive path. The gap between the two legs of the specimen is 2 mm wide and 50 mm long. The specimen was bended about 150°C at the temperature of 100°C, and cooled to the room temperature. A 30 V DC electric field was applied for the electrical actuation. In terms of electric power, approximately 4.1 W was applied during the electrical actuation experiment.

As shown in Figure 11, the electrically induced shape recovery process is slow within the initial 9 s. After about 12 s, the deploying speed of the SMP composite specimen dramatically increases. At about 45 s, the shape recovery process in the specimen is completed and no noticeable deformation is observed after 45 s. The recovered shape of SMP composite is approximately 98% compared with its original shape. The remaining deformation in shape might result from friction between the soft segment and the hybrid fillers. Furthermore, it must also be noted that the rate of shape recovery was strongly dependent on the magnitude of the applied voltage and the electrical properties of SMP composites.

At 45 s, the temperature distribution in the SMP composite specimen was also monitored by an infrared video camera (AGEMA, Thermo-vision 900), and the temperature distribution along two different conductive pathways were plotted in Figure 12. As is shown in Figure 12(a), higher temperature is observed where internal strain is higher during the shape recovery process, which is attributed to the higher local resistivity. The phenomenon is coincident with the above mentioned investigations on the strain-sensitivity of the electrical resistivity. In Figure 12(b), temperature at the contact points between SMP composite specimen and aluminum electrodes is relatively higher due to the high local

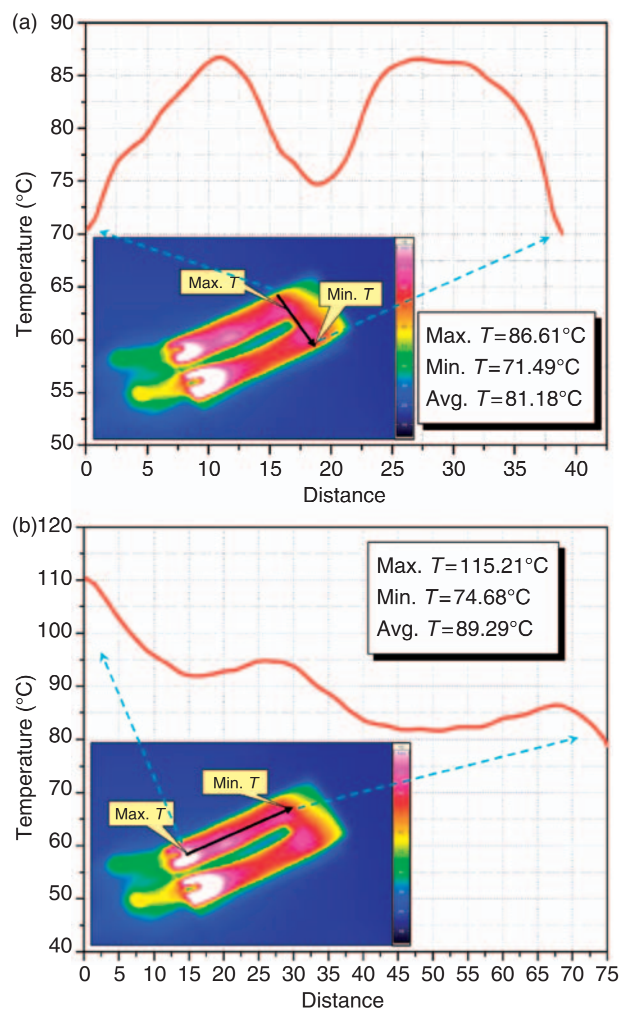


Figure 12. Temperature distribution of the conductive SMP composite driven by loading an electric voltage of 30 V. (a) Temperature distribution along line A; (b) Temperature distribution along line B.

contacting resistivity. The rest curve of the temperature distribution along the conductive pathway is relatively flat, which is the result of homogeneous distribution of hybrid fillers.

CONCLUSIONS

This article presented a new approach to significantly improve the electrical conductivity of styrene-based SMP composites embedded with CNTs. With the same amount of conductive fillers, the electrical resistivity of SMP composites containing both SCFs (1.5 wt%) and CNTs was decreased about 1000 times in comparison with those embedded with CNTs only. The demonstrated temperature and strain sensitivity of the electrical resistivity revealed potentials of the developed conductive SMP composites to be smart sensing materials. Subsequently, results in the isothermal static tensile and flexural investigations showed that the elastic modulus and stretch of the SMP composites were redoubled with the reinforcement of hybrid fillers, which was beneficial for their applications as stress-bearing components or structures, as well as shape recovery forces output. Finally, the shape recovery properties of the developed SMP composites were studied by taking DMA and electrical actuation experiments. The additionally acquired shape-memory capability enabled the conductive polymer composites to possess active shape-changing property, further expanding their application scopes in space, aerospace, electronics, automatics, and chemical industry.

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