

# Preparation, Morphology, and Properties of Silane-Modified MWCNT/Epoxy Composites

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**ABSTRACT:** Both epoxy resin and acid-modified multiwall carbon nanotube (MWCNT) were treated with 3-isocyanatopropyltriethoxysilane (IPTES). Scanning electron microscopy (SEM) and transmission electronic microscope (TEM) images of the MWCNT/epoxy composites have been investigated. Tensile strength of cured silane-modified MWCNT (1.0 wt %)/epoxy composites increased 41% comparing to the neat epoxy. Young's modulus of cured silane-modified MWCNT (0.8 wt %)/epoxy composites increased 52%. Flexural strength of cured silane-modified MWCNT

(1.0 wt %)/epoxy composites increased 145% comparing to neat epoxy. Flexural modulus of cured silane-modified MWCNT (0.8 wt %)/epoxy composites increased 31%. Surface and volume electrical resistance of MWCNT/epoxy composites were decreased with IPTES-MWCNT content by 2 orders and 6 orders of magnitude, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3481–3488, 2010

**Key words:** CNT; epoxy; morphology; mechanical properties; electrical properties

## INTRODUCTION

carbon nanotubes (CNTs) generated many interesting research topics since Ijima<sup>1</sup> identified their structures in 1991. CNTs possess excellent electrical,<sup>2</sup> mechanical,<sup>3</sup> thermal, and magnetic properties.<sup>4–7</sup> Recently, CNT/polymer composites have been investigated including the matrices such as polypropylene (PP),<sup>8</sup> phenolic resin,<sup>9</sup> and polyimide.<sup>10,11</sup>

Epoxy resins are usually used in electronic, paints, electrical insulators, printed circuit boards (PCB), and packaging materials, etc. Our early research has successfully prepared the multiwall carbon nanotube (MWCNT)/epoxy composite, and the thermal, morphological and electrical properties have been investigated.<sup>12</sup> Our previous studies also reported the preparation of polysilsesquioxane (PSSQ) with epoxy resin and blending them with unmodified and acid-modified MWCNT.<sup>13</sup> The molecular motion<sup>13</sup> of PSSQ was reduced by the addition of acid-modified MWCNT.

Carbon nanotube and polymer matrices may be bonded with chemical bonding. The chemical bonding may chemically to enhance the adhesion between CNT and polymer. Our reports<sup>14,15</sup> suggested that carbon nanotube and polymer were connected with amide bonding or via reaction on carbon nanotube surface.<sup>15</sup> Our previous research<sup>15</sup> has successfully prepared the MWCNT/waterborne polyurethane nanocomposite that carbon nanotube and waterborne polyurethane was bonded with covalent bonding and ionic bonding. The mechanical and thermal properties of waterborne polyurethane were enhanced due to the addition of MWCNT.

In this research, both multiwall carbon nanotube and epoxy were treated with silane. Multiwalled carbon nanotube and epoxy were bonded with silane and assembled with SiO<sub>x</sub>. The main objective of this research is to investigate the improvement of mechanical properties and to study the molecular motion and morphology of the silane-modified MWCNT/epoxy hybrid composites.

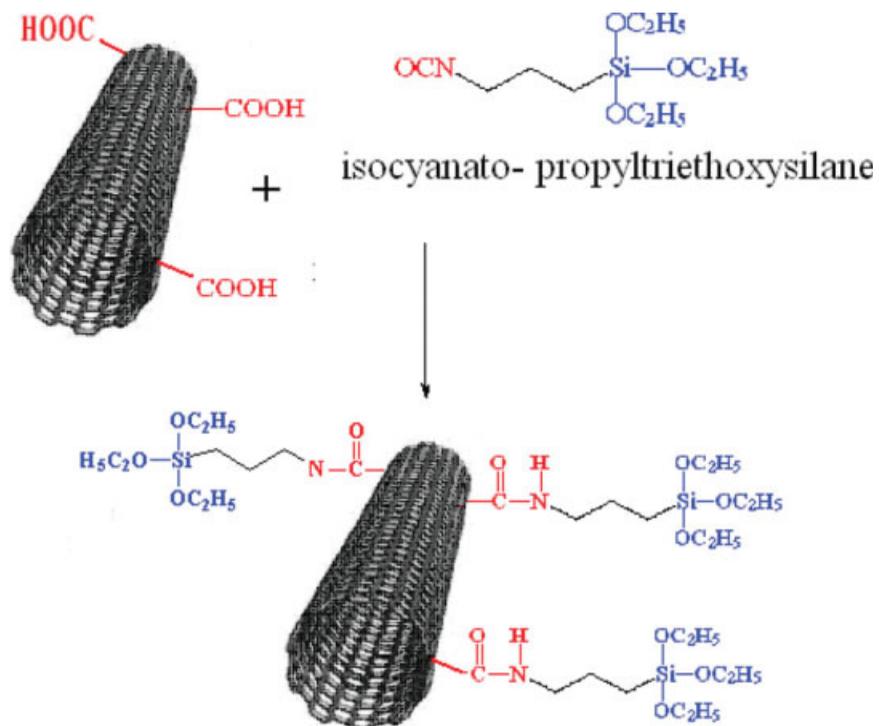
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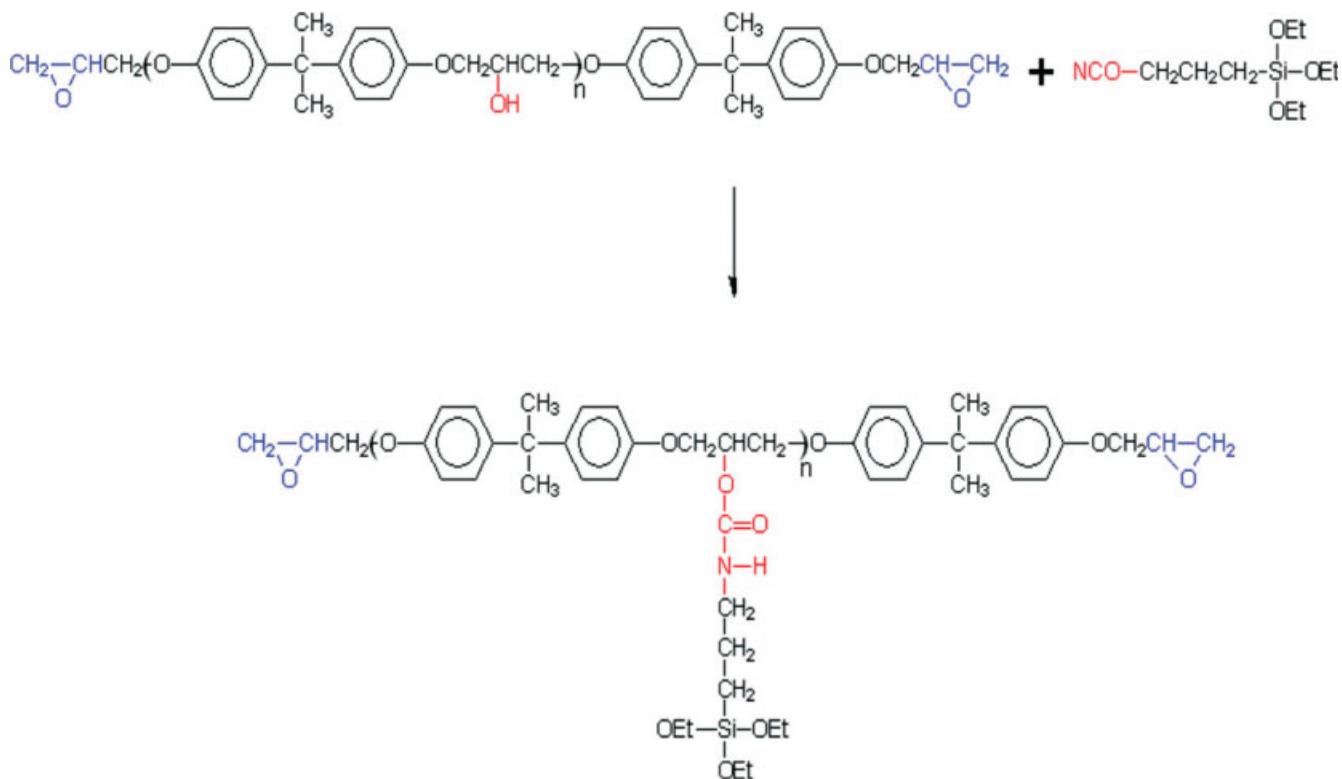
## EXPERIMENTAL SECTION

### Materials

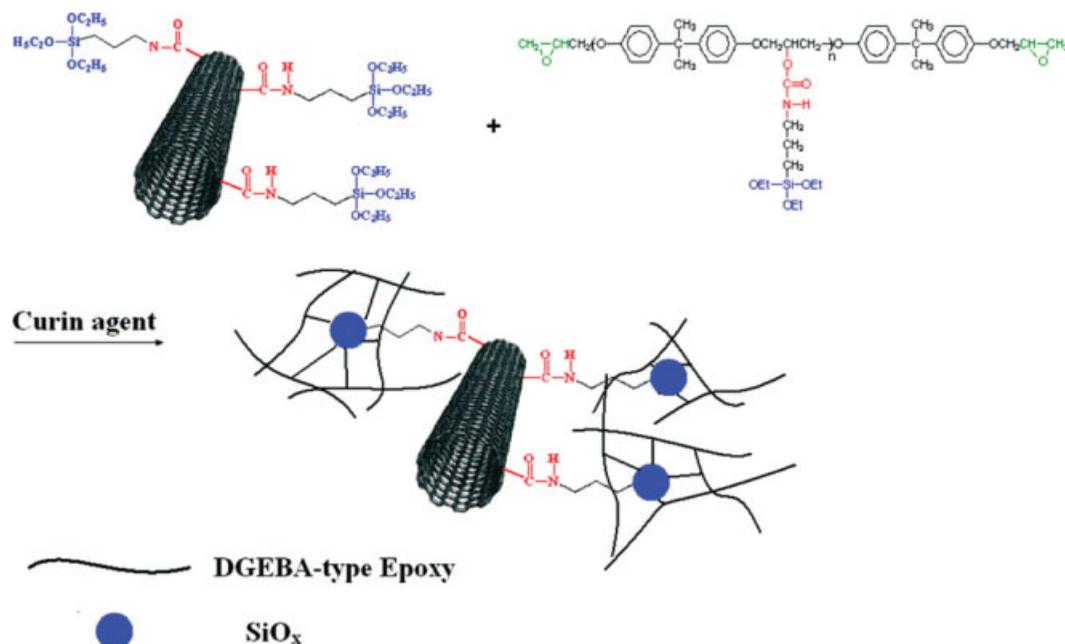
Multiwalled carbon nanotubes were obtained from the Nanotech Port Company, Shenzhen, China. The



**Scheme 1** Modified MWCNT by IPTES. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Scheme 2** Modification of DGEBA-type epoxy by IPTES.<sup>17</sup> [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Scheme 3** Preparation of silane-modified MWCNT/epoxy composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

diameter of carbon nanotube is 40–60 nm, length is 0.5–40  $\mu\text{m}$ , specific surface area is 2300  $\text{m}^2/\text{g}$ . Epoxy (DGEBA type), Epon 828 was obtained from Nan Ya Plastics Corp. Taiwan. 3-Isocyanatopropyltriethoxysilane (IPTES) was obtained from United Chemical Technologies, Inc., Bristol, CT. Triethylamine (TEA) was supplied by Lancaster Company Fairfield, OH. Dibutyltindilaurate was used as catalyst, which was obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. 4,4'-Diaminodiphenyl sulfone was obtained from Chris KEV Company, Inc. Terrance Leawood, KS.

#### Modification of the MWCNT

MWCNTs were treated with a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  at 50°C for 24 h. After acid treatment, the MWCNT was washed using deionized water, filtered, and dried at 100°C.

#### Preparation of silane-modified MWCNT/epoxy hybrid material

Epoxy was mixed with 3-IPTES and the acid-modified MWCNT was then heated at 60°C for 7 h with TEA. The mole ratio of epoxy and total amount of IPTES was 1 : 1. The IPTES may be reacted and grafted on the acid-modified MWCNT surface (Scheme 1) and the other part of IPTES may be bonded with the epoxy (Scheme 2). The method of modification of DGEBA-type Epoxy has been reported elsewhere.<sup>16–18</sup> Dibutyltindilaurate was used as catalyst. 4,4'-Diaminodiphenyl sulfone was

used as curing agent. The mole ratio of epoxy and 4,4'-diaminodiphenyl sulfone was 2 : 1, which was added to the mixture and cured at 200°C for 4 h (Scheme 3).

### PROPERTIES MEASUREMENT

#### Fourier transform infrared spectroscopy

Fourier transform infrared spectra (FTIR) of MWCNT were recorded between 400 and 4000  $\text{cm}^{-1}$  on a Nicolet Avatar 320 FTIR spectrometer, Nicolet Instrument Corporation, Madison, WI. The precursors were coated on a  $\text{CaF}_2$  plate. A minimum of 32 scans was signal-averaged with a resolution of 2  $\text{cm}^{-1}$  at the 4000–400  $\text{cm}^{-1}$  range.

#### <sup>29</sup>Si solid-state nuclear magnetic resonance spectra of cured structure of silane-modified MWCNT/epoxy composites

High-resolution solid-state <sup>29</sup>Si nuclear magnetic resonance (NMR) experiments were performed from a BRUKER DSX 400MHz. The spectra of <sup>29</sup>Si CP/MAS NMR of the composites were used to characterize the degree of condensation of cured Epoxy hybrid network with various carbon nanotube contents.

#### Morphological properties

Morphological properties were investigated by a scanning electron microscope Hitachi, FE-SEM (S-4200, Japan) and a transmission electronic microscope (TEM) JEOL-2000FX (Japan).

## Mechanical properties measurements

### Tensile property

Tensile strength was tested by using an Instron machine Model 4488 at room temperature. Test procedure was followed the ASTM-D638. Dimensions of the test specimen are 120 mm × 13 mm × 3 mm. The crosshead speed was 5 mm/min.

### Flexural property

Flexural strength was tested by using an Instron machine Model 4488 at room temperature. Test procedure was followed the ASTM-D790. Dimensions of test specimen are 120 mm × 13 mm × 3 mm. The crosshead speed was 5 mm/min.

## Electrical properties measurements

Surface and volume electrical resistivities were measured by a ULTRA Mesohmeter SM-8220, DKK TOA Corporation, Tokyo, Japan. The surface and volume electrical resistances of the silane-modified MWCNT/epoxy composites were measured after the addition of various contents of MWCNT. The charge time was 30 s, and the current stress of the measurements was 100 V. An average value was obtained from five to six measurements for each sample.

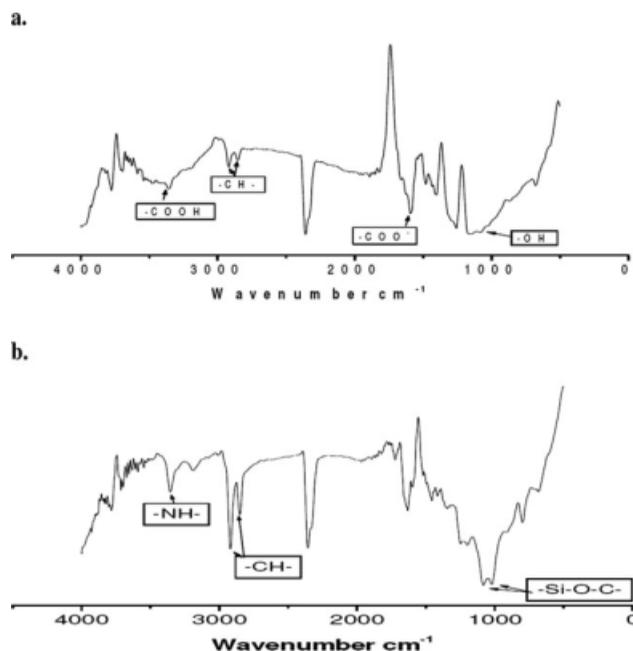
## RESULTS AND DISCUSSION

### Fourier transform infrared spectroscopy

Figure 1(a) shows the FTIR spectra of acid-modified carbon nanotube, the wave number at 1610 ~ 1550  $\text{cm}^{-1}$  was the absorption of  $\text{COO}^-$  asymstretch. The wave number at 1075 ~ 1010  $\text{cm}^{-1}$  was the absorption of  $-\text{OH}$  in primary alcohol. The wave number at 3000 ~ 2800  $\text{cm}^{-1}$  was the absorption of  $-\text{CH}$  stretch. The wave number at 3650 ~ 3000  $\text{cm}^{-1}$  was the absorption of  $-\text{COOH}$  stretch. These observations verify that MWCNT surface will forms  $-\text{COOH}$  functional group by acid treatment.

The acid-modified MWCNT was reacted with IPTES. Figure 1(b) presents the FTIR spectra of the isocyanatopropyltriethoxysilane-modified MWCNT. The wave number at 1100  $\text{cm}^{-1}$  was the absorption of  $-\text{SiO}$  stretch; the wave number at 3530 ~ 3400  $\text{cm}^{-1}$  was the absorption of  $-\text{NH}$  stretch. The characteristic absorption bands of the  $-\text{SiO}$  stretch appeared at 1100  $\text{cm}^{-1}$  and  $-\text{NH}$  stretch was appeared at 3530 ~ 3400  $\text{cm}^{-1}$ , indicating that MWCNT surface had been modified by silane.

Figure 2 shows the FTIR spectra of the mixture of epoxy and IPTES. FTIR characteristic peak of  $-\text{NCO}$  groups of IPTES (wave number at 2270  $\text{cm}^{-1}$ ) decreased gradually with the reaction time and



**Figure 1** FTIR spectra of (a) acid-modified MWCNT; (b) isocyanatopropyltriethoxysilane-modified MWCNT.

finally were disappeared after 7 h of reaction time at 60°C. The FTIR spectra show the IPTES was complete reacted with the epoxy after 7 h of reaction time at 60°C.

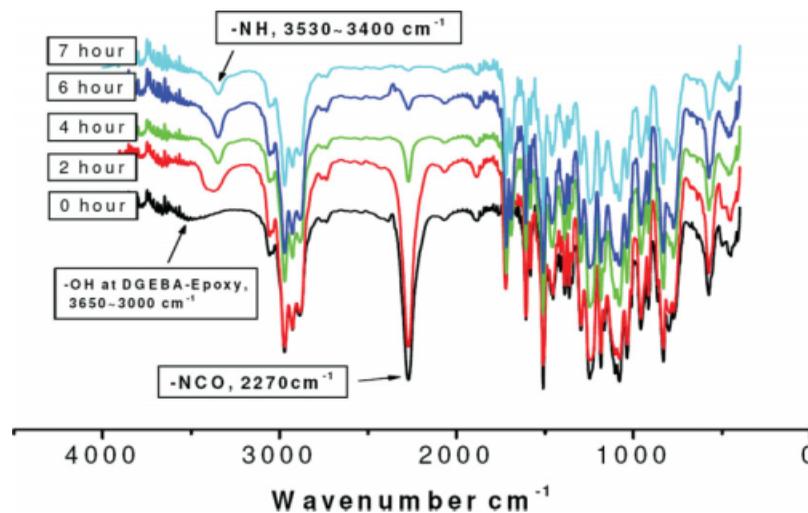
### $^{29}\text{Si}$ solid-state nuclear magnetic resonance of cured structure of silane-modified MWCNT/epoxy composites

Figure 3 summarizes the  $^{29}\text{Si}$  solid-state NMR spectra of cured (a) neat epoxy resin, (b) silane-modified MWCNT/epoxy composites. It indicates that trisubstituted siloxane bonds ( $T^2$  shift,  $\delta$  -59.839 ppm, and  $T^3$  shift,  $\delta$  -67.002 ppm) are presented in the neat epoxy resin and silane-modified silane modified MWCNT/epoxy. Trisubstituted siloxane bonds are defined as a silicon atom possesses four bonds, three bonds are bonded with three oxygen atoms and the fourth bond may be bonded with another carbon atom<sup>19</sup> [Fig. 3 (c)].

To investigate the effect of MWCNT content on the cured structures of the composites, it is necessary to calculate the degree of condensation of siloxane structures in the cured network.<sup>19-21</sup> The degree of condensation can be explained by the percentage of every type of structure ( $T^n$ ) according to the following equation proposed by Shea et al.<sup>19</sup>:

$$\text{Degree of condensation of } T \text{ distribution} = \frac{[(1.0)(\% \text{ area } T^1) + (2.0)(\% \text{ area } T^2) + (3.0)(\% \text{ area } T^3)]}{3}$$

The degree of condensation of  $T$  distribution of silane-modified epoxy composites without MWCNT



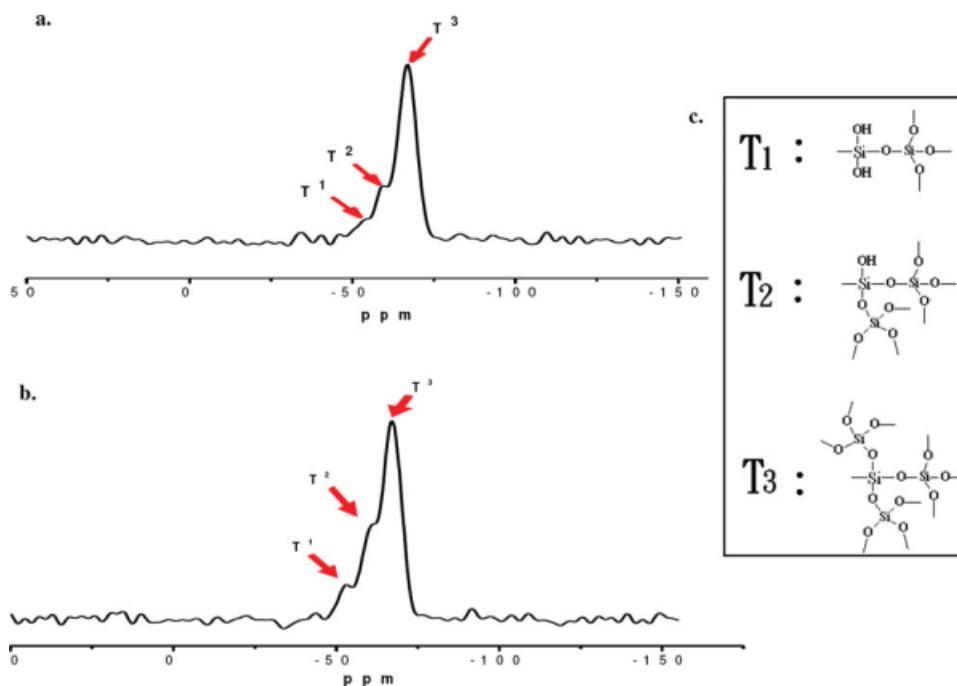
**Figure 2** IR of FTIR spectra of the reaction between epoxy resin and isocyanatopropyltriethoxysilane. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

and with 1 wt % silane-modified MWCNT were 88% and 84%, respectively. The silane-modified MWCNT reduced the degree of condensation of *T* distribution of epoxy composites may be due to the steric hindrance of the MWCNT.

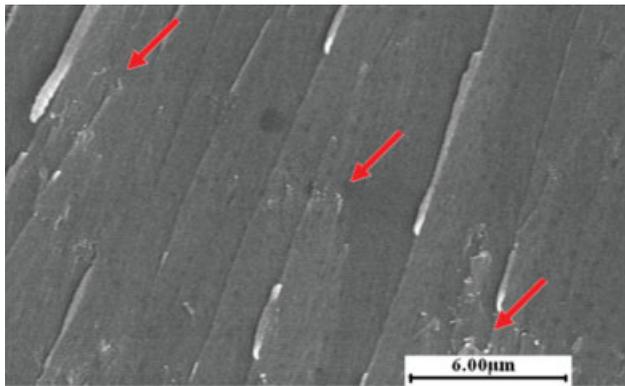
### Morphological properties

Figures 4 illustrate the scanning electron microscopy (SEM) images of the cross section of silane-modified

MWCNT/epoxy composites. Most of the MWCNTs were embedded in the epoxy matrix and only a few of them were pulled out. Figure 4 shows only a few of MWCNT cluster can be seen in the silane-modified MWCNT/epoxy composites. The micrographs of MWCNT/epoxy composites show uniform and co-orientation dispersed. Figure 5 illustrates the TEM microphotographs of the silane-modified MWCNT/epoxy composites. The TEM microphotographs show that the MWCNT was well dispersed in the epoxy matrix.



**Figure 3** The solid-state  $^{29}\text{Si}$  NMR spectra of (a) neat epoxy resin, (b) 1.0 wt % silane-modified MWCNT/epoxy nanocomposites, (c) trisubstituted siloxane bonds (*T* shift)<sup>19</sup>. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** SEM microphotograph of the 1.0 wt % MWCNT/epoxy composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Mechanical properties

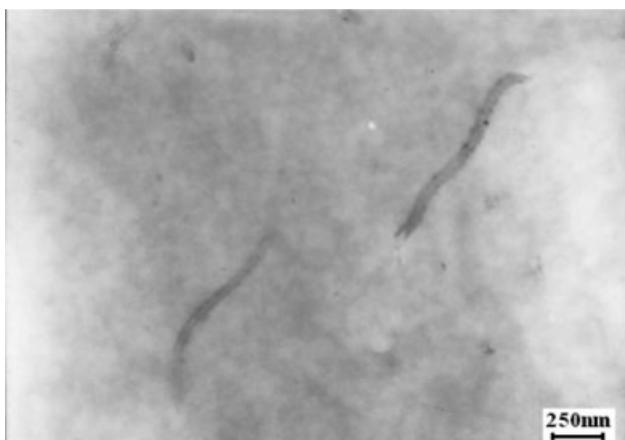
#### Tensile properties

Typical stress–strain plots for pure epoxy and silane-modified MWCNT/epoxy composites are shown in Figure 6. Figure 7(a) reveals that the tensile strength of cured silane modified MWCNT/epoxy composites increased by 41% from 6.67 MPa (neat epoxy) to 9.44 MPa (1.0 wt % silane-modified MWCNT/epoxy).

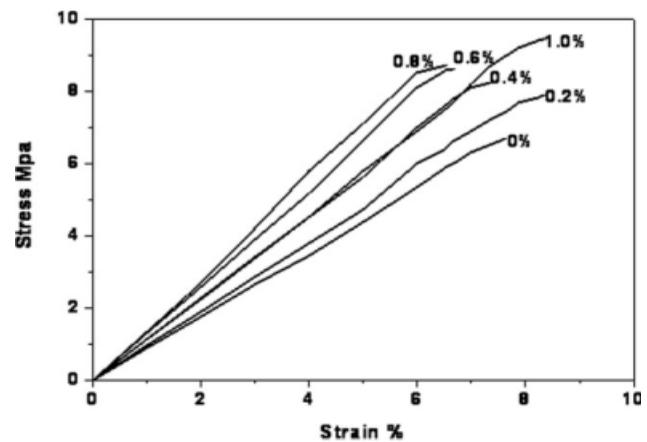
Figure 7(b) indicates that the Young's modulus of cured silane-modified MWCNT/epoxy composites increased by 52% from 0.88 GPa (neat epoxy) to 1.34 GPa (0.8 wt % silane-modified MWCNT/epoxy), and to 1.13 GPa (1.0 wt % silane-modified MWCNT/epoxy).

#### Flexural properties

Figure 8(a) demonstrates that the flexural strength of cured silane-modified MWCNT/epoxy composites increased by 145% from 14.0 MPa (neat epoxy) to

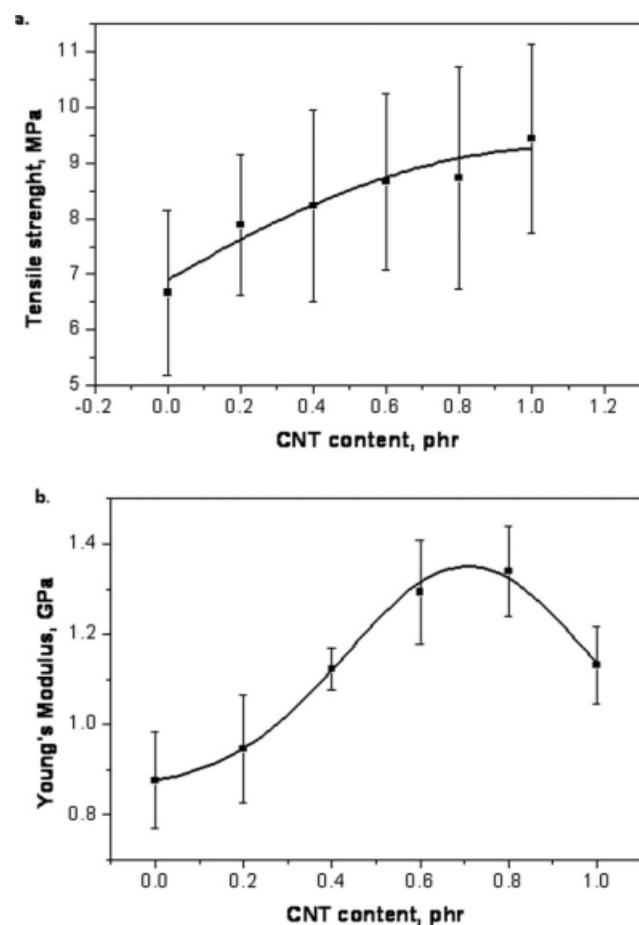


**Figure 5** TEM microphotograph of the 1.0 wt % MWCNT/epoxy composites.

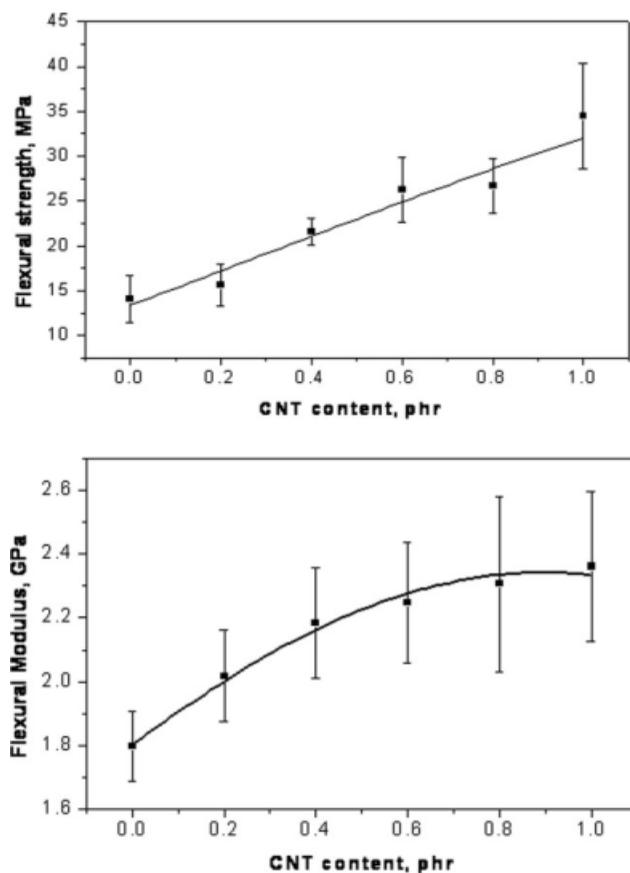


**Figure 6** Stress–strain plots of silane-modified MWCNT/epoxy/nanocomposite.

34.5 MPa (1.0 wt % silane-modified MWCNT/epoxy). Figure 8(b) shows that the flexural modulus of cured silane modified MWCNT/epoxy composites increased by 31% from 1.80 GPa (neat epoxy) to 2.36 GPa (1.0 wt % silane-modified MWCNT/epoxy).



**Figure 7** Effect of MWCNT content on the (a) tensile strength, (b) Young's modulus of silane-modified MWCNT/epoxy/nanocomposite.



**Figure 8** Effect of MWCNT content on the (a) flexural strength, (b) flexural modulus of silane-modified MWCNT/epoxy/nanocomposite.

CNTs have good mechanical properties such as high tensile strength and modulus. Figure 4 SEM microphotograph presents the silane-modified MWCNT are almost co-orientation and well dispersion in matrix, which a small amount of CNT added to the polymer matrix can enhance the mechanical properties significantly.

Since silane-modified MWCNT have high surface area and silane-modified MWCNT can reacted with silane-modified epoxy. When silane-modified MWCNT and silane-modified epoxy form  $\text{SiO}_x$  bonding enhances the adhesive force between carbon nanotube and polymer matrix.

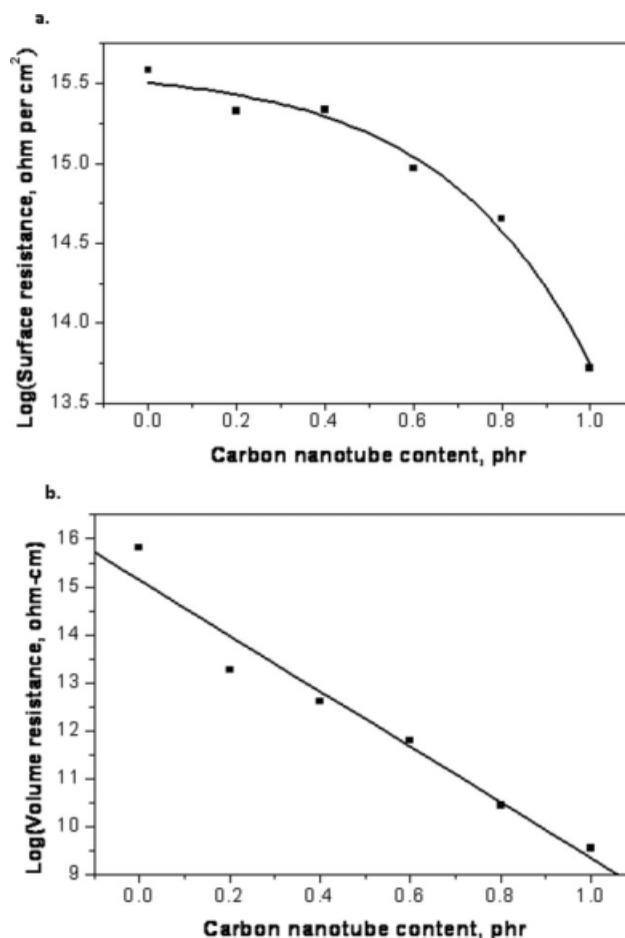
When the high modulus MWCNT filler was introduced to polymer matrix, which can improve composites hardness also enhance the modulus properties. These effects can improve the silane-modified MWCNT/epoxy composites tensile and flexural properties.

The improvement of flexural strength was more significant than that of tensile strength. The flexural strength increased 145% when MWCNT content was 1 wt % whereas the tensile strength increased 41% when MWCNT content was 1 wt %. The affinity of the MWCNT to the polymer matrix was improved

when MWCNT and epoxy were modified by IPTES. The mechanical properties depend on the affinity of the reinforcements or filler to the polymer matrix. When both of the acid-treated MWCNT and the epoxy were modified with the silane, the silane-modified MWCNT/epoxy composites bonded with the  $\text{SiO}_x$  functional groups form three dimension cross-link enhance the interaction force between MWCNT and epoxy. The silane-modified MWCNT and the epoxy bonded with the  $\text{SiO}_x$  functional groups form interpenetrated network structure of the composites resulting in enhanced properties.

### Electrical properties

Figure 9(a) shows the surface electrical resistance of MWCNT/epoxy composites decreased only 2 orders of magnitude from  $3.83 \times 10^{15} \Omega/\text{cm}^2$  (neat epoxy) to  $5.24 \times 10^{13} \Omega/\text{cm}^2$  (1.0 wt % MWCNT content). Figure 9(b) shows the volume resistance decreased 6 orders of magnitude from  $6.45 \times 10^{15} \Omega/\text{cm}$  (neat epoxy) to  $3.48 \times 10^9 \Omega/\text{cm}$  (1.0 wt % MWCNT content).



**Figure 9** Effect of MWCNT content on the (a) surface and (b) volume electrical resistance of silane-modified MWCNT/epoxy nanocomposite.

The improvement of volume resistance was more significant than that of surface resistance. Most of the assembled MWCNTs are well dispersed in the epoxy matrix and only few of them migrated to the surface, hence, the volume resistance of the composites was improved more significant than that of the surface resistance. Furthermore, the lengths of MWCNTs were shortened and the number of defects increases during acid modification. Some researches reported that acid-modified MWCNT showed less improvement in electrical conductivity of MWCNT/polymer composites.<sup>11</sup>

### CONCLUSIONS

Diglycidyl ether of bisphenol A (DGEBA) epoxy and acid-treated carbon nanotube was modified with IPTES and mixed with epoxy then cured to form silane-modified MWCNT/epoxy hybrid material. SEM and TEM examination of DGEBA epoxy and silane-modified MWCNT nanocomposites revealed that MWCNTs were embedded in the matrix and well dispersed. Considerable enhancement of tensile and flexural properties and decrease in surface and volume resistance were obtained with small quantities of isocyanatopropyl silane. Tensile strength of cured silane-modified MWCNT/epoxy composites increase from 6.67 MPa (the neat epoxy) to 9.44 MPa (1.0 wt % silane-modified MWCNT/epoxy). Young's modulus of cured silane-modified MWCNT/epoxy composites increased from 0.88 GPa (neat epoxy) to 1.34 GPa (0.8 wt % silane-modified MWCNT/epoxy), and to 1.13 GPa (1.0 wt% silane-modified MWCNT/epoxy). Flexural strength of cured silane-modified MWCNT/epoxy composites increased from 14.0 MPa (neat epoxy) to 34.5 MPa (1.0 wt % silane-modified MWCNT/epoxy). Flexural modulus of cured silane modified MWCNT/epoxy composites increased from 1.80 GPa (neat epoxy) to 2.36 GPa (1.0 wt % silane-modified MWCNT/epoxy). Surface electrical resistance of MWCNT/epoxy com-

posites decreased from  $3.83 \times 10^{15} \Omega/\text{cm}^2$  (neat epoxy) to  $5.24 \times 10^{13} \Omega/\text{cm}^2$  (1.0 wt % IPTES-MWCNT). Volume resistance decreased from  $6.45 \times 10^{15} \Omega/\text{cm}$  (neat epoxy) to  $3.48 \times 10^9 \Omega/\text{cm}$  (1.0 wt % IPTES-MWCNT).

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