Dynamic mechanical analysis of carbon nanotube-reinforced nanocomposites

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ABSTRACT

Background: To predict the mechanical properties of multiwalled carbon nanotube (MWCNT)–reinforced polymers, it is necessary to understand the role of the nanotube-polymer interface with regard to load transfer and the formation of the interphase region. The main objective of this study was to explore and attempt to clarify the reinforcement mechanisms of MWCNTs in epoxy matrix.

Methods: Nanocomposites were fabricated by adding different amounts of MWCNTs to epoxy resin. Tensile test and dynamic mechanical analysis (DMA) were conducted to investigate the effect of MWCNT contents on the mechanical properties and thermal stability of nanocomposites.

Results: Compared with the neat epoxy, nanocomposite reinforced with 1 wt% of MWCNTs exhibited an increase of 152% and 54% in Young's modulus and tensile strength, respectively.

Conclusions: Dynamic mechanical analysis demonstrates that both the storage modulus and glass transition temperature tend to increase with the addition of MWCNTs. Scanning electron microscopy (SEM) observations reveal that uniform dispersion and strong interfacial adhesion between the MWCNTs and epoxy are achieved, resulting in the improvement of mechanical properties and thermal stability as compared with neat epoxy.

Keywords: Dynamic mechanical analysis, Multiwalled carbon nanotube, Nanocomposite, Storage modulus

Introduction

Epoxy resin reinforced with fillers shows good stiffness, specific strength, dimensional stability and chemical resistance, and it has become an attractive structural material in industries such as aerospace, automobile and sporting goods, where material weight is an important factor. Carbon nanotubes (CNTs) are widely used for nanoreinforcing a variety of polymer matrices, because of their excellent mechanical, electrical and thermal properties. These superior properties coupled with recent developments in nanotechnology and nanofabrication techniques have triggered extensive research worldwide in CNT-based nanocomposites. Qian et al [1] reported that elastic modulus and tensile strength were increased by 42% and 25%, respectively, when 1 wt% of CNTs was added to polystyrene matrices. Shen et al [2] and Kim et al [3] have found a significant improvement (greater than

100%) of both flexural and tensile strength with the addition of 1 wt% of multiwalled carbon nanotubes (MWCNTs). Allaoui et al [4] achieved an increase in the thermal conductivity of MWCNT-epoxy resin nanocomposites by about 9 times when 4 wt% of MWCNT was added. Biercuk et al [5] reported a 125% increase in the thermal conductivity of epoxy with the addition of 1 wt% of single-walled carbon nanotubes loading.

CNTs possess an ultimately high aspect ratio (length/diameter) resulting in an intrinsic van der Waals force among tubes. These forces lead to a substantial agglomeration of tubes generating voids and reducing the strength of the nanocomposite as a result of the stress concentration [6]. Practical uses of CNTs in epoxy resin nanocomposites significantly depend on the level of homogeneous dispersion of individual CNTs in the polymer matrix and the interfacial adhesion between the polymer matrix and CNTs [7]. CNTs can be functionalized covalently or noncovalently with various polymers. Noncovalent interactions such as the π–π interaction enable the absorption of polymers onto the CNT surfaces [8-12]. Chemical functionalization [13-18] can create functional groups on the surface of CNTs and form covalent bonding with the polymer matrix. However, strong acid treatment would cut off the CNTs' length and limit their application as a high-performance filler [7]. Viet et al [19] proposed a theoretical model based on the shear-lag model and global force equilibrium to predict the effective Young's modulus of single- and multi-walled carbon nanotube-epoxy composites. Ma et al [20] investigated the effects of CNT loading

and magnetic field on the fracture toughness, glass transition temperature and electrical properties of epoxy composites containing aligned carbon nanotubes. Ghosh et al (21) prepared MWCNT-reinforced epoxy matrix using an innovative ultrasonic dual-mixing process which consisted of ultrasonic mixing with simultaneous magnetic stirring. Lee and Park (22) investigated the effect of MWCNTs on the electrical properties of a stretchable carbon composite electrode. Weidt and Figiel (23) presented a 3D nonlinear computational model to predict the compressive behavior of epoxy–carbon nanotube nanocomposites, taking into account the particle waviness and van der Waals interactions at the polymer–particle interface. Tan and Xu (24) investigated the conductive properties and mechanism of various polymers doped with carbon nanotube-polyaniline hybrid nanoparticles.

To predict the mechanical properties of MWCNT-reinforced polymers, it is necessary to understand the role of the nanotube-polymer interface with regard to load transfer and the formation of the interphase region. The main objective of this study was to explore and attempt to clarify the reinforcement mechanisms of MWCNTs in epoxy matrix. In this work, different amounts of MWCNTs were dispersed within the epoxy resin. An ultrasonicator was used to process the dispersion of MWCNTs in the epoxy matrix. The influence of MWCNT content on the mechanical properties of MWCNT-epoxy nanocomposites was investigated. Tensile tests were conducted to evaluate the Young's modulus and tensile strength of the nanocomposites. Dynamic mechanical analysis was performed to determine the storage modulus, loss modulus and glass transition temperature. Scanning electron microscopy (SEM) was used to examine the fracture surface and reveal the dispersion of MWCNTs in the polymer matrix. A better understanding of the thermal and mechanical properties of the nanocomposite is useful for quality control and product development.

Materials and methods

Materials

Commercial MWCNTs supplied by Golden Innovation Business Co., Taiwan, were used in this study. The MWCNTs were 50 to 90 nm in diameter and 5 to 15 μm in length. Table I lists the specifications of the MWCNTs provided by the manufacturer. The morphology of pristine MWCNTs was analyzed using a field emission scanning electronic microscope (FESEM) as shown in Figure 1. It can be observed that the MWCNTs are entangled with each other. The polymer matrix consists of epoxy resin (bisphenol A diglycidyl ether) and hardener (tetraethylenepentamine 80%, fatty acid 20%). Distilled water was used in the synthesis process as necessary.

Fabrication of MWCNT-epoxy nanocomposites

The liquid epoxy (3.42 g) was put in a small breaker and placed in a preheated oven at a temperature of 60°C for 30 minutes. Then, a desired amount of MWCNTs (17.1, 28.5, 45.6 or 57 mg) was incorporated into the liquid epoxy. The mixture was gently stirred for 10 minutes. After stirring, it was placed in an ultrasonic bath at a temperature of 50°C for

TABLE I - Specifications of MWCNTs

Diameter	50-90 nm
Length	5-15 μm
Purity of MWCNT	$\geqq$95%
Ash	$\leqq$0.2 wt%
Specific surface area	40~300 m^2/g
Amorphous carbon	<3%

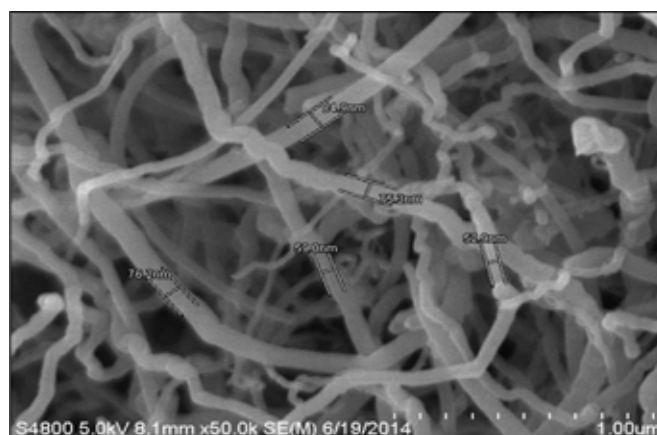MWCNTs = multiwalled carbon nanotubes.

Fig. 1 - Field emission scanning electronic microscope.

3 hours to disaggregate the MWCNTs and achieve good dispersion. The suspension was degassed in a vacuum chamber at a pressure of 20 mm Hg for 3 hours. Then, the hardener (2.28 g) was added to the MWCNT-epoxy solution, and softly stirred for about 10 minutes. After that, the solution was placed in a vacuum chamber at a pressure of 20 mm Hg for 30 minutes to remove any bubbles created by the stirring. The nanocomposite suspension was cast into a dog-bone mould to fabricate the tensile test specimen, as shown in Figure 2. The specimen was postcured in a preheated oven at a temperature of 50°C for 24 hours. Then the specimen was removed from the mold and cooled to room temperature. Four sets of nanocomposites were fabricated using the same procedures, with MWCNT contents of 0.3, 0.5, 0.8 and 1.0 wt%, respectively. As the content of MWCNTs becomes higher than 1.0 wt%, the viscosity of the liquid epoxy is significantly increased, resulting in a failure of the dispersion. Thus, specimens with MWCNTs higher than 1.0 wt% were not included in this work. Samples of neat epoxy were also prepared for comparison. The top and bottom surfaces of the specimens were mechanically polished to eliminate the surface roughness and any defects, using a grinding machine.

Characterization

Tensile tests were conducted according to ASTM D638 to characterize the mechanical properties of the nanocomposites; these properties included the Young's modulus,
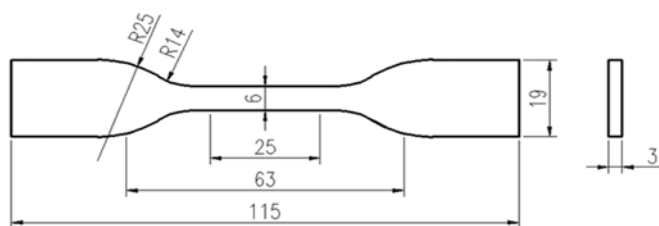
Fig. 2 - Tensile testing specimen (units are mm).

Fig. 3 - Stress-strain curves of neat epoxy and nanocomposite with different multiwalled carbon nanotube (MWCNT) loadings.

TABLE II - Mechanical properties of MWCNT/epoxy nanocomposites

	MWCNT wt%				
	0	**0.3**	**0.5**	**0.8**	**1.0**
Young's modulus, GPa	0.477	0.584	0.695	0.847	1.20
Yielding strength, MPa	8.39	10.5	10.9	12.3	12.9
Tensile strength, MPa	11.6	12.9	13.6	16.1	16.5
Fracture strain, %	12.1	4.24	7.10	4.20	4.12
Fracture modulus, MPa	1.08	0.392	0.876	0.503	0.547

MWCNTs = multiwalled carbon nanotubes.

tensile strength and fracture strain. Tests were performed at ambient temperature using a universal testing machine (Hounsfield model H10KS, 10 kN load cell) with a constant crosshead speed of 3 mm/min. To evaluate the dispersion of the MWCNTs in the polymer matrix, the fracture surface of the nanocomposite was investigated using FESEM (Hitachi model s-4800). Dynamic mechanical analysis (DMA) can be used to determine the storage modulus E', loss modulus E" and damping coefficient tanδ as a function of temperature, frequency or time. The storage modulus is relative to the elastic modulus, while the loss modulus is used to characterize the viscous properties of polymer composites. In this study, DMA was performed using a Metravib model DMA 450, operating in a 3-point bending (flexural) mode at a frequency of 1 Hz with a scanning rate of 10°C/min from -20°C to 150°C. The DMA specimen of dimension 48 × 6.5 × 2.6 mm, taken from the center section of the tensile test specimen, was placed in the 3-point bending fixture, and then enclosed in a thermal chamber. Frequency, amplitude and an appropriate temperature range were applied to the specimen.

Results and discussion

Tensile testing

The as-prepared test specimens were polished and machined to form a tensile test specimen as shown in Figure 2. Three tests were performed for each sample. The average of the 3 measured values was calculated for each sample, and the average of the measurements was reported. Figure 3 shows the stress-strain curves from the tensile tests for neat epoxy and nanocomposites with 0.3, 0.5, 0.8 and 1.0 wt% of MW-CNTs. The Young's modulus is obtained from the slope of the linear region of the stress-strain curve. The yield strength is determined using the 0.2% offset method. The area under the stress-strain curve represents the strain energy density and can be used to evaluate the toughness of the materials. Other mechanical properties such as tensile strength and fracture strain can also be extracted from the stress-strain curve.

The experimental results of the mechanical property testing for neat epoxy and nanocomposites with various loadings of MWCNTs are summarized in Table II. It appears that the Young's modulus, yield strength and tensile strength of the epoxy were greatly improved by the incorporation of MWCNTs. The strain at break tended to decrease as the content of MWCNTs increased, indicating that the addition of MWCNTs made the nanocomposite stiffer and somewhat more brittle in comparison with the neat epoxy. There was a
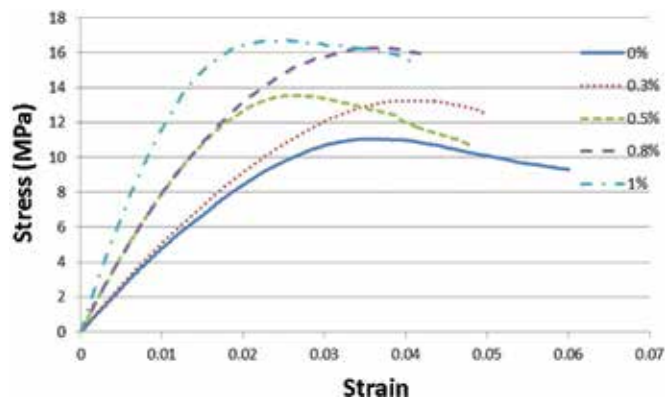
significant increase in Young's modulus of up to 150% with 1.0 wt% MWCNT loading, and a moderate increase in tensile strength up to 42%. Conversely, the strain at fracture decreased from 12.1% to 4.12% as the loading of MWCNTs increased from 0 wt% to 1.0 wt%.

The dispersion of MWCNTs in the epoxy matrix was examined using FESEM. The SEM images of the fracture surface of neat epoxy and nanocomposite with 1.0 wt% MWCNT loading are presented in Figure 4A and B, respectively. It appears that the neat epoxy exhibited a clean and smooth surface. Incorporation of MWCNTs into the epoxy matrix increased the surface roughness. The fracture surface shown in Figure 4B reveals that MWCNTs were well dispersed in the epoxy matrix. MWCNTs that had bonded with the epoxy matrix were not totally pulled out, and they remained partially within the epoxy matrix. This indicates that strong interfacial adhesion existed between the MWCNT and epoxy matrix. Load and stress transfer from the epoxy to MWCNTs were improved by this strong adhesion which led to significantly enhanced mechanical properties.

Dynamic mechanical analysis

DMA was employed to determine the storage modulus E', loss modulus E" and damping coefficient tanδ of the nanocomposites as a function of temperature. Figure 5 shows the DMA plots of storage modulus (E') versus tem-

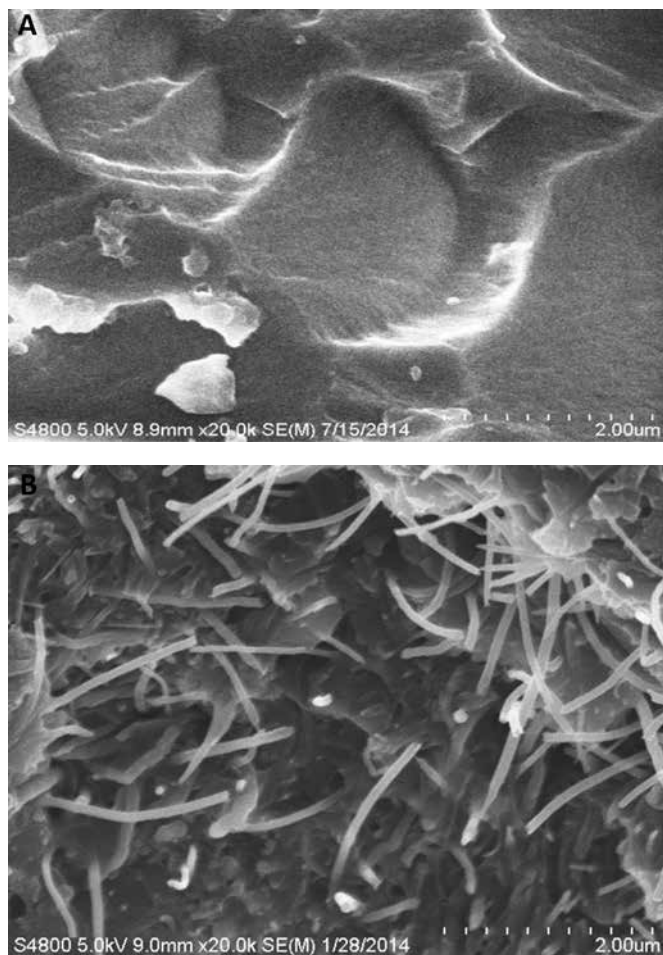**Fig. 5 -** Storage modulus (E') vs. temperature for neat epoxy and nanocomposite with different multiwalled carbon nanotube (MWCNT) loadings.
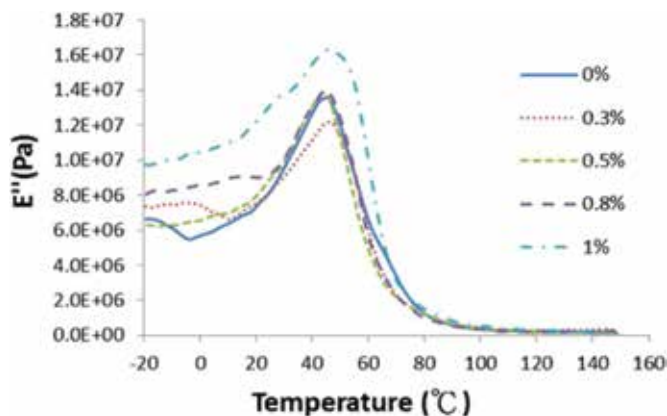
Fig. 6 - Loss modulus (E") vs. temperature for neat epoxy and nanocomposite with different multiwalled carbon nanotube (MWCNT) loadings.

Fig. 4 - SEM images showing the fracture surfaces of neat epoxy (**A**) and nanocomposite with 1.0 wt% of multiwalled carbon nanotubes (MWCNTs) (**B**).

perature for various MWCNT loadings. The storage modulus increased with increased MWCNT loading because of the polymer-MWCNT interaction; at a molecular level, the adsorption of the polymer chains on the MWCNT's surface reduced the mobility of molecules. The storage modulus of neat epoxy was 0.183 GPa and increased gradually by 52% to 0.287 GPa at 30°C when MWCNT loading was 1 wt%. The storage modulus decreased as the temperature increased, due to energy dissipation involving cooperative motions of the polymer chain.

Figure 6 shows the loss modulus (E") versus temperature for nanocomposites with various levels of MWCNT contents. Similar to the storage modulus, the loss modulus was found to increase with the increase of MWCNT loading. The addition of 1.0 wt% of MWCNTs yielded a 45% increase in the loss modulus at 30°C compared with the neat epoxy. It can be seen that the storage modulus of the nanocomposite decreased rapidly, while the loss modulus reached a maximum when the nanocomposite was heated to the glass transition temperature (T_g) region.

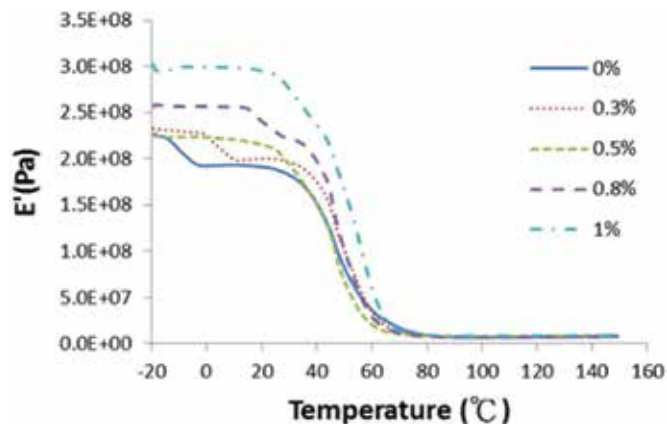The loss modulus is used to describe the dissipation of energy into heat caused by friction between CNT-CNT and CNT-polymer interactions when the nanocomposite is subjected to external forces. The damping coefficient (tanδ) is defined as the ratio of the loss modulus to the storage modulus. It can be considered an indicator of how efficiently a material loses energy to molecular rearrangements and internal friction. Figure 7 presents the tanδ curves of the nanocomposites with various amounts of MWCNT. The glass transition temperature (T_g) can be determined from the peak position of the tanδ curve. The glass transition temperature of neat epoxy is 65°C and slightly increases to 67°C with 1 wt% MWCNT loading.

The enhancement of the glass transition temperature can be interpreted as a reduction of the mobility of the epoxy molecular in the proximity of MWCNTs, due to the interfacial interaction between the MWCNTs and epoxy matrix. The strong interfacial interaction can be attributed to a large specific surface area of MWCNT within the polymer matrix. Immobilization of epoxy matrix around the nanotubes causes mechanical stiffening resulting in an increase of the thermal stability. A notable observation is that the addition of
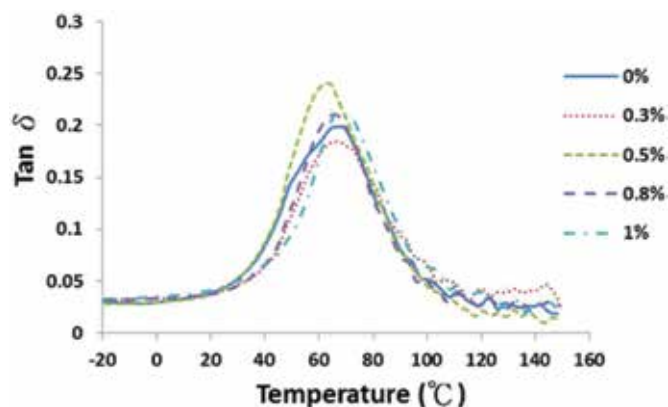
Fig. 7 - Damping coefficient (tanδ) vs. temperature for neat epoxy and nanocomposite with different multiwalled carbon nanotube (MWCNT) loadings.

MWCNTs to epoxy resin showed a slight increase in the glass transition temperature. This indicates that the addition of MWCNTs does not affect the relaxation behavior of the nanocomposite significantly.

Conclusions

To quantify the reinforcing mechanisms of MWCNTs in epoxy-based nanocomposites, tensile testing and dynamic mechanical analysis were conducted with MWCNT loadings varying from 0.3 wt% to 1.0 wt%. Morphology of the nanocomposite was characterized by FESEM images to investigate the dispersion and interfacial adhesion of MWCNTs in the epoxy resin. Experimental results showed that nanocomposites prepared with 1 wt% MWCNTs exhibit a 152% increase in Young's modulus, a 54% increase in tensile strength and a 52% increase in storage modulus, compared with the neat epoxy. It is clear that a significant stiffening effect on the nanocomposite was achieved by the addition of MWCNTs. This can be attributed to the good dispersion and strong interfacial bonding between the MWCNTs and epoxy matrix. Both the load and the stress transfer from the epoxy to the MWCNTs were improved by the strong adhesion between them, leading to significant enhancement of mechanical properties. Immobilization of epoxy matrix around the nanotubes due to the interfacial interaction causes mechanical stiffening resulting in an increase of thermal stability.

Disclosures

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