Macromolecular Research, Vol. 14, No. 4, pp 456-460 (2006)

# Effects of Morphology on the Electrical and Mechanical Properties of the Polycarbonate/Multi-Walled Carbon Nanotube Composites

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*Received April 27, 2006; Revised July 7, 2006*

**Abstract:** The electrical, morphological, and mechanical properties of polycarbonate (PC)/multi-walled carbon nanotube (MWNT) composites were studied by electrical conductivity, electromagnetic interference shielding efficiency (EMI SE), scanning electron microscopy, and tensile strength measurements. In the electrical property analysis of the PC/MWNT composites, the percolation threshold of the PC/MWNT composites was observed between 1.5 and 2.5 wt% MWNT content. From the electrical conductivity and EMI SE studies, the theoretical values of the EMI SE were in good agreement with the experimental values of the EMI SE. From the morphology of the PC/MWNT composites, it was observed that MWNT is dispersed homogenously in the PC matrix. From the electrical conductivity and morphological studies, it was suggested that the percolation threshold of the PC/MWNT composites is related with the morphological results in that MWNT is apparently interconnected to form an electrical pathway. The mechanical properties of the PC/MWNT composites peaked at the MWNT content of 2.5 wt%.

*Keywords*: multi-walled carbon nanotube composites, electrical properties, morphology, mechanical properties.

## Introduction

Since the discovery of the carbon nanotube (CNT), considerable studies have been focused on the CNT for the filler in the polymer/CNT composites because of its superior electrical and mechanical properties.[1-12] In particular, the polymer/CNT composites for the application to the electrostatic discharge (ESD) and electromagnetic-radio frequency interference shielding (EMI SE) materials has been widely studied because of its excellent electrical properties and high aspect ratio.[6,13] For example, the CNT showed high electrical conductivity up to $10^3$ S/cm.[13] Also, the CNT has very large aspect ratio, as high as 1,000-10,000. This high aspect ratio allows the percolated structure, which provides a conductive path for charge to flow in the polymer/CNT composites, at very low volume content of the CNT. According to the theoretical prediction, the percolation threshold of the cylindrical shaped filler with aspect ratio of 1000 was at 0.05 vol% in the polymer/filler composites.[14] Sandler *et al.*[6] also reported the very low percolation threshold at about 0.1 vol% of the CNT in the epoxy/CNT composites by the measurements of the electrical conductivity. Therefore, the polymer/CNT composites requires small amounts of the CNT to achieve the conductivity compared to about 20 vol% for the carbon black which has been typically used as the conductive filler.

For the polymer/conductive filler composites, the prediction of the EMI SE from the electrical conductivity was suggested by Colaneri and Shacklette.[15] According to Colaneri and Shcklette, the EMI SE properties of the polymer/filler composites have been influenced by several factors such as nature of the filler, size and the distribution of the filler. Also the prediction of the EMI SE was successfully performed when the conductivity was relatively uniform, which was obtained by uniform dispersion of the filler. In this case, the prediction of the EMI SE can be used when the experimental data of the EMI SE are not available because of the difficulties of the sample preparations by high loadings of the fillers.

In this study, the electrical and mechanical properties of

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the polycarbonate (PC)/ multi-walled carbon nanotube (MWNT) are reported by the measurements of the electrical conductivity, EMI SE, and tensile strength. In particular, the theoretical values of the EMI SE of the PC/MWNT composites, which is calculated from the electrical conductivity, are compared with the experimental values of the EMI SE, which is obtained from the vector network analyzer, of the PC/MWNT composites.

## Experimental

**Materials.** A MWNT was supplied by the Hyperion Catalysis International, Cambridge, MA. as a form of the PC/ MWNT masterbatch. Hyperion masterbatch consists of the PC/MWNT (85/15 wt%). The MWNT was vapor grown and typically consists of 8-15 graphitic layers.[3,8] Typical diameter of the MWNT is ranged from 10 to 15 nm, while length is between 1 and 10 $\mu$m.[3,8] The Hyperion masterbatch was diluted with the PC supplied by LG Chem. with the commercial designation of PC 201 15. The characteristics of the PC and Hyperion masterbatch are summarized in Table I.

**Composite Preparations.** PC/MWNT composites were prepared by melt mixing using twin screw extruder. The PC/MWNT composites, ranged from 0.5 to 15 wt% MWNT content, were prepared by diluting the Hyperion masterbatch with the PC. The temperatures of the extruder were set at 240 and 270 °C in feeding and barrel zone, respectively. Samples were compression molded using hot press at 260 °C for 5 min. Before sample preparation, all the samples were dried under vacuum (<1 mmHg) at 100 °C for 1 day.

**Electrical Conductivity.** For measuring the electrical conductivity, the four-probe method was used to eliminate the contact resistance. Four thin gold wires (0.05 mm thick and 99% gold) were attached in parallel on the samples by conducting graphite paint.

**EMI SE.** The EMI SE was measured by ASTM D4935-90 techniques using vector network analyzer. The sample was placed into an Eletro-Metrics EM-2107 sample holder at room temperature. The EMI SE was measured between 50 MHz and 1.5 GHz frequency range.

**Scanning Electron Microscopy (SEM).** The morphology of the PC/MWNT composites without $O_2$ plasma etching was obtained by scanning electron microscopy (model: Hitachi S-4300) after Pt coating. The samples were fractured at the cryogenic condition.

The morphology of the $O_2$ plasma etching samples were observed by the Hitachi S-4800 at 5 kV accelerating voltage. Before the SEM measurements with $O_2$ etching, the PC in the PC/MWNT composites was degraded selectively by $O_2$ plasma etching for 5 min. Also, the etched samples were conductively coated by using the Pt.

**Mechanical Properties.** The mechanical properties of the PC/MWNT composites were investigated using an universal testing machine (Instron 4467). Tensile test was performed according to the ASTM D638. The speed of cross-head movement for tensile test was 5.0 mm/min, and 7 specimens were measured and averaged.

**Table I. Characteristics of PC and MWNT Masterbatch Used in This Study**

| Sample | $\overline{M_n}$ | $\overline{M_w}$ | MWD | $T_g$ (°C)[a] |
|---|---|---|---|---|
| PC[b] | 11,000 | 30,000 | 2.7 | 156.6 |
| MWNT Masterbatch[c] | - | - | - | 146.0 |

[a]Measured in our laboratory by DMTA. [b]Supplied by LG Chem. Co (PC 201 15). [c]Supplied by Hyperion Catalysis International, Cambridge, MA. (PC/MWNT=85/15 wt%).

## Results and Discussion

**Electrical Properties.** Figure 1 shows the electrical conductivity of the PC/MWNT composites with the MWNT content. For the PC/MWNT composites at 0.5 wt% MWNT content, the electrical conductivity shows about $10^{-10}$ S/cm. For the PC/MWNT composites at 1.5 and 2.5 wt% MWNT content, the electrical conductivity increases dramatically and shows about $10^{-3}$ and $10^{-2}$ S/cm, respectively, which is considered to be a satisfactory results of the ESD materials. This increase of the electrical conductivity suggests the formation of the interconnected structure of the MWNT in the PC/MWNT composites. Therefore, the percolation threshold of the PC/MWNT composites could be considered at about 1.5~2.5 wt% MWNT content. Similar results were reported by Pötschke *et al.*[8] for the PC/MWNT composites by electrical conductivity and rheological measurements, respectively.

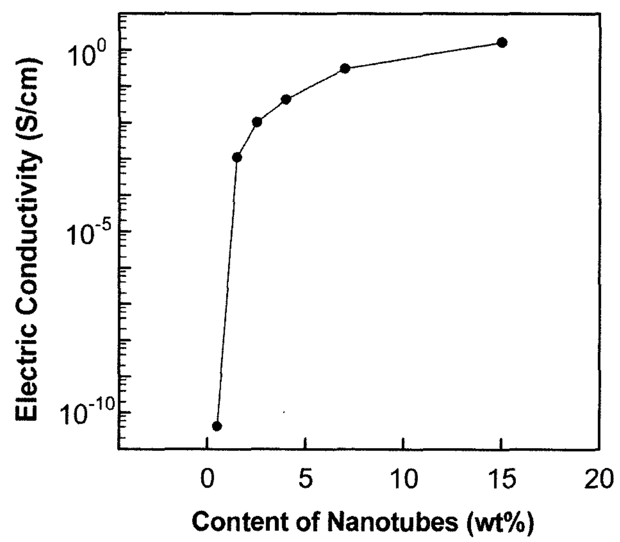


**Figure 1.** Electrical conductivity of the PC/MWNT composites with the MWNT content.

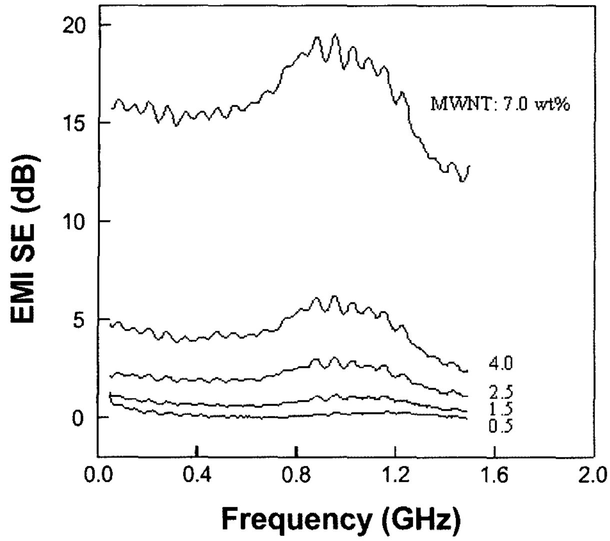


**Figure 2.** Electromagnetic-radio frequency interference shielding of the PC/MWNT composites with the MWNT content.

Figure 2 shows the EMI SE of the PC/MWNT composites with the MWNT content (0.5 to 7.0 wt%). The sample of the PC/MWNT composites with 15.0 wt% MWNT content was not able to prepare since the PC/MWNT (15.0 wt%) composite was too brittle. The EMI SE is defined in terms of the ratio of power of incident and transmitted EM wave as follows:[16]

$$\text{EMI SE} = 10 \log (P_I/P_T) \quad (1)$$

where $P_I$ and $P_T$ are the power of incident and transmitted EM waves, respectively. The unit of the EMI SE is given in dB. Theoretical value of the EMI SE can be calculated by applying the electrical conductivity to eq. (2):[15]

$$\text{EMI SE} = 20\log\left(1 + \frac{1}{2}\sigma d Z_o\right) \quad (2)$$

where $\sigma$ is the electrical conductivity, $d$ is the sample thickness, and $Z_o$ is the free space impedance (constant: 377 $S^{-1}$).

In Table II shows the experimental and theoretical values of the EMI SE of the PC/MWNT composites with MWNT content. From Figure 2 and Table II, the theoretical values of the EMI SE are in good agreement with the experimental values of the EMI SE with the MWNT content. Eq. (2) will valid when the uniform distribution of the conductive filler in the polymer composites is obtained.[15] In this case, a reliable value of the average electrical conductivity will be obtained. For the PC/MWNT composites at 7.0 wt% MWNT content, both the experimental and theoretical values of the EMI SE show about 15 dB. At 15.0 wt% MWNT content, the theoretical value of the EMI SE is about 30 dB. The comparison between the experimental and theoretical values of the EMI SE of the PC/MWNT composites shown in Table II is the first experimental study of the PC/MWNT composites.

**Table II. Theoretical and Experimental EMI SE of the PC/MWNT Composites with MWNT Content**

| MWNT Content (wt%) | Theoretical EMI SE (dB) | Experimental EMI SE at 0.6 GHz (dB) | Experimental EMI SE at 1.2 GHz (dB) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.5 | $2.0 * 10^{-9}$ | $2.0 * 10^{-2}$ | $2.1 * 10^{-1}$ |
| 1.5 | 0.08 | 0.59 | 0.83 |
| 2.5 | 1.28 | 1.94 | 2.04 |
| 4.5 | 4.03 | 4.13 | 4.40 |
| 7.0 | 15.49 | 15.82 | 15.95 |
| 15.0 | 29.69 | - | - |

**Morphology.** Figure 3 shows the scanning electron micrographs of the cryogenically fractured cross-sectional surfaces

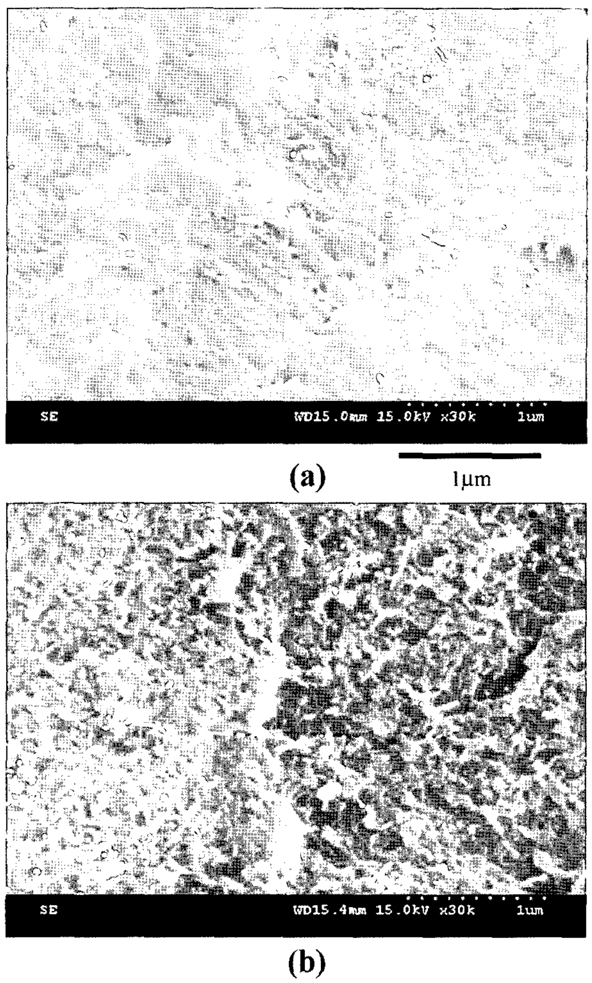


**Figure 3.** Scanning electron micrographs of the cryogenically fractured cross-section surfaces for the PC/MWNT without $O_2$ plasma etching for the 2.5 and 15.0 wt% MWNT content: (a) 2.5 wt% MWNT and (b) 15.0 wt% MWNT.

of the PC/MWNT composites without $O_2$ plasma etching for the 2.5 and 15.0 wt% MWNT content. From Figure 3, it is observed that the MWNT seems to be distributed evenly in the PC matrix. However, the distribution of the MWNT is not observed clearly without $O_2$ plasma etching since the MWNT has high aspect ratio and curved structure. Therefore, we have conducted SEM observations with $O_2$ plasma etching.

Figure 4 shows the scanning electron micrographs of the cryogenically fractured cross-sectional surfaces of the PC/MWNT composites with 2.5 wt% MWNT content after $O_2$ plasma etching for 5 min. In the high magnification image (Figure 4(b)), it is shown that the MWNT is dispersed homogenously in the PC matrix. The MWNT is appeared to connect closely and forms a pathway between the MWNT. From the results of the electrical conductivity shown in Figure 1 and morphological results shown in Figure 4, it is suggested that the percolation threshold of the PC/MWNT composites is closely related with the morphological results that the MWNT is appeared to connect each other to form a electrical pathway. Therefore, it is considered that the interconnected MWNT shown in Figure 4(b) could be the pathway for the electric charge to flow.

Figure 5 shows the scanning electron micrographs of the cryogenically fractured cross-sectional surfaces of the PC/MWNT composites with the 15.0 wt% MWNT content after $O_2$ plasma etching for 5 min. From Figure 5(b), it is observed that the MWNT is dispersed through out the PC matrix without any significant agglomeration of the MWNT. From Figures 4 and 5, the distance between the MWNT in the PC/MWNT composites (15.0 wt% MWNT) is observed to be much closer compared the PC/MWNT (2.5 wt% MWNT)

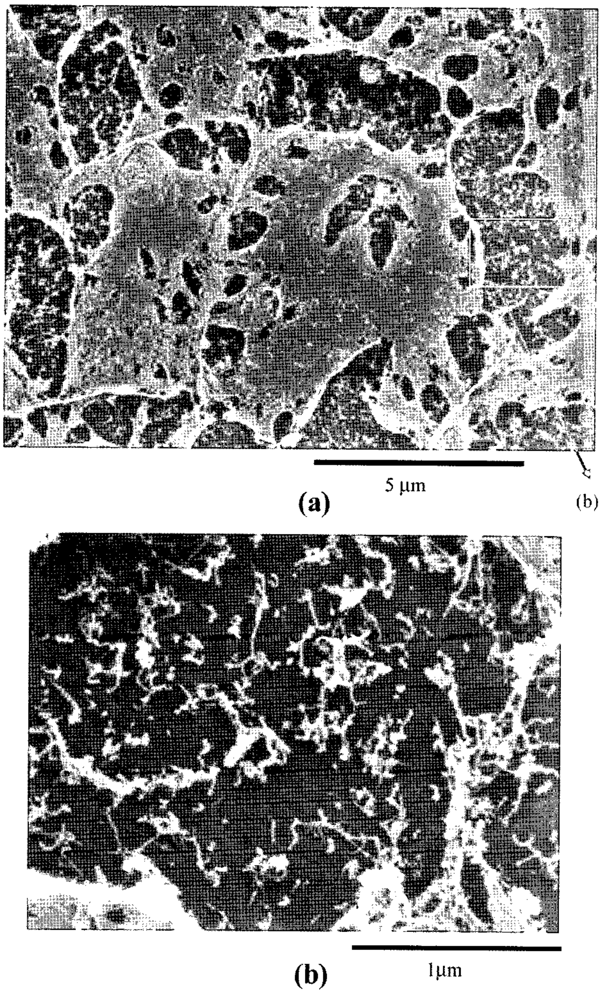


**Figure 4.** Scanning electron micrographs of the cryogenically fractured cross-section surfaces for the PC/MWNT composites at 2.5 wt% MWNT: (a) low magnitfication and (b) high magnification.

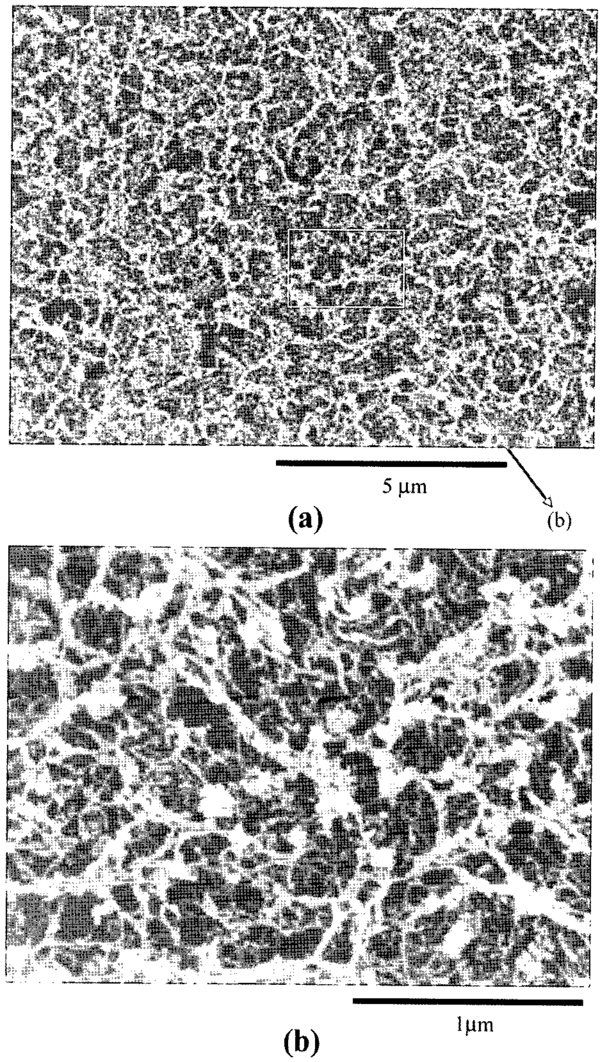


**Figure 5.** Scanning electron micrographs of the cryogenically fractured cross-section surfaces for the PC/MWNT composites at 15.0 wt% MWNT: (a) low magnification and (b) high magnification.

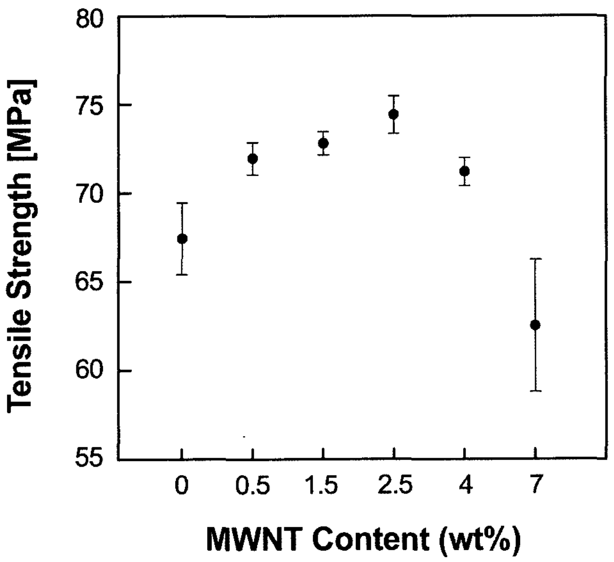


**Figure 6.** Tensile strength of the PC/MWNT composites with the MWNT content.

composites. According to our $T_g$ measurements of the PC/MWNT masterbatch by dynamic mechanical thermal analyzer shown in Table I, the $T_g$ of the PC used in the masterbatch was found to be 146.0 °C which is 10 degrees lower than the $T_g$ of the PC used as a matrix in this study. It is believed that the dispersion of the MWNT may be improved when the MWNT is mixed with the PC which has a lower $T_g$. Also, from Figures 4 and 5, it is suggested that the dilution of the highly concentrated PC/MWNT masterbatch with high shear stress using twin screw extruder is a good method for obtaining the homogeneous dispersion.

**Mechanical Properties.** Figure 6 shows the tensile strength of the PC/MWNT composites with the MWNT content. In Figure 6, when the MWNT content is up to 2.5 wt%, the tensile strength of the PC/MWNT composites is increased from 67 to 74 MPa with the increase of the MWNT content. When the MWNT content is higher than 2.5 wt%, it is observed that the tensile strength of the PC/MWNT composites is decreased from 74 to 62 MPa. When the MWNT is increased, it is thought that the decrease in the ductility and the increase in the brittleness of the PC/MWNT composites is occurred because the MWNT prevents the mobility of the PC matrix. Therefore, it is shown that the tensile strength is observed maximum value at the 2.5 wt% MWNT content in the PC/MWNT composites.

## Conclusions

In this study, the electrical, morphological and mechanical properties of the PC/MWNT composites were investigated by electrical conductivity, EMI SE, SEM, and tensile strength measurements. In the studies of the electrical properties of the PC/MWNT composites, the percolation threshold of the PC/MWNT composites was observed between 1.5 and 2.5 wt% MWNT content. From the results of the EMI SE of the PC/MWNT composites, the theoretical values of the EMI SE were in good agreement with the experimental values of the EMI SE.

From the results of the morphology of the PC/MWNT composites, it is observed that the MWNT is dispersed homogenously in the PC matrix. From the results of the electrical conductivity and morphology of the PC/MWNT composites, it is suggested that the percolation threshold of the PC/MWNT composites is related with the morphological results that the MWNT is appeared to connect each other to form a electrical pathway. From the results of the mechanical properties of the PC/MWNT composites, the tensile strength is observed maximum value at the 2.5 wt% MWNT content.

**Acknowledgements.** This study was supported by research grants from the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), an official KOSEF-created engineering research center (ERC) at Korea University, Seoul, Korea. Also, we thank Mr. Jeongmin Kim for his help in the use of SEM.

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