

# Preparation and Thermal, Electrical, and Morphological Properties of Multiwalled Carbon Nanotube and Epoxy Composites

Siu-Ming Yuen,<sup>1</sup> Chen-Chi M. Ma,<sup>1</sup> Hsin-Ho Wu,<sup>2</sup> Hsu-Chiang Kuan,<sup>1</sup>  
Wei-Jen Chen,<sup>1</sup> Shu-Hang Liao,<sup>1</sup> Chia-Wen Hsu,<sup>1</sup> Han-Lang Wu<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, National Tsing-Hua University, Hsin-Chu 30043, Taiwan

<sup>2</sup>Union Chemical Laboratories, Industrial Technology Research Institute, Hsin-Chu 30055, Taiwan

Received 4 January 2005; accepted 23 May 2006

DOI 10.1002/app.25140

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Multiwalled carbon nanotube (MWCNT)/epoxy composites are prepared, and the characteristics and morphological properties are studied. Scanning electron microscopy microphotographs show that MWCNTs are dispersed on the nanoscale in the epoxy resin. The glass-transition temperature ( $T_g$ ) of MWCNT/epoxy composites is dramatically increased with the addition of 0.5 wt % MWCNT. The  $T_g$  increases from 167°C for neat epoxy to 189°C for 0.5 wt % CNT/epoxy. The surface resistivity and bulk resistivity are decreased when MWCNT is added to the epoxy resins. The surface resistivity of CNT/epoxy composites decreases

from  $4.92 \times 10^{12} \Omega$  for neat epoxy to  $3.03 \times 10^9 \Omega$  for 1 wt % MWCNT/epoxy. The bulk resistivity decreases from  $8.21 \times 10^{16} \Omega \text{ cm}$  for neat epoxy to  $6.72 \times 10^8 \Omega \text{ cm}$  for 1 wt % MWCNT/epoxy. The dielectric constant increases from 3.5 for neat epoxy to 5.5 for 1 wt % MWCNT/epoxy. However, the coefficient of thermal expansion is not affected when the MWCNT content is less than 0.5 wt %. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1272–1278, 2007

**Key words:** multiwalled carbon nanotubes; epoxy resin; composites; morphology; electrical properties

## INTRODUCTION

Carbon nanotubes (CNTs) have generated much interesting research since Iijima identified their structures<sup>1</sup> in 1991. CNTs possess excellent electrical,<sup>2</sup> mechanical,<sup>3</sup> thermal, and magnetic properties<sup>4</sup> and have low density, high strength, high toughness, high surface areas, and flexible and high chemical stability.<sup>5–7</sup>

Recently, CNT/polymer composites have been investigated including matrices such as polyethylene,<sup>8–10</sup> polypropylene,<sup>11</sup> poly(methyl methacrylate),<sup>12</sup> poly(vinylcarbazole), and polyamide.<sup>13</sup> Epoxy resins are usually applied in electronics, paints, electrical insulators, printed circuit boards, and packaging materials. Several studies have been conducted to improve the properties of epoxy incorporated with CNTs.<sup>14–33</sup> Bae et al. added acid modified CNTs to liquid-crystal epoxy and studied their surface properties, cure kinetics,<sup>14</sup> and mechanical and thermal properties.<sup>19</sup> The addition of CNTs to epoxy can improve the mechanical properties of the epoxy<sup>21,23–27,32</sup> because of the excellent mechanical properties of CNTs.<sup>33</sup>

Nanocomposites can be used as antistatic materials if their surface electrical resistivity is lower than  $10^{-9} \Omega/$

square. When the surface electrical resistivity of the nanocomposites is lower than  $10^{-6} \Omega/\text{square}$ , they can be used for electrostatic discharge. The CNT nanocomposites can be used as shielding materials for electromagnetic interference or radio frequency interference if the surface electrical resistivity is lower than  $10^{-4} \Omega/\text{square}$ . The electrical resistivities of CNT/epoxy nanocomposites can be adjusted by controlling the CNT content of the material. CNTs also have excellent thermal conductivity, so adding CNTs to epoxy can improve thermal conductivity of the nanocomposites.<sup>18,31</sup> The thermal conductivity of pure CNTs can be up to 2800 W/m K.<sup>33</sup> It is anticipated that, with the addition of CNTs into the epoxy resin, the electrical and mechanical properties of nanocomposites may be enhanced.

In this research, multiwalled CNT (MWCNT)/epoxy composites were prepared and the thermal, morphological, and electrical properties were investigated. Characteristics such as the glass-transition temperature ( $T_g$ ), thermal expansion coefficient, electrical resistivity, dielectric constant, and morphological properties of CNT/epoxy composites are discussed.

## EXPERIMENTAL

### Material

MWCNTs were obtained from the Nanotech Port Company (Shenzhen, China). The method of preparation of the MWCNTs was the chemical vapor deposition method. The purity of the CNTs was 95%. The

Correspondence to: C.-C.M. Ma (ccma@che.nthu.edu.tw).

Contract grant sponsor: National Science Council, Taiwan; contract grant number: NSC 93-2216-F-007-022.

diameter of the CNTs was 40–60 nm, the length was 0.5–40  $\mu\text{m}$ , and the specific surface area was 40–3000  $\text{m}^2/\text{g}$ . The electrical resistivity of the MWCNTs was about  $10^{-4} \Omega$ . A diglycidyl ether of bisphenol A (DGEBA) type epoxy resin was obtained from the Nan Ya Plastics Corp. 4,4'-Diaminodiphenyl sulfone was obtained from the Chris KEV Company, Inc. (Terrance Leawood, KS).

### Preparation of CNT/epoxy nanocomposites

DGEBA-type epoxy and 4,4'-diaminodiphenyl sulfone were dissolved in acetone. The weight ratio of epoxy to 4,4'-diaminodiphenyl sulfone was 3 : 1. The CNTs were dispersed in acetone. Epoxy and CNT solutions were mixed and 4,4'-diaminodiphenyl sulfone solution was added. The blend was placed on an aluminum plate after being completely stirred. Solvent was removed completely at  $40^\circ\text{C}$ . Then, the blend was cured at  $150^\circ\text{C}$  for 4 h, followed by postcuring at  $180^\circ\text{C}$  for 1 h.

### Property measurements

Glass-transition temperature and thermal expansion coefficient

The  $T_g$  and thermal expansion coefficient were measured by thermomechanical analysis (TMA) on a TA

Instruments TMA 2940. The temperature rising rate was  $10^\circ\text{C}/\text{min}$ .

### Thermal conductivity

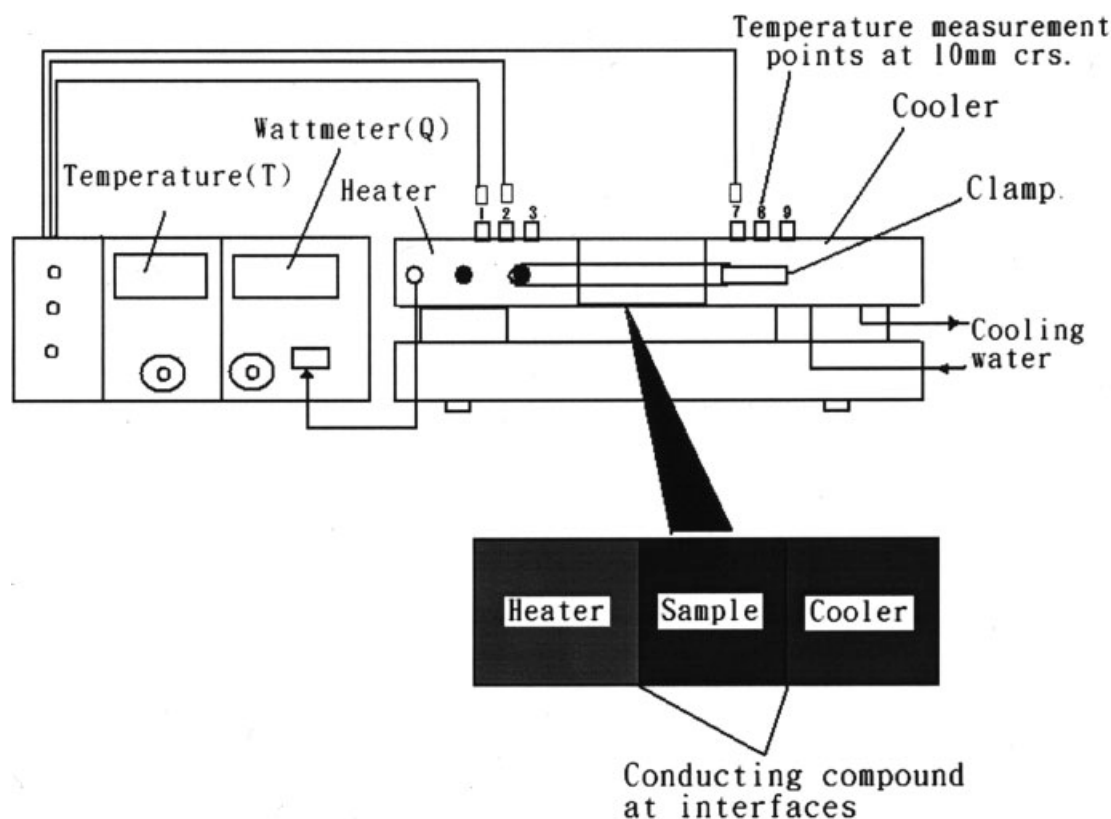
The thermal conductivity was tested with an H940 heat conduction unit (see setup, Fig. 1), and the sample dimensions were  $10 \times 10 \times 1 \text{ mm}$ .

### Electrical resistivity

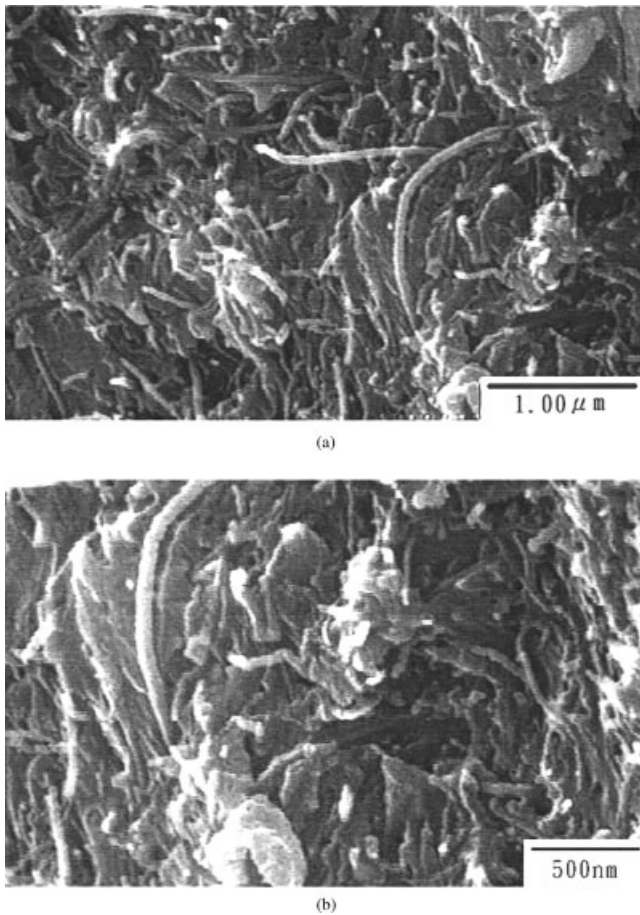
The surface and bulk (dc) electrical resistivity were measured by an ULTRA Mesohmeter SM-8220 from DKK TOA Corporation. The electrical resistivity was measured at room temperature ( $25^\circ\text{C}$ ).

### Dielectric constant

The dielectric constant was measured by a radio frequency-impedance/material analyzer (HP-4291B), which was calibrated by a poly(tetrafluoroethylene) standard. The frequency of the sample was measured at 1 GHz. The dielectric constant was measured at room temperature ( $25^\circ\text{C}$ ).



**Figure 1** The setup of the thermal conductivity measurement.



**Figure 2** An SEM microphotograph of the 1 wt % MWCNT/epoxy nanocomposite at original magnifications of (a)  $\times 30,000$  and (b)  $\times 45,000$ .

### Morphological properties

The morphological properties were evaluated by scanning electron microscopy (SEM) on a Hitachi FE-SEM S-4200.

## RESULTS AND DISCUSSION

### Morphological property

The dispersion of CNTs in the epoxy resin was observed by SEM microphotographs (Fig. 2). The high resolution SEM shows that the mixture of CNTs and epoxy resin was mixed well. Observation of the cross section of the CNT/epoxy composites revealed that some of the CNTs were aggregated. The CNTs were mostly buried inside the epoxy matrix and part of the CNT clusters could be seen.

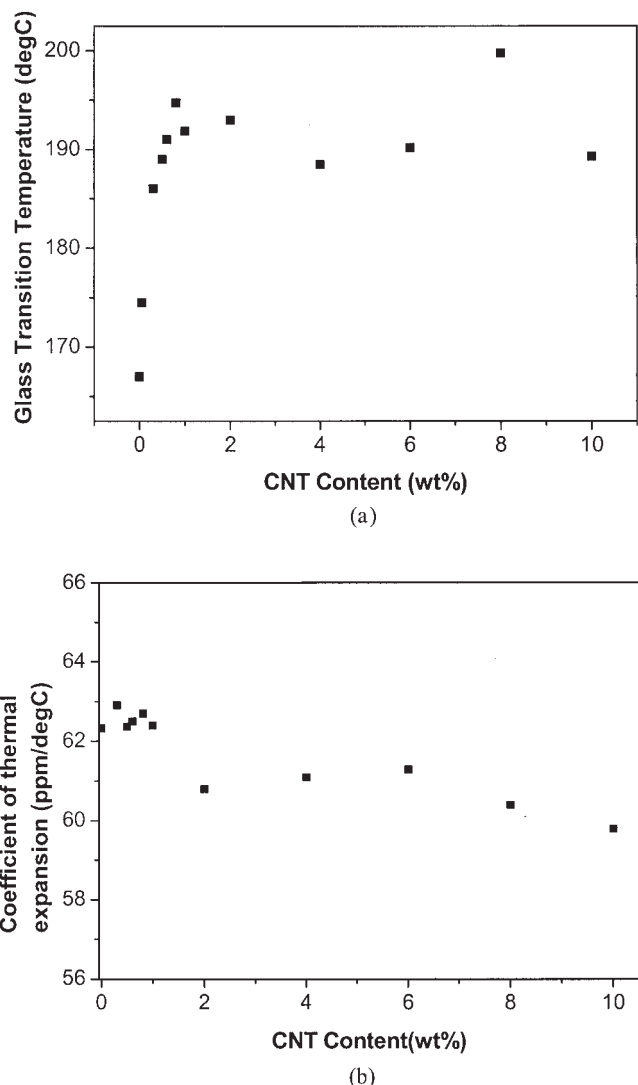
### Thermal properties

Figure 3(a) shows the effects of the CNT content on the  $T_g$  of the composites. The  $T_g$  values increased

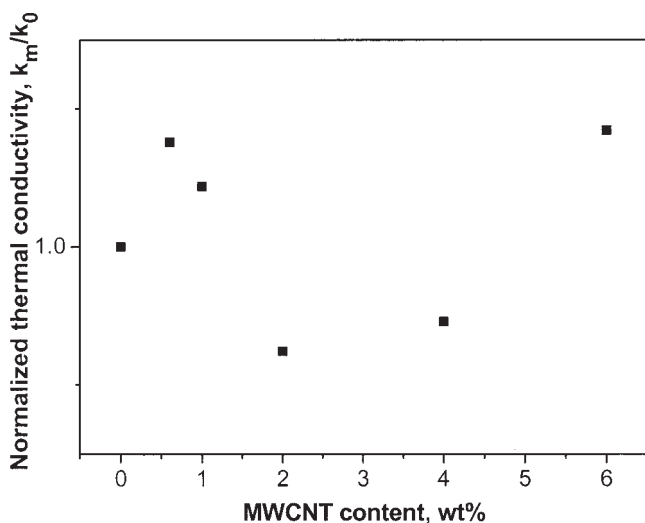
from  $167^\circ\text{C}$  for neat epoxy to  $189^\circ\text{C}$  for 0.5 wt % CNT/epoxy and further to  $192^\circ\text{C}$  for 1.0 wt % CNT/epoxy. The  $T_g$  increased rapidly when the content of CNT was below 0.1 wt % and increased slowly at higher CNT content (0.5 wt %). The well-dispersed CNTs may limit the motion of the polymer chain. When the MWCNT content was higher than 2.0 wt %, the adhesion between the MWCNTs and epoxy was reduced.

Figure 3(b) shows that the effect of the CNT content on the thermal expansion coefficient was insignificant. The thermal expansion coefficient of the composites decreased slightly with MWCNTs from 62.33 ppm/ $^\circ\text{C}$  for neat epoxy to 59.80 ppm/ $^\circ\text{C}$  for 10.0 wt % MWCNT/epoxy.

Figure 4 summarizes the normalized thermal conductivity of the MWCNT/epoxy nanocomposites. Normalized thermal conductivity is defined as the ra-



**Figure 3** The effect of the CNT content on the (a) glass-transition temperature ( $T_g$ ) and (b) thermal expansion coefficient of the MWCNT/epoxy nanocomposites.



**Figure 4** The effect of the MWCNT content on the normalized thermal conductivity of the MWCNT/epoxy nanocomposites;  $k_m$ , thermal conductivity of nanocomposites;  $k_0$ , thermal conductivity of neat epoxy.

ratio of the thermal conductivity of the nanocomposites to the thermal conductivity of the neat epoxy. Although MWCNTs possess excellent thermal conductivity, the thermal conductivity of MWCNT/epoxy nanocomposites was not improved significantly by the MWCNT content. Xu et al.<sup>34</sup> compared the theoretical and experimental data of the thermal conductivity of single-walled CNT (SWCNT) filled poly(vinylidene fluoride) (PVDF) composites at room temperature. They found that the experimental data of the thermal conductivity of SWCNT-filled PVDF were lower than the theoretical data. Xu et al. postulated that the poor thermal conductivity of the CNT/polymer composites was due to the nonuniform size of the MWCNTs, and their vacancy and dislocation in MWCNT may affect the thermal conductivity.<sup>34</sup> The high resistance between the nanotube–matrix or nanotube–nanotube interface may also affect the thermal conductivity of the nanocomposites.<sup>34</sup>

### Electrical properties

Figure 5(a,b) illustrates the effect of the MWCNT content on the surface and bulk resistivity of the MWCNT/epoxy nanocomposites. The solid lines connecting symbols are guides for the eyes. As can be seen in Figure 5(a), the surface electrical resistivity of MWCNT/epoxy composites decreased from  $2.88 \times 10^{12} \Omega$  for 0.4 wt % MWCNT/epoxy to  $6.69 \times 10^9 \Omega$  for 0.6 wt % MWCNT/epoxy, and it then decreased slowly when the MWCNT content was higher than 0.6 wt %. The bulk resistivity decreased from  $8.21 \times 10^{17} \Omega \text{ cm}$  for neat epoxy to  $7.57 \times 10^9 \Omega \text{ cm}$  for 0.6 wt % MWCNT/epoxy, and it decreased slightly when

the MWCNT content was higher than 0.6 wt % [Fig. 5(b)].

In classical percolation theory, the electrical conductivity of a filled material follows a power law relationship, as shown in Eq. (1)<sup>30,35,36</sup>:

$$\sigma_{DC} = \sigma_0(P - P_c)^t \quad (1)$$

where  $\sigma_{DC}$  is the electrical conductivity of the nanocomposites,  $\sigma_0$  is the electrical conductivity of the MWCNT itself,  $P_c$  is the volume fraction of the percolation threshold,  $P$  is the volume fraction of the filler, and  $t$  is the critical exponent.

In the current case, the density of the MWCNTs can only be estimated approximately; the mass fraction of the MWCNTs is preferred instead of the volume fraction. Otherwise, the electrical conductivity can be defined as the inverse electrical resistivity. To search out the three-dimensional percolating systems, the bulk electrical resistivity was used instead of the electrical conductivity. The  $t$  is the absolute value of the slope of the plot of  $\log(\rho_{DC})$  versus  $\log(P - P_c)$ . The modified percolation theory becomes

$$\rho_{DC} = \rho_0(M - M_c)^t \quad (2)$$

where  $\rho_{DC}$  is the bulk electrical resistivity of the nanocomposites,  $\rho_0$  is the bulk electrical resistivity of the MWCNT itself,  $M_c$  is the mass fraction of the percolation threshold, and  $M$  is the mass fraction of the filler.

The theoretical predictions of  $t$  related to the system dimensions showed values ranging from 1.6 to 2.0.<sup>30,35,36</sup> Experimental values of 0.7–3.1 have been reported.<sup>35,36</sup> As shown in Figure 5(b), the electrical conductivity of MWCNT/epoxy nanocomposites is in good agreement with the percolation behavior as proposed by Eq. (2). The best fitting to the experimental values resulted in a  $P_c$  value of 0.6 wt % and a  $t$  value of 2.9.

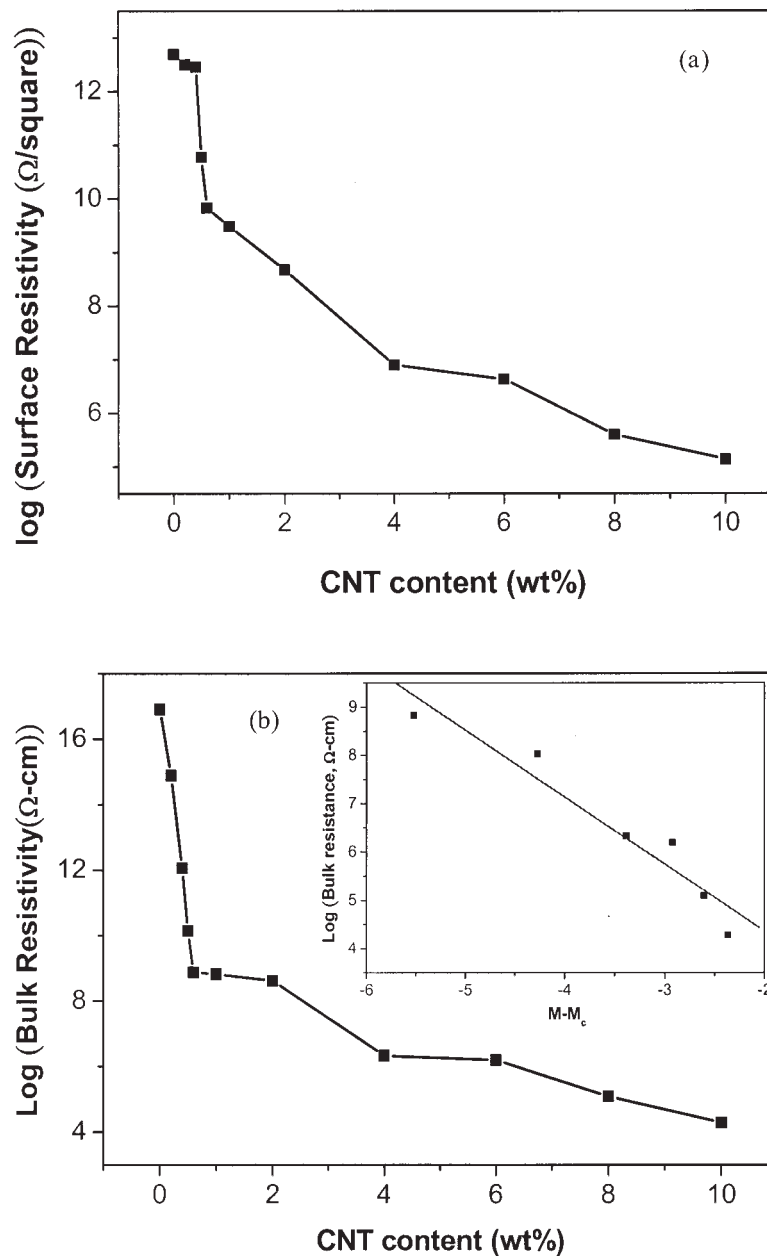
The inclusion of a conductive filler can alter the dielectric characteristics of the polymer medium in which they are dispersed.<sup>37–42</sup> The MWCNTs will affect the dielectric properties of the nanocomposites containing between 0 and 1.0 wt % CNTs.

The relative dielectric constant (or permittivity) is a measurement of the extent to which the electrical charge distribution in a material can be polarized by the application of an electrical field. In an alternating electric field, the samples can be characterized by a complex dielectric constant or permittivity ( $\epsilon^*$ )<sup>41,42</sup>:

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (3)$$

where  $\epsilon'$  is the real part of the dielectric constant or the common dielectric constant of the material and  $\epsilon''$  is the imaginary part of the dielectric constant.<sup>42,43</sup>





**Figure 5** The effect of the CNT content on the (a) surface resistivity and (b) bulk resistivity of the MWCNT/epoxy nanocomposites.

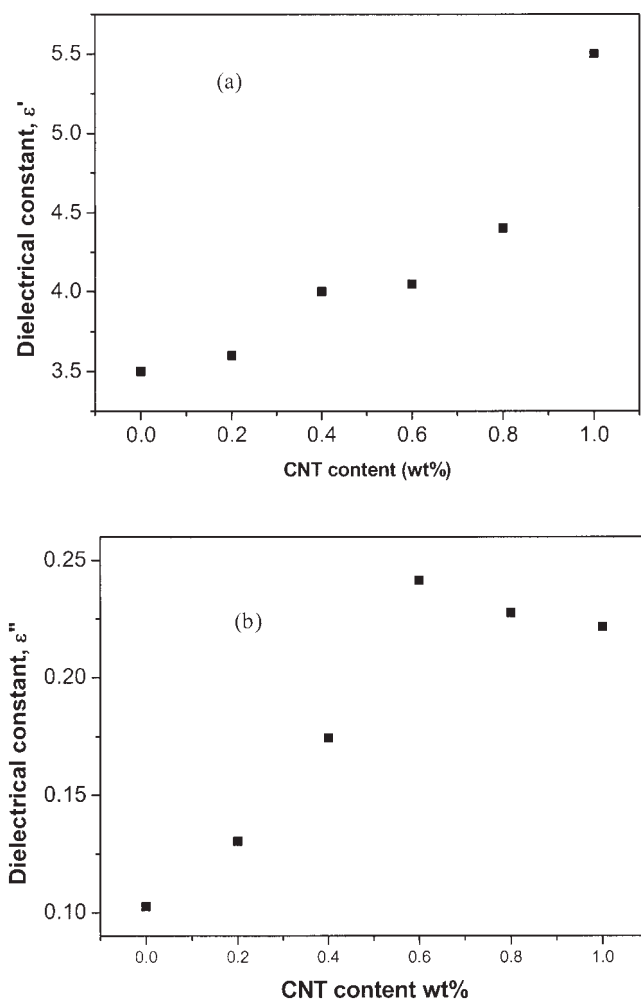
The  $\epsilon'$  represents the polarizability capacitive (or capacitive behavior) of the material, whereas the  $\epsilon''$  represents the energy losses due to polarization and conduction.<sup>41,42</sup>

Figure 6(a) shows that the  $\epsilon'$  of the MWCNT/epoxy increased from 3.5 for neat epoxy to 5.5 for 1 wt % MWCNT content epoxy. Figure 6(b) illustrates that the  $\epsilon''$  of the MWCNT/epoxy increased from 0.10 for neat epoxy to 0.24 for 0.6 wt % MWCNT content epoxy, and the  $\epsilon''$  decreased slightly to 0.22 when the MWCNT content was 0.8 and 1.0 wt % under the 1-GHz testing frequency. The  $\epsilon'$  of MWCNT/epoxy nanocomposites increased slightly at low MWCNT content and rapidly at higher MWCNT content, and the  $\epsilon''$  increased rap-

idly at low MWCNT content and decreased slightly at higher MWCNT content. The  $\epsilon'$  was similar to the change in electrical resistivity: it increased sharply when the MWCNT content was higher than 0.6 wt %. The enhancement of the dielectric constant can be explained according to percolation theory, which was similar to the electrical resistivity.<sup>43,44</sup>

$$\epsilon \propto (P_c - P)^{-s} \quad (4)$$

where  $P_c$  and  $P$  are the volume fraction of the filler at the threshold and the volume fraction of the sample, respectively, and  $s$  is the dielectric constant critical exponent. However, the volume fraction of the MWCNT



**Figure 6** The effect of the MWCNT content on the dielectric constants: (a) the real part ( $\epsilon'$ ) and (b) imaginary parts ( $\epsilon''$ ) of the MWCNT/epoxy nanocomposites.

can only be estimated approximately. The percolation theory can be modified and expressed as Eq. (5):

$$\epsilon\alpha(M_c - M)^t \quad (5)$$

where  $M_c$  and  $M$  are the mass fraction of the filler at the threshold and the mass fraction of the sample, respectively, and  $t$  is the modified dielectric constant critical exponent. In this work, the  $M_c$  was about 0.006 (0.6 wt %) and  $t$  was 3.7. The percolation threshold of the two-phase random spherical filler composite is about 0.16.<sup>43,44</sup> The percolation threshold of the MWCNT/epoxy nanocomposites was much lower than that of the two-phase random spherical filler composite.<sup>43</sup> This is because the MWCNTs are tube shaped, not spherical, which led to the formation of a conductive path at lower content.<sup>44</sup>

## CONCLUSIONS

MWCNT/epoxy nanocomposites were successfully prepared and the properties were investigated. SEM

microphotographs showed that most of the MWCNTs were well dispersed, but some of the MWCNTs aggregated. The surface resistivity of the MWCNT/epoxy composites decreased from  $4.92 \times 10^{12} \Omega$  for neat epoxy to  $3.03 \times 10^9 \Omega$  for 1 wt % MWCNT epoxy. The bulk resistivity decreased from  $8.212 \times 10^{17} \Omega \text{ cm}$  for neat epoxy to  $6.72 \times 10^9 \Omega \text{ cm}$  for 1 wt % MWCNT epoxy. The  $T_g$  of the nanocomposites increased from  $167^\circ\text{C}$  for neat epoxy to  $189^\circ\text{C}$  for 0.5 wt % MWCNT epoxy. The  $\epsilon'$  value increased from 3.5 for neat epoxy to 5.5 for 1 wt % MWCNT epoxy, and the  $\epsilon''$  value increased from 0.10 for neat epoxy to 0.24 for 0.6 wt % MWCNT content epoxy. The addition of MWCNTs to the epoxy resin enhanced the electrical properties,  $T_g$ , and dielectric constant. However, the effects on the thermal conductivity and thermal expansion of MWCNT/epoxy was insignificant.

This research was financially supported by the National Science Council, Taiwan.

## References

- Iijima, S. *Nature* 1991, 56, 354.
- Sandler, J.; Shaffer, M.; Prasse, T.; Bauhofer, W.; Schulte, K.; Windle, A. H. *Polymer* 1999, 40, 5967.
- Geng, H.; Rosen, R.; Zheng, B.; Shimoda, H.; Fleming, L.; Liu, J. Z. *Adv Mater* 2002, 14, 1387.
- Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic: San Diego, CA, 1996.
- Beguín, F.; Ehrburger, P. Special issue on carbon nanotubes. *Carbon* 2002, 40, 1619.
- Subramoney, S. *Adv Mater* 1998, 10, 1157.
- Yakobson, B. I.; Smalley, R. E. *Am Sci* 1997, 85, 324.
- Pötschke, P.; Arup Bhattacharyy, R.; Janke, A. *Polymer* 2003, 44, 8061.
- McNally, T.; Pötschke, P.; Halley, P.; Murphy, M.; Martin, D.; Bell, S. E. J.; Brennan, G. P.; Bein, D.; Lemoine, P.; Quinn, J. P. *Polymer* 2005, 46, 8222.
- Tang, W.; Santare, M. H.; Advani, S. G. *Carbon* 2003, 41, 2779.
- Seo, M.-K.; Lee, J.-R.; Park, S.-J. *Mater Sci Eng A* 2005, 404, 79.
- Yang, Z.; Dong, B.; Huang, Y.; Liu, L.; Yan, F.-Y.; Li, H.-L. *Mater Lett* 2005, 59, 2128.
- Zeng, H.; Gao, C.; Wang, Y.; Watts, P. C. P.; Kong, H.; Cui, X.; Yan, D. *Polymer* 2006, 47, 113.
- Bae, J.; Jang, J.; Yoon, S. H. *Macromol Chem Phys* 2002, 203, 2196.
- Du, J.-H.; Ying, Z.; Bai, S.; Li, F.; Sun, C.; Cheng, H.-M. *Int J Nanosci* 2002, 1, 719.
- Allaoui, A.; Bai, S.; Cheng, H. M.; Bai, J. B. *Compos Sci Technol* 2002, 62, 1993.
- Eitan, A.; Jiang, K.; Dukes, D.; Andrews, R.; Schadler, L. S. *Chem Mater* 2003, 15, 3198.
- Choi, E. S.; Brooks, J. S.; Eaton, D. L.; Al-Haik, M. S.; Hussaini, M. Y.; Garmestani, H.; Li, D.; Dahmen, K. *J Appl Phys* 2003, 94, 1.
- Bae, J. J.; Yoon, S. H. *J Mater Chem* 2003, 13, 676.
- Gojny Florian, H.; Nastalczyk, J.; Roslaniec, Z.; Schulte, K. *Chem Phys Lett* 2003, 370, 820.
- Zhu, J.; Kim, J. D.; Peng, H.; Margrave, J. L.; Khabashesku, V. N.; Barrera, E. V. *Nano Lett* 2003, 3, 1107.
- Sandler, J. K. W.; Kirk, J. E.; Kinloch, I. A.; Shaffer, M. S. P.; Windle, A. H. *Polymer* 2003, 44, 5893.

23. Hsiao, K.-T.; Alms, J.; Advani, S. G. *Nanotechnology* 2003, 14, 791.
24. Valentini, L.; Puglia, D.; Frulloni, E.; Armentano, I.; Kenny, J. M.; Santucci, S. *Compos Sci Technol* 2004, 64, 23.
25. Li, Q.; Zaiser, M.; Koutsos, V. *Phys Stat Sol A* 2004, 201, R89.
26. Breton, Y.; Déésarmot, G.; Salvétat, J. P.; Delpeux, S.; Sinturel, C.; Béguin, F.; Bonnamy, S. *Carbon* 2004, 42, 1027.
27. Ren, Y.; Fu, Y. Q.; Liao, K.; Li, F.; Cheng, H. M. *Appl Phys Lett* 2004, 84, 2811.
28. Lau, K.-T.; Lu, M.; Lam, C.-K.; Cheung, H.-Y.; Sheng, F.-L.; Li, H.-L. *Compos Sci Technol* 2005, 65, 719.
29. Barrau, S.; Demont, P.; Maraval, C.; Bernes, A.; Lacabanne, C. *Macromol Rapid Commun* 2005, 26, 390.
30. Kim, Y. J.; Shin, T. S.; Choi, H. D.; Kwon, J. H.; Chung, Y.-C.; Yoon, H. G. *Carbon* 2005, 43, 23.
31. Miyagawa, H.; Mohanty, A. K.; Drzal, L. T.; Misra, M. *Nanotechnology* 2005, 16, 118.
32. Suhr, J.; Koratkar, N.; Koblinski, P.; Ajayan, P. *Nature Mater* 2005, 4, 134.
33. Treacy, M. M. J.; Ebbesen, T. W.; Gibson, J. M. *Nature* 1996, 381, 678.
34. Xu, Y.; Ray, G.; Abdel-Magid, B. *Composites A* 2006, 37, 114.
35. Stauffer, D. *Introduction to the Percolation Theory*; Francis & Taylor: London, 1991; p 1.
36. Hu, G.; Zhao, C.; Zhang, S.; Yang, M.; Wang, Z. *Polymer* 2006, 47, 480.
37. Tsangaris, G. M.; Kouloumbi, N.; Kyvelidis, S. *Mater Chem Phys* 1996, 44, 245.
38. Zois, H.; Apekis, L.; Omastova, M. *Macromol Symp* 2001, 170, 249.
39. Brosseau, C.; Boulic, F.; Queffelec, P.; Bourbigot, C.; Mest, Y. L. *J Appl Phys* 1997, 81, 882.
40. Xiao, M.; Sun, L.; Liu, J.; Li, Y. *Polymer* 2002, 43, 2245.
41. Kaya, A.; Fang, H. Y. *J Environ Eng* 1997, 123, 169.
42. Lee, J. H.; Oh, M. H.; Park, J.; Lee, S. H.; Ahn, K. H. *J Hazard Mater* 2003, B105, 83.
43. Nan, C. W. *Prog Mater Sci* 1993, 37, 1.
44. Zhu, B.-K.; Xie, S.-H.; Xu, Z.-K.; Xu, Y.-Y. *Compos Sci Technol* 2006, 66, 548.