Original Article

Mechanical and shape recovery properties of shape memory polymer composite embedded with cup-stacked carbon nanotubes

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Abstract

This study investigated the mechanical and shape recovery properties of a styrene-based shape memory polymer composite reinforced by cup-stacked carbon nanotubes. Due to their unique morphology, cup-stacked carbon nanotubes could be well dispersed in the polymer matrix and offer remarkable benefits in the load transfer between the reinforcement fillers and shape memory polymer. Under the same amount of fillers, shape memory polymer composites embedded with cup-stacked carbon nanotubes exhibit superior mechanical properties in comparison with those embedded with multiwalled carbon nanotubes and carbon nanofibers. The elastic modulus, tensile strength, and flexural strength of the 2 wt% cup-stacked carbon nanotube–reinforced shape memory polymer composite increased by 61%, 66%, and 84%, respectively. It was also found that the glass transition temperature of shape memory polymer composite decreased from 61.9°C to 52.8°C by introducing 2 wt% cup-stacked carbon nanotubes, indicating that the shape recovery process could be triggered more easily by external stimulus due to the role of reinforcement fillers. Finally, under the external resistance load, the developed shape memory polymer composite was successfully driven to recover their shapes under thermal stimulus. The cup-stacked carbon nanotubes were proved to be a promising candidate for the polymer reinforcement.

Keywords

Carbon fiber, mechanical properties, polymer matrix composites, smart materials

Introduction

As an emerging class of thermoset polymers, shape memory polymers (SMPs) additionally possess dualshape (or multishape) capability, referring to the shape recovery from temporary shapes to the permanent shapes after SMPs are exposed to external stimulus (Huang et al., 2010; Leng et al., 2009, 2011; Nji and Li, 2012; Pretsch, 2010; Xie, 2011; Xu and Li, 2011; Yu et al., 2012), such as electricity (Leng et al., 2007, 2008a, 2008b, 2008d; Liu et al., 2009b), light (Lendlein et al., 2005), magnetic fields (Buckley et al., 2006; Mohr et al., 2006; Schmidt, 2006), and solvents (Huang et al., 2005; Leng et al., 2008c; Lv et al., 2008, 2009). Currently, two mechanisms for the shape memory behaviors in SMPs are developed and accepted by researchers: glass transition and phase evolution. The first one is used to explain the shape memory effect (SME) in amorphous polymers, where mobility of polymer chains undergoes significant change upon the alternation of temperature (Diani et al., 2006;

Liu et al., 2007; Nguyen et al., 2008; Westbrook et al., 2010). In the second mechanism, the SME is attributed to the formation of phases during cooling, which serve to lock the temporary shape, and a loss of the phases due to heating when shape recovery occurs (Barot et al., 2008; Beloshenko et al., 2005; Ge et al., 2011;

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Gunes and Jana, 2008; Gunes et al., 2008; Hu, 2007; Long et al., 2009). Compared with other shape memory materials, SMPs exhibit excellent properties, such as high strain recovery (up to 400%), low density, low cost, easy shape procedure, and easy control of recovery temperature (Diani et al., 2011; DiOrio et al., 2011; Lan et al., 2009; Mya et al., 2011).

However, pure SMPs are not suitable for many practical applications that require particular functions, for example, high stiffness and strength, high recovery force, self-healing (Nji and Li, 2010), and good electrical conductivity. Thus, shape memory polymer composites (SMPCs) have been extensively studied to meet the various requirements in practical applications (Gunes and Jana, 2008; Gunes et al., 2008; Xu et al., 2010). Among all the fillers that have been recruited as reinforcements in SMPs, carbon nanotubes (CNTs) have stood out 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, especially their mechanical properties (Cadek et al., 2002; Coleman et al., 2006; Ni et al., 2007).

The most challenging issue in the application of CNTs as the reinforcement of polymer composites is their dispersion in the matrices. Existing arts in this realm include ultrasonic bath, mechanical stirring, dispersing agent assistance, and chemical (i.e. covalent) functionalization. Generally, the ultrasonic bath is considered to be the most efficient and convenient way to achieve a good dispersion of CNTs. However, when it comes to a polymer matrix, it is unacceptable to disperse CNTs ultrasonically for a long time and in high output power because this will generate excessive thermal energy and cause local curing in some polymer matrices. During the relatively long-time curing cycle of polymer composites, previously separated CNTs further reaggregate due to the strong van der Waals forces and Brownian motion, which would result in a material with agglomerations (acting as defects in the matrix) and thus low mechanical properties. However, the interphase performance and load transfer efficiency between traditional CNTs and polymer matrix are limited due to the seamless columned morphology of traditional single-walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs). It should also be noted that increasing the CNT content is not a universal solution to make up for the disadvantages resulting from the poor CNT dispersion because excessive amount of CNTs (around 4.5 wt%) would increasingly inhibit the polymerizing reaction of some polymers, just as the styrene-based shape memory resin.

Recently, cup-stacked CNTs (CSCNTs) attract a great deal of attention as a superior candidate for the polymer modifier (Endo et al., 2002, 2003(a), 200(b), 2008; Hasobe et al., 2007; Hayashi et al., 2007; Iwahoria et al., 2005; Kim et al., 2002; Liu et al., 2009a;

Njuguna et al., 2009; Terrones et al., 2002; Yokozeki et al., 2005, 2007, 2008, 2009). The growth conditions of CSCNT can be precisely controlled in production method such as chemical vapor deposition (CVD) through the use of a floating reactant method (Endo et al., 2002; Liu et al., 2009a; Yokozeki et al., 2005, 2007, 2008). The stacking morphology of truncated conical graphene sheets exhibits an angle to the axis, and almost every portion of the graphene sheet edges is exposed to the outside. Compared with MWCNTs and carbon nanofibers (CNFs), CSCNTs have novel structural characteristics such as a larger hollow core and a larger portion of open ends than other CNTs. Almost every portion of the graphene sheet edges is exposed to the outside, which is expected to affect their surface energies and offer advantages in the load transfer between CSCNTs and polymer matrix and prevent the graphene sheet sliding (Endo et al., 2002; Yokozeki et al., 2007, 2008, 2009). Another advantage offered by the unique morphology of CSCNTs is their good dispersion in the polymer matrix, resulting from the excellent interphase and increased interaction between CSCNTs and the polymer.

In view of these, CSCNTs were selected as reinforcement filler in this article to improve the mechanical, thermomechanical, and shape recovery properties of styrene-based SMP composite. To clearly demonstrate their superior reinforcement effect, SMP composites filled with MWCNTs and CNFs were also prepared under the same amount of fillers. The different SMP composites were evaluated in terms of their isothermal mechanical properties, dynamic mechanical performance, thermal stability, glass transition characteristic, and thermal conductivity that are important for their practical applications. Finally, under the external resistance load, the developed SMP composite with 2 wt% CSCNTs was successfully driven to recover their shapes under thermal stimulus. The investigated CSCNTs could be utilized in other polymer composite systems where a good dispersion of CNTs is hard to achieve.

Investigated material and fillers

In our study, the styrene-based shape memory resin (Veriflex[®]S VF 62) with a density of 0.92 g/cm³ was purchased from Cornerstone Research Group, Inc. (Dayton, OH, USA), which is a two-part, fully formable thermoset SMP resin system. Typical mechanical and thermal properties of the pure SMP were obtained from the supplier and presented in Table 1.

The chosen CSCNTs were synthesized by CVD using a floating reactant method, featuring with an average outer diameter of 100 nm, an average inner diameter of 70 nm, and an average aspect ratio of 50.

SMP composites filled with different amounts of CSCNTs (0.5, 1, 1.5, and 2 wt%) were prepared. For

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

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

SMP: shape memory polymer.

comparisons, SMP composites filled with MWCNTs and CNFs were also prepared under the same amount of fillers. The MWCNTs were purchased from Shenzhen Nanometer Gang Co., Ltd, with an average length of 1 μ m and diameter of 100 nm. The vapor-grown CNFs were supplied from Chengdu Organic Chemicals Co. Ltd, Chinese Academy of Sciences. The nanofibers have an average diameter of 100 nm and an average aspect ratio of 50, which are comparable with those of CSCNTs.

The SMP composites filled with specified amount of reinforcement fillers (CSCNTs, MWCNTs, and CNFs) were prepared in the following steps. First, the shape memory resin was mixed with cross-link agent at a weight ratio of 24:1. Second, reinforcement fillers were mixed with the blend and stirred well. The suspension was then placed in a high-energy sonicator (SONICS-44349N) at an output amplitude of 60% for a total of 40 min, at an intervals of 10 min. Third, the mixture was placed in an air-tightened box to completely remove the air bubble and then transferred into a close mold. Fourth, the resin 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 the temperature was ramped to 90°C at 5°C/h. After holding for 3 h at 90°C, the temperature was then ramped to 110°C at 10°C/h. Within 2 h, the reaction was essentially completed, and the specimen was finally cooled to room temperature at 10°C/h.

Results and discussion

Morphology observation by scanning electron microscope

The investigated raw CSCNTs could be synthesized by a floating reactant method using ferrocene or iron pentacarbonyl as a catalyst precursor, hydrogen sulfide as a cocatalyst, and natural gas as a carbon feedstock in a continuous process (Endo et al., 2002). The micromorphology and the structure illustration of the CSCNTs are shown in Figure 1. The morphology was observed by a scanning electron microscope (SEM; CamScan MX2600) in a vacuum condition. As revealed in Figure 1(a), the CSCNTs appear as relatively long straight nanofibers with entirely hollow core along the length direction, which is considered as the main characteristic compared with that of conventional columntype nanofibers. The size of the hollow core is directly



Figure 1. (a) Morphology of the investigated raw CSCNTs under SEM observation and (b) structure illustration of the raw CSCNTs.

CSCNTs: cup-stacked carbon nanotubes; SEM: scanning electron microscope.



Figure 2. Freeze-fracture surface morphology of SMP composites filled with CSCNTs and MWCNTs: (a) dispersion of CSCNTs in the SMP composite and (b) MWCNT aggregates in the SMP composite.

SMP: shape memory polymer; CSCNTs: cup-stacked carbon nanotubes; MWCNTs: multiwalled carbon nanotubes.

determined by the size of the metal particle at the growth direction of the CSCNTs and is related to the catalytic particle, the type of carbon feedstock, and the reaction temperature (Endo et al., 2002). The cupstacked morphology of the CSCNTs has been previously reported (Endo et al., 2002, 2003(a), 200(b); Yokozeki et al., 2005), and its schematic view is plotted in Figure 1(b). As shown in this figure, the structure of CSCNTs consists of numerous truncated conical graphitic sheets that form various angles with the length direction. Compared with MWCNTs, which are composed by certain concentric tubular graphitic sheets, the outer and the inner surfaces of the CSCNTs are covered entirely by open edges, which in turn leads to a superior load transfer efficiency between the CSCNTs and polymer matrix. Due to the strong atomic bond among carbon atoms in each conical graphitic sheets, CSCNTs possess higher modulus compared to the conventional CNFs. It should also be noted that although CSCNTs have lower strength and modulus than SWCNTs, their aspect ratio could be much larger by controlling the synthesizing method. Therefore, dispersion of CSCNTs into the polymers results in the superior reinforcement effect in the mechanical properties of the polymers.

SEM was also used to study the distribution of CSCNTs and MWCNTs in the developed SMP composites in a vacuum condition. After coating with gold, the freeze-fracture surfaces of the SMP composites incorporated with 0.5 wt% CSCNTs and 0.5 wt% MWCNTs reveal their nanopatterns and are shown in Figure 2. Here, all the SMP composite samples are prepared under the same condition that follows the synthesis procedures as mentioned above. It is observed that CSCNTs are well dispersed and separated from each other in the SMP composite (Figure 2(a)). Besides, due to their particular morphology, an excellent interphase and higher load transfer efficiency are expected between the CSCNTs and SMP, which will increase the mechanical properties of the developed SMP composites. However, as shown in Figure 2(b), MWCNT aggregates are observed in the SMP composite. Because the SMP composites were cured at a high temperature, the Brownian motion of MWCNTs would be significantly increased. Furthermore, the strong van der Waals forces among MWCNTs at closing spaces also led to the agglomerations during the long-time curing cycle, which would act as defects in the SMP composites and thus decrease their mechanical properties.

Mechanical properties

Isothermal static stress-strain tests. To demonstrate the strengthening effect of the CSCNTs, the isothermal static stress-strain tests were conducted under room temperature of 25°C. Specimens with dimensions of 65 \times 14 \times 3 mm³ were cut out from the fabricated SMP composites with different CSCNT concentrations (varied from 0.5 to 2 wt%).

The tests were operated on a Zwick/Roell servomechanical test frame where an Instron[®] clip-on extensioneter 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 and within the ISO 6892:1998 Standard.



Figure 3. Stress-strain curves of pure SMP and SMP composite filled with different weight fractions of CSCNTs. SMP: shape memory polymer; CSCNTs: cup-stacked carbon nanotubes.

Figure 3 reveals the representative relationship between internal tensile strain and stress of the pure SMP and SMP composite filled with CSCNTs. The modulus of elasticity was calculated from the slope of the initial linear part of the stress-strain curve, while the maximum stress at failure was taken as the tensile strength. It can be observed that each stress-strain curves are linear up to about 80% of the failure load, indicating that the material behaves fairly elastic. In fact, the developed SMP composites could be considered as isotropic material due to the high randomicity of the CSCNTs' dispersion. Under the temperature of 25°C, which is much lower than the glass transition temperature (T_{α}) of SMP, the viscoelastic behavior of the SMP composite is negligible, and the elastic modulus increases along with the addition of CSCNT content. At this stage, CSCNTs are well bonded with the SMP matrix. Then, with the increase in external load, the slope of the curves decreases considerably before they reach the climax. This is because that the extruded CSCNTs were observed on the fracture surface of the developed SMP composites, and thus, the occurrence and propagation of microcracks initiated by the debonding between matrix resin and fillers is considered to be the major failure mechanism. When the internal strain increases to a critical level, the yielding phenomenon is observed and the ultimate tensile strength is subsequently reached.

As presented in Figure 3, after doping 2 wt% CSCNTs into pure SMP, the elastic modulus of the SMP composite increased from 1.24 to 1.99 GPa, with an increase of 61%. The corresponding tensile strength increased from 22.96 to 38.12 MPa, increased by 66%. And the maximum tensile strain before fracture decreased from 3.1% to 2.11%. It should also be noted that the elastic modulus and strength of the SMP composites would not be continuously increased with the



Figure 4. Curves of tensile modulus versus weight fraction of different fillers (CSCNT, MWCNT, and CNF). CSCNT: cup-stacked carbon nanotube; MWCNT: multiwalled carbon nanotube; CNF: carbon nanofiber; SMP: shape memory polymer.

addition of CSCNTs because excessive amount of CSCNTs would also increasingly inhibit the polymerizing reaction of the styrene-based shape memory resin.

To clearly demonstrate the outstanding mechanical reinforcement effect of CSCNTs, isothermal static stress-strain tests were also conducted on SMP composites filled with MWCNTs and CNFs, and the results were compared with those of CSCNT-filled SMP composites. The corresponding tensile modulus of each SMP composites is summarized in Figure 4, and the data are all calculated as the average of at least three samples. With 2 wt% MWCNTs and CNFs, the tensile modulus of the SMP composite increased from 1.24 GPa (pure SMP) to 1.79 and 1.61 GPa, respectively. However, when compared with those of CSCNT-filled SMP composites, an obvious decline is observed under the same weight fraction of fillers (varied from 0.5 to 2 wt%). This result experimentally validates the increased interaction and superior load transfer efficiency between CSCNTs and SMP.

Isothermal static flexural properties. The isothermal static flexural behavior of SMP bulk and SMP-based composites was studied to determine their shape memory behaviors 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 ($65 \times 14 \times 3 \text{ mm}^3$) were cut out from the prepared SMP composites. The specimen dimensions and weight fractions of CSCNTs were the same as those in



Figure 5. Curves of flexural stress versus flexural strain in the SMP composites filled with various weight fractions of CSCNTs. SMP: shape memory polymer; CSCNT: cup-stacked carbon nanotube; CNF: carbon nanofiber.

the static tensile tests. In the integrated testing software, the output ports were selected as load and displacement, and the corresponding flexural strength, flexural stress, and flexural strain were calculated according to ISO 6892:1998 Standard. The maximum stress at failure was taken as the tensile strength.

Figure 5 reveals the representative relationships between flexural stress and strain in the developed SMP composites. By adding 2 wt% CSCNTs into SMP, the flexural strength increased from 31.01 to 58.50 MPa, with an increase of 88.65%. The maximum flexural strain before material failure decreased from 2.66% to 2.01%. Compared with that of pure SMP, the flexural stress in the developed SMP composites increases proportionally to the weight fraction of CSCNTs.

For comparison, isothermal static flexural tests were also conducted on SMP composites filled with MWCNTs and CNFs, and the results are given in Figure 6. The data are all calculated as the average of at least three samples. Under the reinforcement of 2 wt% MWCNTs and CNFs, the flexural strength of the SMP composite increased from 31.01 (pure SMP) to 45.1 and 40.1 MPa, respectively. Similar to the results obtained in the isothermal static stress-strain tests, the flexural strength of the SMP composite filled with CSCNTs is also found to increase significantly compared with those of SMP composites filled with MWCNTs and CNFs under the same amount of reinforcement fillers. The above-mentioned isothermal tensile and flexural test results indicated that SMP composites reinforced by CSCNTs could be more effective in strengthening SMP composites.

Thermal stability

Before probing the SME for SMPs, it is important to evaluate their thermal stability properties. Here, the



Figure 6. Curves of flexural strength versus weight fraction of different fillers (CSCNT, MWCNT, and CNF). CSCNT: cup-stacked carbon nanotube; MWCNT: multiwalled carbon nanotube; CNF: carbon nanofiber; SMP: shape memory polymer.

thermogravimetric analysis (TGA) is applied to investigate the thermal stability of the prepared SMP composites filled with different amounts of CSCNTs, MWCNTs, and CNF. The weight of the specimen is about 6–8 mg. The weight loss of specimens was tested from room temperature to 700°C at a heating rate of 20°C/min. Before the experiments, all the specimens were kept in oven at 120°C for 8 h to fully remove the moisture to avoid its interference on the weight characterization. In order to sensitively distinguish the critical point of the decomposition (e.g. onset point, peak point, and end point during decomposition), the curve of differential thermal gravimetric (DTG) analysis was employed.

During the TGA on the pure SMP and CSCNTreinforced SMP composites, the dependence of DTG values on the temperature is investigated and shown in Figure 7, where the curves' fluctuation denotes the weight loss rate of the specimens. We also summarized the critical point of the decomposition (onset point, peak point, and end point during decomposition) in Table 2 for a clear illustration among different specimens. It can be seen that for the pure SMP, the curve is fairly stable before the temperature is ramped to 368°C (onset point), indicating that the material is chemically stable. Then, the SMP starts to degrade. After the curve reaches its peak point at about 458°C, SMP is completely degraded at about 501°C (end point), namely, the decomposition process of the SMP. Curves of CSCNT-reinforced SMP composites exhibit similar fluctuation trend. However, the incorporation of CSCNTs into SMP offers a thermally stabilizing effect since the onset point occurs at a higher temperature with increase in CSCNT amount. The SMP composite containing 2 wt% CSCNTs starts to degrade at about 389°C, which is 21°C higher than that of pure SMP.

	Onset point (°C)	Peak point (°C)	End point (°C)
Pure SMP	368	458	501
SMP + 0.5 wt% CSCNT	373	461	504
SMP + 1 wt% CSCNT	380	470	509
SMP + 1.5 wt% CSCNT	386	471	521
SMP + 2 wt% CSCNT	389	487	534

Table 2. Critical temperatures points (onset point, peak point, and end point) during the decomposition process.

SMP: shape memory polymer; CSCNT: cup-stacked carbon nanotube.



Figure 7. Differential thermal gravimetric values versus temperature during the thermogravimetric analysis. The curves were slightly shifted vertically for better visualization. SMP: shape memory polymer; CSCNT: cup-stacked carbon nanotube.

Besides, it is significant that the peak points, which reveal the rate limit of the weight loss, shift toward a higher temperature as the CSCNT content increases. The similar trend was also found for the end points of the decomposition, implying that the SMP composites end combustion at higher temperature with the gradual incorporation of CSCNTs. The improved thermal stability of the SMP composite is attributed to both the excellent thermal stability of CSCNTs and their interactions with the polymer matrix. This experimental observation is consistent with previous reports on the polymer composites embedded with CNTs and CNFs (Cho and Yoon, 2001; Du et al., 2003; Xiong et al., 2006). The glass transition range of the SMP and their composites in this study is around 50°C-80°C, while the temperature range for triggering the SMP is usually between T_g and $T_g + 30^{\circ}$ C. That is, the induced temperature to actuate the SME is much lower than the onset temperature of decomposition.

Since the onset point represents the temperature at which the investigated materials start to degrade, it could be utilized to evaluate their thermal stability. The critical onset temperatures during the decomposition process of pure SMP and SMP composites



Figure 8. Curves of onset temperature versus weight fraction of different fillers (CSCNT, MWCNT, and CNF). CSCNT: cup-stacked carbon nanotube; MWCNT: multiwalled carbon nanotube; CNF: carbon nanofiber; SMP: shape memory polymer.

incorporated with different types of fillers (CSCNT, MWCNT, and CNF) are summarized and plotted in Figure 8. Clearly, all the three types of fillers could enhance the thermal stability of the pure SMP by increasing its onset temperature. However, under the same weight fraction of filler, CSCNT-filled SMP composites exhibit higher onset temperature in comparison with that of MWCNT- and CNF-filled SMP composites, indicating a more profound effect of CSCNTs. Besides, it is also observed that all the recorded onset temperatures are much higher than the glass transition temperature to actuate the SME in the pure SMP and SMP composites.

Dynamic mechanical analysis

The storage modulus of SMP composite 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 dynamic mechanical properties of the SMP composites reinforced by different amounts of CSCNTs were determined using a NETZSCH DMA 242C (NETZSCH, Germany) equipment. All the specimens, with the same dimensions of $35 \times 12 \times 4 \text{ mm}^3$, were tested under the three-point



Figure 9. Curves of storage modulus and loss tangent under various temperatures versus weight fractions of CSCNTs. CSCNTs: cup-stacked carbon nanotubes; SMP: shape memory polymer.

bending mode at a constant heating rate of 10° C/min, an oscillation frequency of 1 Hz, and an examined temperature range of 10° C– 120° C. They were initially locked into a deformation of 0% with zero initial force. The storage modulus and loss tangent of composites as a function of temperature are presented in Figure 9.

The data show that for an SMP composite with a certain amount of CSCNT content, the storage modulus far below T_{σ} is about two orders of magnitude larger than that above T_g . For instance, the SMP composite with 2 wt% CSCNTs exhibits a storage modulus of 1964.7 MPa at 20°C, while it is just 95.53 MPa at 120°C. In this figure, the T_g could be 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 about 58°C–65°C. T_{φ} moves to a lower temperature with an increase in the CSCNT content. However, within the entire range of testing temperature, the storage modulus of the SMP composites increases along with the addition of CSCNT content. This is because the reinforcement fillers could be well bonded with the SMP matrix due to the cupstacked morphology of CSCNTs. Besides, the typical size of CSCNTs is of the same order as the size of segments in polymer network. The friction interactions among CSCNTs and macromolecule segments help SMP composites to resist external loading, resulting in an improved thermomechanical properties. Based on the dynamic mechanical analysis (DMA) results, the shape recovery force or moment of the SMP composites during a specified shape recovery cycle could be calculated by using the classic material mechanics theories. Because of the increased storage modulus of the CSCNT-filled SMP composite under various temperatures, a higher shape recovery stress would be generated during the glass transition process.



Figure 10. DSC scans of SMP composites with different weight fractions of CSCNTs.

DSC: differential scanning calorimetry; SMP: shape memory polymer; CSCNTs: cup-stacked carbon nanotubes.

Shape recovery behavior

Differential scanning calorimetry. The glass transition temperature (T_g) of a noncrystalline material refers to the critical temperature at which the material changes its behavior from glassy state to rubbery state. When it comes to SMP, T_g is the switching temperature where the modulus of SMPs begins to significantly decrease and SMPs begin to show the SME. Similar to other types of SMP materials, T_g also plays an essential role in shape memory performance of styrene-based SMP. Therefore, T_g was primarily determined in this section before the following investigations on the shape memory behavior of the SMP composites.

The NETZSCH Instrument DSC 204F1 was applied to study the thermal properties of composites in a nitrogen environment. In this study, the midpoint of the temperature range, where the glass transition of the SMP composite occurs, was defined as T_g . During the measurement, the specimens were heated from 5°C to 110°C, then cooled down to 5°C, and again heated up to 110°C at a scanning rate of 10°C/min. The thermal transitions in the second thermal scan were used for analysis. The influence of the CSCNTs on the T_{σ} of SMP composites is presented in Figure 10 as a function of CSCNT content. Compared with the T_g of pure SMP (62°C), T_g of SMP composite with 2 wt% CSCNTs decreased to 52.8°C. Such an influence on T_g can be attributed to the decrease of SMP segments per unit volume in composite than that of pure SMP matrix.

Thermal conductivity. Traditionally, polymeric materials possess an intrinsically low thermal conductivity on the

10 S

Figure 11. Thermal conductivity of the SMP composites as a function of weight fraction of different fillers (CSCNT, MWCNT, and CNF).

SMP: shape memory polymer; CSCNT: cup-stacked carbon nanotube; MWCNT: multiwalled carbon nanotube; CNF: carbon nanofiber.

order of 0.15 < k < 0.30 W/mK for most cases, which makes them good insulators for numerous applications. However, thermally stimulated SMPs require a relatively high conductivity to achieve responsive sensitivity. In this study, thermal conductivity of the CSCNT-filled SMP composite was tested to evaluate the influence of CSCNTs on the thermal sensitivity of the SMP composites.

Figure 11 presents the relationship between thermal conductivity of the SMP composites and weight fractions of different fillers (CSCNT, MWCNT, and CNF). The thermal conductivity of pure SMP is approximately 0.17 W/m K at room temperature. In comparison, SMP composites possess higher thermal conductivity, and the value is significantly increased with the addition of reinforcement fillers. For example, the thermal conductivity of SMP composite filled with 2 wt% CSCNTs increases to 0.33 W/m K. This is because due to a higher content of SMP matrix per unit, pure SMP needs more heating energy to complete shape recovery process than the SMP composites with the same heating progress and specimen dimensions. However, under the same amount of reinforcement fillers, SMP composites filled with CSCNTs possess a higher thermal conductivity comparing with that of SMP composites filled with MWCNTs and CNFs, which is, respectively, attributed to the relatively larger aspect ratio of CSCNTs and the superior thermal properties of CNTs. The relative lower energy consumption and improved capability to absorb and conduct thermal energy make shape recovery process of SMP composites much quicker than that of pure SMP. This increase suggests that the CSCNTs are beneficial as components for polymer with respect to thermal conductivity.

Figure 12. Series of photographs showing the macroscopic shape recovery process of SMP composite filled with 2 wt% CSCNTs.

110 S

SMP: shape memory polymer; CSCNTs: cup-stacked carbon nanotubes.

Shape recovering behavior. The above-mentioned investigations revealed that CSCNTs could benefit the SMP material by improving the mechanical and thermomechanical properties, decreasing the glass transition temperature, and increasing the thermal conductivity. In the following study, the shape recovery behavior of SMP composites filled with 2 wt% CSCNTs being driven by thermal energy was carried out and monitored by video camera, as shown in Figure 12. The demonstrated specimen was cut out from the prepared SMP composite with a dimension of 80 \times 20 \times 3 mm³. A 1 g weight was attached on the end of the specimen to test the shape recovery properties under external resistance load. The thermal energy was generated by passing electric current through two resistance heating films attached on the top and bottom surfaces of the specimen. The applied electric current is 1 A.

As shown in Figure 12, the thermally induced shape recovery process in the investigated SMP composite is slow within the initial 10 s. Then, the deploying speed of the SMP composite specimen dramatically increases. At about 100 s, the shape recovery process in the specimen is completed, and no noticeable deformation is observed after 100 s. By using the testing method the authors previously developed (Lan et al., 2009), the recovered shape of SMP composite is observed to be approximately 97% compared with its original shape. The remaining deformation in shape results from the external resistance load and the friction between the soft segment of SMP and the CSCNTs. Furthermore, it must also be noted that the rate of shape recovery of the SMP composites was strongly dependent on the magnitude of the applied voltage in the resistance heating films. If we quantitatively define the total shape recovery time of the SMP composite as the time point that corresponds to the 95% shape recovery ratio, Table 3 lists the shape recovery time of the pure SMP and three SMP composites with 2 wt% reinforcement fillers as a function of applied electric current on the resistance heating films. The results indicated that the



Electric current (A)	Shape recovery time	Shape recovery time (s)			
	SMP/CSCNTs	SMP/MWCNTs	SMP/CNFs	Pure SMF	
1	97.3	114.3	126.0	150.9	
5	84.6	95.1	109.5	137.2	
7.5	77.3	81.4	93.8	112.2	

Table 3. Shape recovery time of the pure SMP and three SMP composites with 2 wt% reinforcement fillers as a function of electric current.

SMP: shape memory polymer; CSCNT: cup-stacked carbon nanotube; MWCNTs: multiwalled carbon nanotubes.

developed SMP composite with CSCNTs possesses excellent shape recovery rate and ratio and hence could provide superior recovery abilities in their practical applications.

Conclusion

In this article, CSCNTs were recruited as reinforcement fillers in a styrene-based SMP composite. Compared with traditional MWCNTs and CNFs, CSCNTs could be well dispersed and warrant superior interface bonding and load transfer efficiency between the SMP matrix and the cup-stacked nanostructure. SMP composites containing different amounts (varied from 0.5 to 2 wt%) of reinforcement fillers (CSCNTs, MWCNTs, and CNFs) were prepared. The isothermal static mechanical tests indicated that the elastic modulus, tensile strength, and flexural strength of the CSCNT-reinforced SMP composites increased by 61%. 66%, and 84%, respectively, with 2 wt% CSCNTs. The glass transition temperature of SMP composite decreased from 61.9°C to 52.8°C by embedding 2 wt% CSCNTs, indicating that the shape recovery process could be triggered more easily by external stimulus due to the role of reinforcement fillers. The applied CSCNTs were also proven to enhance the thermal stability, thermal conductivity, and actuating force output during the shape recovery process. Finally, under the external resistance load, the developed SMP composite with 2 wt% CSCNTs was successfully driven to recover their shapes under thermal stimulus. The investigated CSCNTs could be utilized as other polymer composite reinforcement where CNTs are hard to be well dispersed.

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