MECHANICAL AND ELECTRICAL PROPERTIES OF SHAPE MEMORY POLYMER MATRIX AND CARBON NANOCOMPOSITE

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Abstract

This paper presents the fabrication and characterization, especially mechanical and electrically conductive properties, of a shape memory styrene polymer mixed with multi-walled carbon nanotubes (MWNTs). The composite, which is produced from resin mixing with MWNTs, can be activated directly by passing an electrical current. It is found that MWNTs can incorporate very well with resin after being disposed by nitrohydrochloric acid at even higher than 100°C. The MWNTs must be dispersed using an ultrasonic apparatus for more than 0.5 hour in the solvent, which is able to dissolve the resin. The transition temperature of the composite filled with 8% MWNTs measured by differential scanning calorimetry (DSC) is 49.57°C lower than 53°C of the pure polymer, while the curing temperature is 80°C higher than the 75°C of the pure polymer. The electrical behavior of composite related to conductive networks, and the percolation threshold of MWNTs/SMP nanocomposites sheet were about 5 wt.%; the electrical conductivity of composite filled with 8wt.% MWNTs ranges from 10^{-2}~10^{-1} Ωcm $^{-1}$.

1 Introduction

Shape memory polymers (SMPs) can be fixed into a temporary shape, and then recover their original shape by an external stimulus (e.g., heat), i.e., the shape-memory effect. SMPs have attracted great interest in recent years, owing to their high shape recovery ratio, ease in transforming into another shape and control of recovery temperature, and more importantly, low cost [1-4]. Most of the previous research works are focused on thermoplastic SMPs. However, as we know, most composites, in particular for some special applications, utilize thermoset resins rather than thermoplastic resins, due to the better mechanical performance and environmental durability inherent with thermoset resins [5-7]. However, these thermoset pure SMP without reinforcement are too soft to be suitable for many engineering applications, in which high stiffness and recovery force are required [8]. In comparison with reinforcement using micro-sized particles, nano particles may have greater potential, as the resulted composites can provide a significant improvement in both their thermo and mechanical properties [9-12]. SMP composites filled with highly conductive fillers provide an additional advantage, i.e., the actuation can be induced by passing an electrical current [13,14]. In this paper, we investigate the fabrication and characterization, especially for mechanical and electrical conductive properties, of shape memory composite using the styrene polymer matrix filled with multi-walled carbon nanotubes (MWNTs). The focus is on the influential factors for the evolution of mechanical property and the electrical properties

2 Samples Prepartion

We intend to produce an activate material which can be directly heated by passing an electric current. The selected shape memory polymer is a styrene-based thermoset resin, (specific gravity: 0.88~0.92; boiling temperature: 100~145°C). In order to improve the interfacial bonding between polymer and nanotubes, the MWNTs (10~20 nm in diameter, 50 μm in length) are surface-modified in a mixed solvents of nitric acid (61%) and sulfuric acid (98%) in a ratio of 3:1 at 140°C for 10 minutes, so that covalent bonds can be formed for better adhesion. The full term (IR) experimental result reveals that the hydroxide and the carboxyl appear after modification. After this treatment, the surplus solvent are washed by distilled water till the PH value between 5.5~7 is reached; and then the mixture was treated at 250°C in heater box to distill

MWNTs; the surface-modified MWNTs were mixed with resin, and then proper proportion of the solvent N, N-dimethylformamide (DMF) was added to reduced the viscidity of mixture; mixed by mechanical stir for 30min (500-1000rad/min), followed by high-energy sonication by VCX750 (produced by Sonics&Materials, INC.) for 2 hour; making the DMF volatilization at the temperature of 55~65°C till the mixture reach to a constant weight; at last, the mixture was injected into closed glass mould to cure, at the temperature of 75°C for 24 hour.

The samples contain 0, 2, 5, 8 and 20 wt.% of carbon nanotubes with a constant amount of the styrene-based resin and the hardener (about 3.5 wt.%).

3 Results and Discussion

3.1 Experimental Methods

3.1.1 DSC test: full term (DSC) test was carried out uisng an Instrument 2920MDSC on samples of around weight 7.0 mg. DSC curves of the composites were plotted in Figure 1. The temperature ranged from -50°C to 150°C at a constant heating rate of 10°C/min.

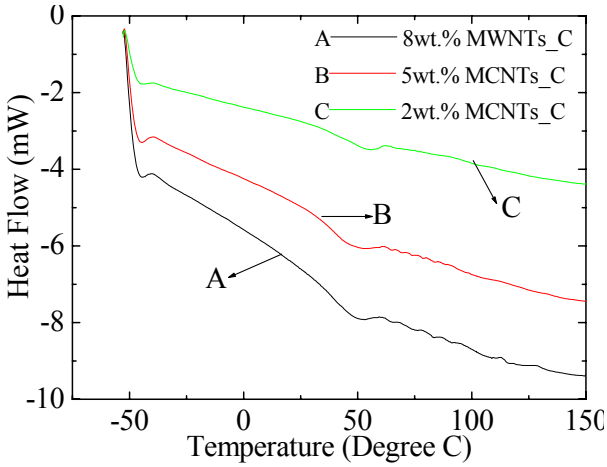

Fig. 1. DSC curves of composites filled with A 8wt.%, B 5wt.% and C 2wt.% MWNTs.

The glass transition temperatures were determined by the standard tangent method as 51.33°C, 49.45°C and 49.57°C for the 2, 5, 8wt.% nanocomposites respectively. As a reference, the glass transition temperature of pure SMP is 53~55°C. Hence, the glass transition temperature of MWNTs/SMPs composites is lower than the pure SMP.

3.1.2 TGA test: the temperature range for Thermal gravity analyzer (TGA) test is from 30°C to 900°C. A Perkin-Elmer Thermal Analysis is used at a constant heating rate of 10°C/min.

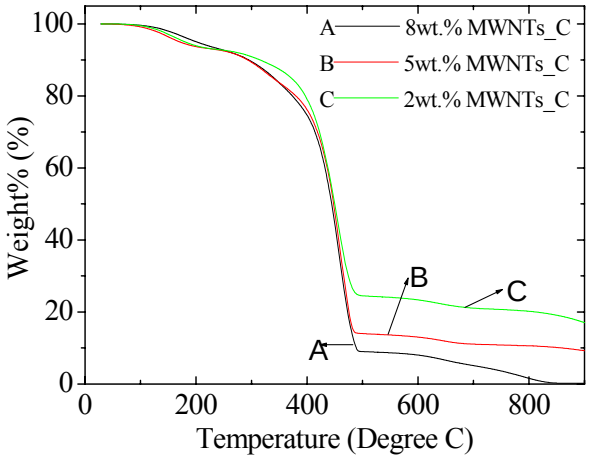

Fig. 2. TGA records of composites filled with (A) 8%MWNTs, (B) 8% and (C) 15% CB.

The weight of 2, 5, 8wt.% MWNTs nanocomposites were 16.249mg, 10.532mg and 12.148mg, respectively. The thermal stability and the transition temperatures were obtained from the TGA curves. It can be seen that MWNTs reinformed SMPs nanocomposite is highly thermal stable, and the thermal degradation temperature higher than 200 °C, while the boiling temperature 100~145 °C of pure SMP. The conductive filler accounts for the thermal degradation mechanism of composite.

3.1.3 Raman spectroscopy: Raman spectra of 8wt.% MWNTs composite sample was recorded with a DILOR LABRAM multi-channel confocal microspectrometer in backscattering mode using an Ar+ laser excitation (514.5 nm, 5 mw; resolution 1cm^{-1}). The integration times were 90 s and 30 s. The Raman spectrum is obtained in the range from 800 to 1700cm^{-1}. As we know, the typical spectra of MWNT is at a band about 1588cm^{-1} (G band) due to the $A_{(g1)}$, $E1_{(g)}$ and $E_{2(g)}$ vibrational modes, and a band at 1357cm^{-1} (D band) arising from the disorder-induced A(g1) mode. The G band is wide and its intensity is lower than twice of that of the D band [15].

A Raman spectrum of 8wt.% MWNT nanocomposite is presented in Fig. 3, which shows three peaks at 1000.8, 1357.24 and 1600.65cm^{-1}, respectively. The range between 1500~600cm^{-1} is defined as finger mark range, from which the structure of styrene polymer is identified. The peaks at1357.24 and 1600.65cm^{-1} reveal the structure of MWNT. Finally, we can estimate the interaction between polymer and the filler from peaks departure.

For the 8wt.% MWNTs nanocomposites, the polymer has large effect on the A(g1) mode, reduce the disorder degree; at the same time, nearly has no effect on $E1_{(g)}$ and $E_{2(g)}$ vibrational modes of MWNTs compared with pure MWNTs Raman spectrum.

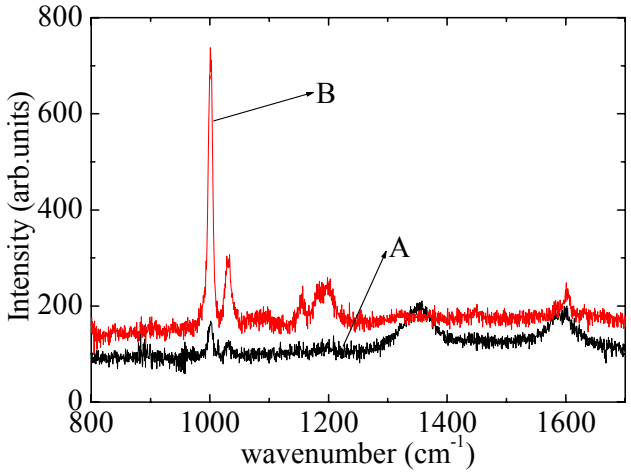

Fig. 3. Raman spectrums of 8wt.% MWNTs composites, the integration time are A 90s, B 30s.

Besides the interaction between polymer and filler, the thermal and electrical conduction of MWNT in composites also can be obtained from Raman spectrum. For MWNTs/styrene-based SMP composite, thermal and electrical conduction arises from the molecular vibration, so the D band obtained from Raman spectrum can be used to explain these properties of MWNTs in composite. Compared with pure MWNTs, the D band arising from the disorder-induced A(g1) mode of 8wt.% MWNTs composite falls down severely, so the thermal and electrical properties of composite is worse than pure MWNT.

3.2 Mechanical Properties Tests

The cured MWNT/SMPs composites were tested for their mechanical properties. Tensile tests were performed at 25°C and at a constant cross-head rate of 5N/mm on an Instron electro-mechanical testing machine. The dimension of samples were 70mm×15mm×3mm. The gauge length was 48mm. Table 1 summarizes the major results of pure SMP and SMP/MWNTs composites. For 8wt.% SMP/MWNTs nanocomposite, its Young modulus increases by 12.1% and the tensile strength by 8.1 as compared with that of the pure SMP. The uniform dispersion, and the adherence between surface-modified MWNTs and polymer interface may be accouted for the improvement of mechanical property. So the mechanical properties of MWNTs reinforce SMP composites are improved compared with pure polymer, and the level of improvement depends on the exact fabrication process.

Table 1. Mechanical properties of tensile tests

Materials	E(GPa)	σ (N/mm)	ε max (%)
Pure SMP	1.16	17.3	2.3
2wt.%MWNTs/SMP	1.21	17.9	2.1
5wt.%MWNTs/SMP	1.25	18.5	1.7
8wt.%MWNTs/SMP	1.30	18.7	1.5

Further investigation is necessary to find the influence of nanotube vs. SMP ratio (in wt%), uniformity of dispersion and interface inherence on the mechanical properties of the nanocomposite. The improvements, together with a proper alignment of the nanotubes, a new generation of nanocomposite may be obtained, which can be highly competitive as compared with the traditional fiber reinforced composites [16].

3.3 Electrical Propertie Tests

The electrical conductivity of all types of samples is investigated using a simple circuit. A multimeter (DT9901C) was applied directly on the samples. The electrical conductivity is calculated by:

$$R = \rho \frac{L}{A} \qquad (1)$$

where: R is the resistivity, 1329 Ω, L is the length of sample, 8.0cm, A is the contact area of electrode and composite(length 2.0cm × width 1.2cm), ρ is the electrical conductivity. Through calculation, the electrical conductivity of 8 wt.% MWNTs/SMP nanocomposite is $1.25\times10^{-2}\,\Omega cm^{-1}$.

Fig. 4. 8.0×2.0×0.2 (cm^3) 8wt.% MWNTs composite (a), and its surface resistivity is 80Ω·cm (b)

The intensity I (0.076 A, when U is 20 V) through the sample thickness e (0.16 cm) and contact area S (5×10^{-3} cm^2) is measured, using a programmable power supply PSP-2010. The DC conductivity is then calculated by equation (2):

$$\sigma = \frac{I}{U}\frac{e}{S}DC \qquad (2)$$

The DC electrical conductivity of nanocomposite is obtained as $1.2\times10^{-2}\ \Omega cm^{-1}$. In order to improve the electrical properties, MWNTs are used. Carbon nanotubes have excellent conductivity, but not for SWNTs, which can be semi-conductive or metallic based on their chirality. The conductivity of MWNTs results from the mean behavior of the different rolled grapheme layers. The electrical conductivity of styrene polymer/MWNT composites is plotted as a function of the 0, 2, 5, 8 and 20 weight percentage of nanotubes added in the matrix (Fig. 5).

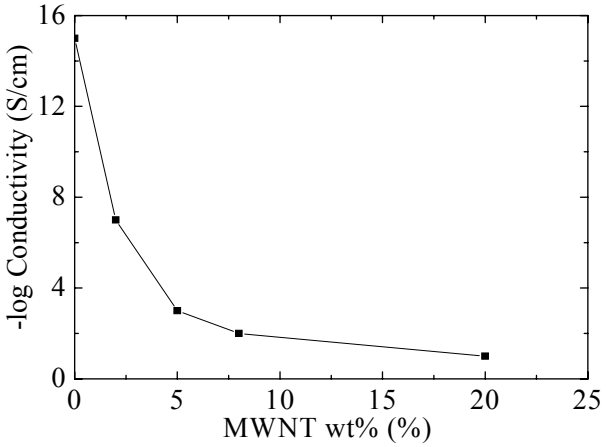

Fig. 5. The conductivity as a function of MWNT weight percentage

Within the range of wt% of CNTs presented in Fig. 4., from 0 to 5 wt.%, the conductivity drops by twelve orders of magnitude, corresponding to the phenomenon of percolation, and thus, a conduction threshold below 2 wt.%. The percolation threshold is a measure of the conductive path formed by the interconnected nanotubes. A high aspect ratio of the interconnection allows reaching this threshold with a small CNT fraction. The conductivity of 20 wt.% composite is fourteen orders of magnitude lower than the pure polymer, and is practically a conductor. The 2 and 5 wt.% composites are semi-conductor with conductivity as high as 10^{-6} and 10^{-3} S/cm, respectively. The addition 8 wt.% of MWNTs is sufficient to transform the polymer composite more suitable for applications requiring electrostatic discharge from the electrical properties measurements, the threshold of a conducting or interconnected network of the CNTs was reached at 2 wt.%.. This study also suggests that it is not helpful to have very high MWNTs concentrations to improve the electrical properties of composites due to a kind of "saturation effect".

The conductivity of a composite depends on many factors, namely, the size, shape and type of filler, and the ratio of the conductive filler in composite etc. But the most important influential one is the formation of conductive network. Without conductive chain; the conductivity of the composite is poor.

As we know the excellent mechanical and electrical properties compared with other conductive fillers, taking micro carbon black and nanoparticles into test, it is found that there were no interfacial bonding between polymer and filler, so the aggradation of filler would occur through the curing process, and thus the mechanical property of composites was bad. At the same time, due to the lower ratio of diameter to length of carbon particles ($1\sim10^1$) compared with MWNTs (more than 10^3), the percolation threshold of particles was 6~10wt.%, while the MWNTs composite was 0.1~9wt.%. The 8wt% micro carbon black composite was $10^{-3}\ \Omega cm^{-1}$, and the 8wt% nanoparticles more than $10^{-4}\ \Omega cm^{-1}$, while the 8wt% MWNTs nanocomposite was $10^{-2}\ \Omega cm^{-1}$.

3.4 The Mechanism Analysis of Shape-Memoty Effect of Polymers

through the study and investigation of SMPs, we find that the shape memory effect can be explained by the strain relaxation theory, the bases are the SMPs and SMPs composites belong to polymer materials, and all the behaviors of polymer can be looked as relaxation. Quoting the Eyring general theory (3) to explain the relation of relaxation time with temerature, because the relaxation process is arose by the part movement of main molecule chain.

$$\tau = \tau_0 e^{\Delta E/RT} \qquad (3)$$

τ_0 is a contant, R is gas contant, T is absolute temperature, and ΔE is the energy of relaxation process. For SMPs and SMPs composites, the ΔE is the activation energy (or crystalization heat) of soft monomer, τ is looked as the recovery time dividing

e. The ΔE can be obtained by the relaxation time at different temperature obeying equation:

$$\Delta E = R\frac{d\ln\tau}{d\left(1/T\right)} \qquad (4)$$

The value of the equations (3) (4) are make relation between shape memory effect and the relaxation process; make a base standard to evaluate the recovery property of SMPs. Table 2. presents the recovery time of 8wt.% MWNTs composite at different temperature.

Table 2. recovery time at differents temperature

absolute temperature (K)	Recovery time (s)	τ (s)
323	202.08	202.08/*e*
328	156.38	156.38/e
333	122.04	122.04/e
338	92.45	92.45/e

The weight of 8wt.% MWNTs composite sample is 8.40g, and its ΔE calculated through equation (3) is 12.3557J/g (1284.99J/mol); through equation (4) is 12.7214J/g (1323.03J/mol). Because the activation energy of polymer equals to the enthalpy which can be calculated from the Endothermic effect of full term DSC curve A (Fig. 1,) is 11.7294J/g (Onset point: 41.37°C, Peak 1 top: 50.71°C). So the shape memory effect can be explained by relaxation behavior is a relaxation process.

4 Conclusions

The MWNT filler improves the properties of SMP composite. The mechanical properties are more determined by the uniformity of dispersion; while the electrical properties are dominated by the conductive chains or network. Therefore, both properties may put up different requirements, which appear contradicted in nature. Nevertheless, a few conclusions can be drawn from the experiments reported in this paper.

1. The reinforcement using MWNT increases the modulus and tensile stress of the SMP composite. The glass transition of the reinforced and unreinforced SMPs is similar. However, the glass transition temperature of the reinforced ones is slightly lower than the one without reinforcement.

2. TGA results reveal that MWNTs nanocomposite has a higher thermal stability than the pure SMP material.

3. Raman spectra show that the polymer has large effect on the A(g1) mode, reduce the disorder degree; at the same time, nearly has no effect on $E1_{(g)}$ and $E_{2(g)}$ vibrational modes of MWNTs. And the reduce of A(g1) mode can be used to explained the thermal conductivity of composites lower than the MWNTs.

4. The percolation threshold of the styrene-based SMP reinforced with MWNTs nanocomposite is 0.1~9%, sometimes it belows 5wt.%. The electrical property of the composites is controlled by the fabrication process. Take the MWNT composite as an example. The conductive fillers, either nanotubes or nanoparticles, must be dispersed by ultrasonic. However, once the conductive filler is dispersed uniformly in the mixture, the chance of forming chain falls down, so the electrical property of composite is poor. The percolation threshold will arise.

5. As compared with carbon black, the carbon nanotube composite has a lower percolation threshold, better mechanical and electrical properties.

6. The relaxation effect which is inherent with polymer and its composite is used to explain the shape memory effect firstly. it not only provides a evaluation criterion for shape memory recovery, and also provides a method for qualitative investigation.

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