Research Article

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Mechanical and shape-memory behavior of shape-memory polymer composites with hybrid fillers

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Abstract

Shape-memory polymer (SMP) materials have several drawbacks such as low strength, low stiffness and natural insulating tendencies, which seriously limit their development and applications. Much effort has been made to improve their mechanical properties by adding particle or fiber fillers to reinforce the polymer matrix. However, this often leads to the mechanical properties being enhanced slightly, but the shape-memory effect of reinforced SMP composites being drastically reduced. The experimental results reported here suggested that the mechanical resistive loading and thermal conductivity of a composite (with hybrid filler content of 7.0 wt%) were improved by 160 and 200%, respectively, in comparison with those of pure bulk SMP. Also, the glass transition temperature of the composite was enhanced to $57.28\,^\circ$C from the $46.38\,^\circ$C of a composite filled with 5.5 wt% hybrid filler, as determined from differential scanning calorimetry measurements. Finally, the temperature distribution and recovery behavior of specimens were recorded with infrared video in a recovery test, where a 28 V direct current circuit was applied. The effectiveness of carbon black and short carbon fibers being incorporated into a SMP with shape recovery activated by electricity has been demonstrated. These hybrid fillers were explored to improve the mechanical and conductive properties of bulk SMP.
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Keywords: electroactive; hybrid fillers; responsive; shape-memory polymer

INTRODUCTION

Shape memory refers to the ability of certain materials to return to their original shape, even after rather severe deformations. The most common materials exhibiting such a property are shape-memory alloys (SMAs), the shape-memory behavior of which is produced by a solid-state phase transformation. Recently, shape-memory polymers (SMPs) have received increased attention in academic and industrial research, due to their distinct advantages of lower density, higher shape recoverability, ease of manufacturing and lower cost, which surpass conventional SMAs.[1-3] Additionally, shape recovery of SMPs can also be triggered by various external stimuli, including heat, light,[1] electricity,[4-9] magnetic fields,[10-12] water[13] and solvents.[14-16] Given the large number of approaches, the technical potential of SMP materials is vast. However, SMP materials have several drawbacks such as low strength, low stiffness and natural insulating tendencies, which seriously limit their development and application. To overcome these drawbacks, much effort has been made to improve the mechanical properties of SMP materials.

The reinforcement of SMPs is usually achieved by adding particle or fiber fillers to reinforce the polymer matrix, and some results and outcomes have already been reported.[17-20] Experimental results suggest that the constrained bending recovery force of SMPs could be increased by 50% with the addition of 20 wt% SiC,[17] while the modulus of elasticity of a woven fiberglass shape-memory polyurethane could be increased by a factor of 4.0.[18,19]

However, in the research referenced, the mechanical properties were enhanced slightly, but the shape-memory effect was drastically reduced. Thus, in the study reported here, hybrid particulate and fibrous carbon fillers were used as reinforcement to improve the mechanical and conductive properties of a styrene-based SMP. The thermomechanical properties and shape-memory behavior of composites were investigated as a function of short carbon fiber content. Furthermore, the temperature distribution and shape-memory behavior of a composite (with hybrid filler content of 7 wt%) were recorded using infrared video. The experimental results can be used as feedback for improving the mechanical properties and shape-memory behavior of SMP composites incorporating hybrid fillers.

EXPERIMENTAL

A styrene-based shape-memory resin, purchased from Cornerstone Research Group Inc. (Ohio, USA), with a density of $0.92\,\mathrm{g\,cm^{-3}}$ was used as the matrix, and was polymerized by adding crosslink agent into the matrix at a constant ratio of 28 : 1. The mean aggregate size of carbon black (CB) particles (AX-010, supplied by Sunny Plaza Trading Co. Ltd) was 4 μm, the mean

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

Property	Value	Method
Mechanical properties		
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^{-1} K^{-1}	

Figure 1. Stress–strain curves of composites filled with various SCF contents in tensile mode.

domain size (X-ray diffraction) was 18–20 nm, with a domain content of 65 wt%. The density was in the range 1.80–1.85 g cm^{-3}. The short carbon fiber (SCF) used, purchased from Jitan Inc., China, had a constant length of 6 mm, a diameter of 7 μm, a density of 1.75 g cm^{-3} and a tensile strength of 2200 MPa.

SMP composites were fabricated according to the following process. Firstly, nano-sized particles were suspended in ethanol solvent using ultrasonic equipment (VCX750, Sonics & Materials Inc.). The suspension was then vacuum filtered using a 0.4 μm membrane filter, and heated to remove any remaining solvent. The SCF was placed in deionized water, mechanically agitated and dried in an oven at a temperature of 120 °C to remove any moisture or resin coating on fiber surfaces. Secondly, crosslink agent was mixed with the resin and mechanically stirred. A measured amount of ultrasonicated CB was added into the mixture, and mechanically stirred for 60 min at a constant of 600 rpm. Then the dried fibrous filler was slowly added into the mixture system and mixed mechanically at a constant 120 rpm. Finally, the mixture was degassed for at least 30 min, transferred into a closed mold made of glass sheets and kept in an oven for 24 h at a constant temperature of 75 °C for curing.

Five different types of samples, pure SMP and SMP composites with various hybrid filler contents, were prepared to determine the synergistic effect of hybrid fillers on the mechanical properties and shape-memory behavior of SMP composites. For comparison, the mechanical and thermal properties of the pure SMP are presented in Table 1.

RESULTS AND DISCUSSION
Isothermal static stress–strain tests
Tensile experiments were performed using a Zwick/Roell servo-mechanical test frame with a series of digital controllers. An Instron clip-on extensometer was used for strain measurements in tensile tests, while the test frame's extension sensor was used in tensile tests. Static tensile tests were performed at a strain rate of 0.005 s^{-1} within the chamber. In calculation of experimental data, the engineering stress and strain were used. Figure 1 shows the stress–strain curves at a testing temperature of 25 °C. The tensile strain was calculated from the ratio of the elongation obtained by the crosshead displacement to the gauge length (50 mm). The samples with dimensions of 120 × 25 × 5 mm were taken from the fabricated SMP composites.

When the temperature is 25 °C, which is approximately 37 °C lower than the glass transition temperature, both pure SMP and SMP composite specimens have small fracture strain, and the
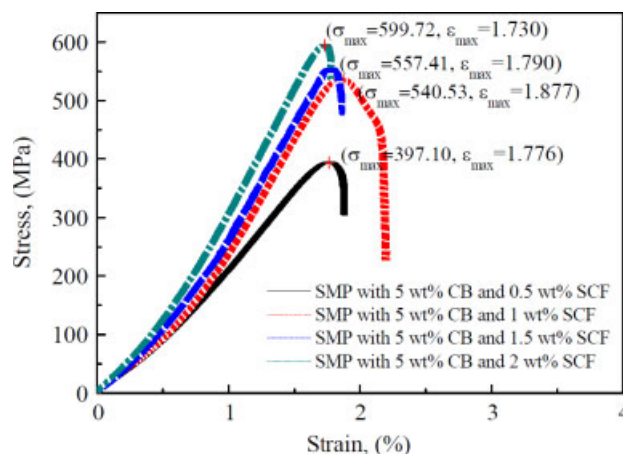
yielding phenomenon is observed in all specimens with various SCF weight fractions. Additionally, the occurrence of necking is also observed clearly in all specimens. However, uniform elongation and considerably large fracture stresses are observed in the specimens filled with 1.0, 1.5 and 2.0 wt% SCF filler.

The yielding phenomenon and ultimate tensile strength (UTS) changes are observed in all specimens, and the UTS gradually increases proportionally to fibrous filler content. As shown in Fig. 1, the UTS of SMP composites filled with 0.5, 1.0, 1.5 and 2.0 wt% SCF filler is 397.10, 540.53, 557.41 and 599.72 MPa, respectively. These results suggest that the tensile strength of composite specimens is regularly improved with an increase in fibrous filler content. It is surmised that the failure behavior of the pure SMP specimen is mainly determined by the ductile deformation. On the other hand, the stress–strain curves of the composite specimens are relatively flat and the composites are more brittle. The reason for these differences might be the occurrence and propagation of cracks initiated by the debonding between matrix resin and filler, which is the major failure characteristic of the filled specimens. Also, the cracks may not propagate easily since the viscous matrix resin becomes hard to flow and the composite materials become brittle. The results of the static tensile tests can be summarized briefly as follows: an obvious increase of the tensile stress is obtained for the composites; the maximum fracture strains of the composites are strongly dependent on the dispersion of hybrid filler; and cracks propagate along the boundary of matrix and fillers.

Isothermal bending stress–strain tests
The bending behavior of bulk SMP and SMP-based composites was studied to determine their shape-memory behavior: recovery time, recovery ratio and bending recoverability.

The flexural strength of the SMP composites was measured using three-point bending tests with a Zwick/Roell servo-mechanical test frame, an Instron clip-on extensometer was used for strain measurements in three-point bending mode and a forced air convective environmental chamber was used for elevated-temperature tests. The static bending tests were performed at a loading speed of 2 mm min^{-1}. The dependence of flexural strength on fibrous filler content was investigated at a testing temperature of 25 °C.

Rectangular samples with dimensions of 150 × 25 × 5 mm were taken from the fabricated SMP composites. The flexural stress of
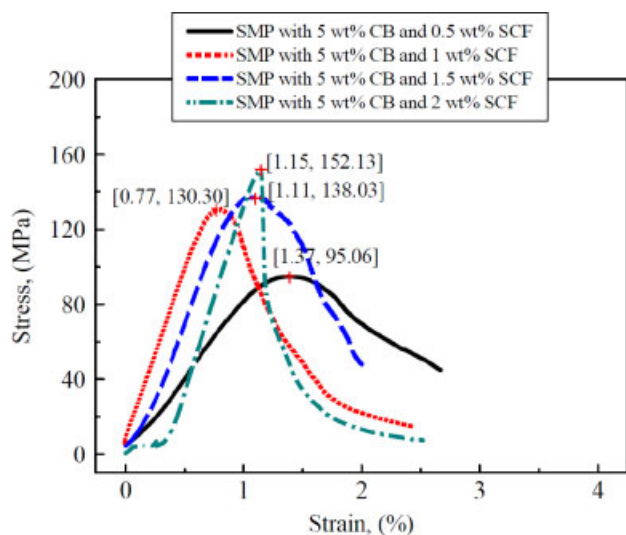
Figure 2. Flexural strength of composites *versus* SCF filler content.

Figure 3. DSC scans of SMP composites and pure SMP.

the 2 wt% SCF sample is higher than that of the 0.5 wt% SCF sample. In general, the flexural stress increases proportionally with the SCF content. As shown in Fig. 2, the flexural modulus of the samples with 0.5, 1, 1.5 and 2 wt% SCF is 95.06, 130.30, 138.03 and 152.13 MPa, respectively. It is observed that the flexural strength of the composites can be significantly improved by adding a small amount of SCF, e.g. the flexural stress increases from 95.06 to 152.13 MPa with an additional 1.5 wt% SCF filler being incorporated. This phenomenon may be mainly attributed to the inherent mechanical properties of the fibrous filler. An obvious increase of the bending strength is obtained for the composites when the fibrous filler content increases. Furthermore, in the bending tests, the bending recovery force of the SMP composites is significantly improved in comparison with that of the pure SMP. In the SMP composites, the typical size of SCF is 7 µm, and the size of macromolecular chains is approximately 1 µm. The typical sizes of SCF filler and macromolecular chains are of the same range. Furthermore, macromolecular chain motion of the SMP composites plays a critical role in mechanical resistive loading. Therefore, the mechanical properties of the SMP composites would be dependent on the SCF filler. The motion of the macromolecular chains would be hindered by the SCF filler through friction interactions, helping the SMP composites to resist external loading, resulting in a significant improvement in mechanical properties.

Differential scanning calorimetry

The temperature at which polymers transform from a glassy state to a rubbery state is called the glass transition temperature (T_g). Polymer segments are assumed to be locked into a glassy state when the polymer segmental motion is limited at temperatures below T_g. Similar to other types of SMP materials, T_g also plays an essential role in the shape-memory behavior of the styrene-based SMP. Thus, it is necessary to confirm T_g prior to shape-memory behavior investigation. DSC is routinely used to determine the transition temperature of polymers.

A Netzsch DSC 204F1 instrument was used to investigate the thermal properties of composites in a nitrogen environment. Since the glass transition always occurs in a temperature range, the midpoint of the temperature range of the scanning curve was defined as T_g in this study. The specimens were heated from
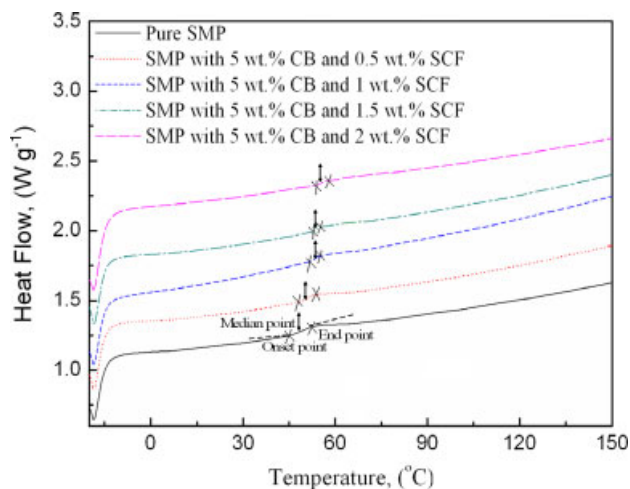
−20 to 150 °C, then cooled to −20 °C and again heated to 150 °C at a scanning rate of 10 °C min^{-1}. The thermal transitions in the second thermal scan were used for analysis. As previous research has demonstrated, T_g of continuous carbon fiber-reinforced SMP composites is higher than that of pure SMP, while nano-sized particulate fillers in composites sometimes have a positive effect on T_g. However, there are few studies on the effect of SCF or hybrid fillers on T_g.[7]

The change of T_g as a function of SCF filler content is shown in Fig. 3. Values of T_g of 46.38, 49.23, 53.82, 55.06 and 57.28 °C are obtained for pure SMP and composites with 0.5, 1.0, 1.5 and 2 wt% SCF, respectively. Experimental measurements show that the glass transition occurs within a temperature range from 45 to 60 °C. Furthermore, the SCF filler has a positive effect in increasing T_g. Note that the relative motion of macromolecule segments is the primary mechanism of the shape-memory effect in the SMPs. The size of typical segments in polymer networks is approximately 10–100 nm. And the characteristic size of CB particles is 18–20 nm. The conductive particles mean that the SMP composites possess a relatively high thermal conductivity. For the same amount of energy, the typical segments of the SMP composite have a faster response time compared pure SMP. Additionally, the total amount of SMP segments per unit in the composite is less than that of pure SMP matrix. Therefore, these two factors make the transition temperature of SMP composites shift to a lower value. On the other hand, the typical size of SCFs is two orders of magnitude greater than the size of segments. These fibrous fillers might block heat transfer, especial in their vertical directions. Thus, thermal behavior of segments is promoted by the nano-size CB, and is prevented by the micro-size fibrous filler. Here, in the hybrid filler-filled composites, T_g is lowered by CB particles and is elevated by the SCF filler.

Dynamic mechanical analysis

The determination of the dynamic mechanical properties was performed with a DMA 242C (Netzsch, Germany), to observe the elastic and loss moduli of the composites as a function of temperature. This method can also be used to detect any change in the measured T_g for polymeric materials. All tests were performed in three-point bending mode at a constant heating rate of 10 °C min^{-1}, and the oscillation frequency was 1 Hz. Samples

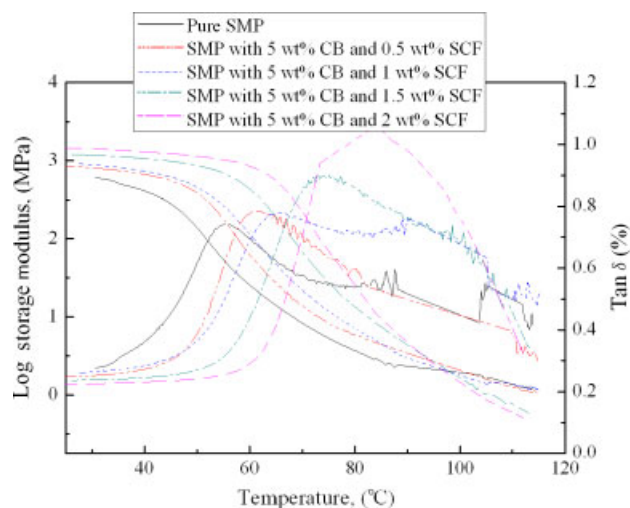**Figure 4.** Storage modulus and tan δ curves of composites at an oscillation frequency of 1 Hz.

Figure 5. Thermal conductivity of the composites with various weight fractions of SCF at 25 °C.

were examined in a temperature interval of 20 to 120 °C, with sample dimensions of 35 × 12 × 4 mm.

Specimens were initially locked into a deformation of 0%. Starting from room temperature and zero initial force, the temperature was ramped up at 10 °C min^{-1}. The storage modulus and tan δ data were recorded against temperature. The storage modulus is the modulus of the elastic portion of a material while loss modulus is the modulus of the viscous portion; tan δ is the ratio of loss modulus to storage modulus.

As shown in Fig. 4, the addition of fibrous filler generally increases the modulus of the composites over the entire temperature range. The data show that the storage modulus of the pure SMP is 604.135 MPa, while the storage modulus of the SMP composite filled with 5 wt% CB and 2 wt% SCF is 1510.14 MPa, at a temperature of 30 °C. Here, the glass transition temperature is defined as the point of intersection between the storage modulus curve and the tan δ curve. Thus, in this manner, the T_g range of the SMP composites is 45–75 °C. T_g moves to a higher temperature with an increase in the fibrous filler content. Alternatively, the peak value of the tan δ curve can also be employed to define T_g. As shown in Fig. 4, the peaks of the tan δ curves of the SMP-based composites are higher than that of pure SMP. Therefore, T_g defined in these two ways increases with increasing fibrous filler content. Note that the typical size of SCFs is approximately the size of macromolecular chains. Therefore, the mechanical and thermomechanical behavior of macromolecular chains would be blocked by the fibrous filler. Additionally, the size of typical segments in the polymer networks is approximately 10–100 nm. And the characteristic sizes of CB particles and their aggregates are 18–20 and 50–500 nm, which is of the same order of magnitude as the size of typical segments. Thus, the mechanical and thermomechanical behavior of segments would be prevented by the particulate fillers. These interactions are considered as friction interactions that would help SMP composites to resist external loading, resulting in a improvement of mechanical and thermomechanical properties.

Thermal response shape-memory behavior

In this study, the thermal response shape-memory effect was evaluated using the shape recovery ratio and shape recovery
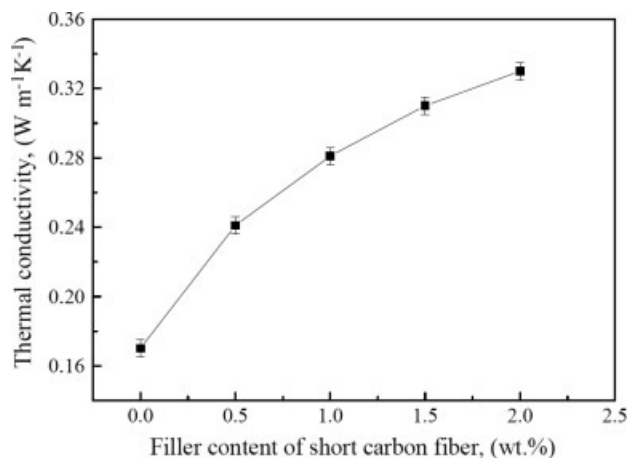
speed. Shape recovery speed refers to the response to external stimuli, and shape recovery ratio is determined by measuring the angle between the straight ends of a bent specimen. In this test, the dimensions of specimens were 100 × 20 × 5 mm. The heating temperature range for the shape-memory effect was set from 50 to 85 °C, which is the range from $T_g - 10$ to $T_g + 20$ approximately for SMP and SMP composites. The heating rate was 5 °C min^{-1}.

Polymeric materials feature an intrinsically low thermal conductivity of the order of $0.15 < k < 0.30$ W m^{-1} K^{-1} in most cases, which makes them good insulators for numerous applications. However, thermally stimulated SMPs require comparatively high conductivity to achieve responsive sensitivity. Figure 5 plots the relationship between thermal conductivity and weight fraction of hybrid fillers. The thermal conductivity of pure SMP is approximately 0.17 W m^{-1} K^{-1} at room temperature. In comparison, SMP composites possess higher thermal conductivity that is improved proportionally to the weight fraction of the hybrid fillers. This increase suggests that the hybrid fillers are beneficial as components for polymer with respect to thermal conductivity. Figure 6 shows the shape recovery ratio of all samples as a function of temperature. The experimental results demonstrate that the composite specimens have faster responsive behaviors in response to temperature. However, this is negligible above 85 °C, due to the fact that the lower stiffness of SMP could not overcome the barrier loading of the fillers.

The thermal absorption and conductivity, which are benefits derived from conductive fillers, are significantly improved by adding CB and SCF fillers into the SMP composites. Additionally, with the same heating program and test sample dimensions, pure SMP needs more heat energy to complete shape recovery than do the composites, due to a higher filler content in the SMP matrix. Therefore, the enhanced absorption and conductibility, and a relatively lower energy consumption make the shape recovery speed of SMP composites much quicker than that of pure SMP. There is a crosslinked structure formed by macromolecular chains in the thermosetting SMP, and the relative motion of macromolecule segments is the primary mechanism of the shape-memory effect in SMPs. In the recovery process, the packed macromolecule segments need to overcome the outer friction to return to the original shape. As is known, the size of typical segments is approximately the same as the characteristic size of CB particles. Therefore, the friction resistance of segments would obviously be influenced by CB particles, which would prevent
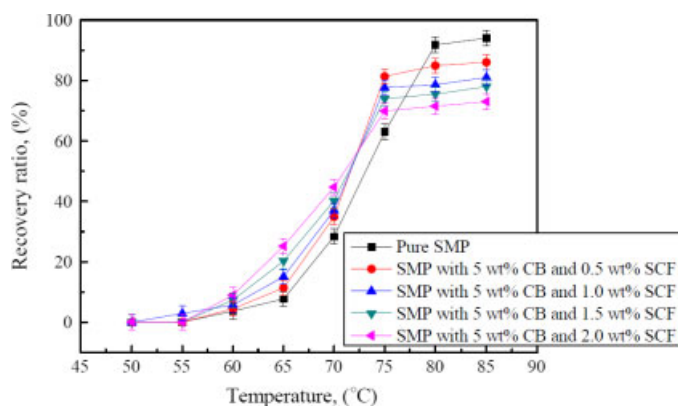
Figure 6. Shape recovery ratio curves of pure SMP and the SMP composites against temperature.

Figure 7. Series of photographs showing the macroscopic shape-memory effect of pure SMP matrix.

shape deformation and recovery behavior. These interactions would result in the CB-filled SMP composites having a lower shape recovery ratio, compared with that of pure SMP.

Shape-memory behavior driven by electricity

In the literature[4,7] it has been shown that the CB particles are dispersed homogeneously within the matrix and serve as interconnections between fibrous fillers, while the SCF fillers act as long-distance charge transporters by forming local conductive paths. As is expected, a synergistic effect of particulate and fibrous fillers makes it easy to form a three-dimensional conductive network in the composites. When a certain level of electrical resistivity of SMP composites has been reached, electrical resistive heating would occur from applied electrical energy. As the internal temperature reaches the switch transition temperature of the SMP composites, shape recovery would be triggered by inductive Joule heating.

For comparison, the shape-memory effect of the SMP matrix is shown in Fig. 7. One sample is shown as an example of thermally induced shape-memory effect. The sample has originally a flat shape (image 1). When the sample is heated above its switch transition temperature, it can be deformed to a desirable shape upon application of an external force. Cooling back below the switch transition temperature, a temporary shape is subsequently fixed (image 2). Then, the sample is reheated above the switch transition temperature again, and the sample starts to recover by itself from the temporary shape to its original shape. Finally, being cooled back below the switch transition temperature again, a second temporary shape of the sample is fixed (image 3). Alternatively, it could return to its original shape (image 4). From a previous thermally induced shape-memory process, it is found that the shape recovery behavior is always inconvenient, uncontrollable and discontinuous. A special heating source needs to be prepared, and the energy loss is very great. To overcome

these drawbacks and limitations, a novel activation approach is required for a shape-memory effect via electrical resistive heating.

As shown in Fig. 8, the shape recovery behavior of SMP materials being driven by electrical current has been achieved. The temperature distribution and shape recovery behavior were recorded using an infrared video camera (AGEMA, Thermo-vision 900). The demonstration specimen incorporated 5 wt% CB and 2 wt% SCF, with dimensions of $300 \times 25 \times 4$ mm. The electrical conductivity of the composite specimen was approximately 1.5 S cm^{-1}, determined using the van der Pauw method. The straight hybrid filler-filled SMP composite sheet is bent into an 'n' shape at a temperature of 85 °C and retains this shape during cooling back to room temperature. No apparent recovery is seen after the deformed sheet is kept in air for 2 h. Then, to carry out shape recovery of the SMP composite driven by electrical current, a 28 V direct current circuit was applied. Figure 8 shows the shape recovery progress. The deformed SMP sheet starts to return to its original shape when a constant electrical current is applied for 5 s. The recovered shape of the SMP composite is approximately 95% compared with its original shape, after 55 s. The remaining deformation in shape might result from friction between the soft segments and the CB particles. Also, the shape recovery speed of the sample in the range 10–40 s is higher than that in other time ranges. Furthermore, it must also be noted that the rate of shape recovery is strongly dependent on the magnitude of the applied voltage and the electrical properties of the composite.

CONCLUSIONS

The proposed approach successfully improved the thermomechanical and conductive properties of SMP materials by the addition of hybrid filler into the matrix. Furthermore, it is demonstrated that thermally responsive shape-memory recovery behavior of the
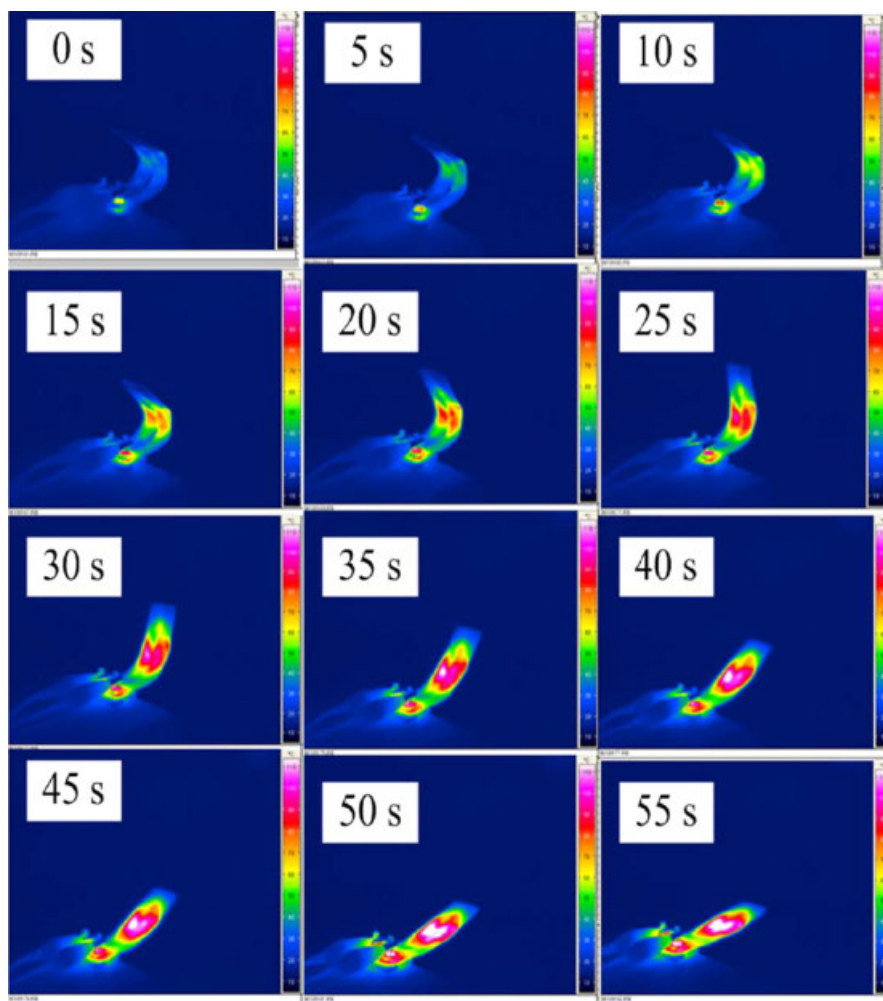
Figure 8. Series of images showing the macroscopic shape-memory effect of the SMP composite with 5 wt% CB and 2 wt% SCF. The permanent shape is a flat strip of composite material, and the temporary shape is deformed as a right-angled shape.

SMP composites has been achieved using electricity, with an appropriate hybrid filler content.

Through systemic investigation, the following conclusions can be drawn. (1) As mechanical bending and dynamic mechanical analysis tests have shown, the static and dynamic thermomechanical properties of the SMP composites are influenced by the conductive fillers. Sometimes, fibrous fillers enhance the mechanical properties of composites more significantly than particulate fillers. (2) Due to the synergistic effect of the fibrous and particulate fillers, the thermal and electrical conductivities of the SMP composites are improved significantly. Fibrous filler has a more effective role in improving electrical conductivity, because it provides continuous paths for electrons. Particulate filler homogeneously improves the thermal conductivity property of the composites. (3) In the shape-memory effect tests, the added filler would worsen the recovery property of the SMP-based composites. Especially for nano-sized filler, individual particles and their aggregates would prevent typical segment motion through friction interaction. This negative interaction would seriously hamper the shape recoverability.

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