

Electromagnetic Interference Shielding Effectiveness of Electroless Nickel-plated MWCNTs/CFs-reinforced HDPE Matrix Composites

Woong-Ki Choi, Myung-Sun Hong, Hae-Seong Lee,[†] Kay-Hyeok An, Joon-Hyuk Bang,[‡]
Young Sil Lee,^{§,*} and Byung-Joo Kim^{*}

R&D Division, Korea Institute of Carbon Convergence Technology, Jeonju 561-844, Korea. *E-mail: kimbj2015@gmail.com

[†]Dept. of Nano Advanced Materials Engineering, Jeonju Univ., Jeonju 560-759, Korea

[‡]Dept. of Polymer-Nano Science & Technology, Chonbuk Nat'l Univ., Jeonju 561-756, Korea

[§]Cheil Industries Inc., 332-2 Gocheon-Dong, Uiwang 437-711, Korea. *E-mail: youngsil2249.lee@samsung.com

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In this work, the electromagnetic interference shielding effectiveness (EMI-SE) of carbon nanotube/carbon fiber-reinforced HDPE matrix composites are investigated with various preparation conditions, such as the carbon fiber and carbon nanotube content, the presence of metal additives, as well as mixing speed and time. It was found that the EMI-SE of the composites increased with filler contents and metal additives. These results indicate that the content and length of carbonaceous fillers determine the electric networks in the composites, resulting in the control of the EMI-SE of the composites.

Key Words : HDPE, CNTs, CFs, EMI-SE, Electrical conductivity

Introduction

Plastics are now widely used to produce plastic materials for housings and enclosures due to their advantages, such as light weight, design flexibility, low cost, mass production capability, good processability, and so on. However, when plastics housings are used, a serious problem with electromagnetic interference (EMI), which could cause noise signals and even the malfunctioning of electronic appliances, is encountered due to their poor electrical conductivity. An effective technique to overcome the EMI problem is to improve the electrical conductivity of plastics by the mixing of conductive fillers into the polymer matrix.^{1,2} Various fillers, including carbon blacks (CBs),^{3,4} carbon fibers (CFs),^{5,6} metal powder,^{7,8} metal coating on surface of carbon fiber,⁹⁻¹¹ and multi-walled carbon nanotubes (MWCNTs),¹²⁻¹⁴ stainless steel fiber,^{15,16} and others, have been investigated as materials for EMI shielding. Although good shielding capability could be obtained by higher CF and MWCNT content, difficulties in producing composites with a high fiber volume fraction occur when extrusion or injection molding is used. The use of electroless metal deposition on CF and CNT surfaces also provides the polymer composites with high strength and modulus.^{17,18}

Electroless nickel deposition is frequently used in metal coating. The morphology, structure, and properties of nickel-plated CFs produced by electroless techniques have been investigated by several researchers.¹⁹⁻²³ However, few studies have focused on the effects of different metal coatings on the EMI-SE of metal-coated filler (CNTs and CFs) polymer matrix composites.²⁴⁻²⁷

Recently, well-dispersed PTT/MWCNT composites with varying amounts of MWCNTs were prepared by melt compounding. The EMI-SE was found to increase with increasing

MWCNT loading.²⁸

Therefore, in this work, the high conductive fillers (CFs and Nickel-plated CNTs) were used to increase the electric conductivity of composites for the improved EMI-SE of the composites. Nickel-plated CNTs and CFs contents were considered. Furthermore, the study was intended to determine structure-property relationships.

Experimental Section

Materials. Multi-walled carbon nanotubes (MWCNTs) fabricated by a CVD method were donated by the Nano-solution Co., Ltd, of Korea. The purity of the MWCNTs was 95 wt %. The diameter and average length of the MWCNTs were < 10 nm and < 20 μ m, respectively. The 1.5 inch chopped carbon fiber (CFs, TZ-307) was provided by Taekwang Industries, Ltd., Korea. High-density polyethylene (HDPE, 2200J) was provided by Honam Petrochemical Co., Korea.

Nickel-Plated Carbon Nanotubes. A two-step pretreatment consisting of sensitization and activation was used to catalyze the MWCNTs. The sensitizer and activator were stannous chloride/hydrochloric acid and palladium chloride/hydrochloric acid, respectively, which assisted with the formation of a nucleus to plate the metal onto the surface of the MWCNTs. The sensitized MWCNTs were added to the solution of the reducing agent. Nickel chloride was used as the source of metal ions, sodium hypophosphite was the reducing agent, and sodium citrate was used as a complexing agent to control the pH of the bath during the plating process. The electroless plating was performed on a hot plate with a magnetic stirrer while the temperature of the bath was maintained at 60 ± 2 °C. Samples were prepared with a plating time of 30 min. Finally, the MWCNTs were washed several times with distilled water and dried in an oven at

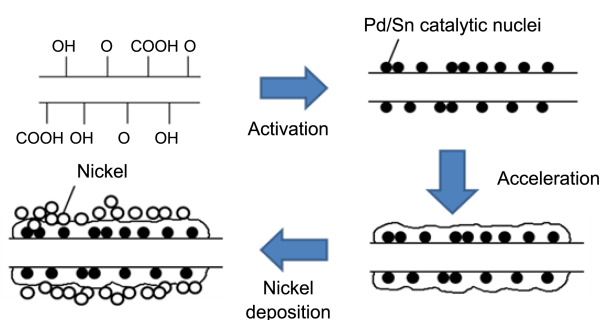


Figure 1. The electroless nickel-plated process for MWCNTs.

100 °C for 24 h. The electroless nickel-plated process for MWCNTs are shown in Figure 1. The content of the nickel-plated samples was determined by thermogravimetric analysis (TGA).

Sample Preparation. The composites were prepared by three kinds methods. One series was prepared as a function of CF contents from 10 to 40 wt %. Another series was prepared as a function of CNT contents from 1 to 10 wt % with fixed CF 30 wt %. The other series used Ni-coated (4 wt %) CNTs with the same process described above. The composites were prepared in the hot press at 180 °C for 30 min under 7.5 MPa pressure.

Analyses. The morphology of the nickel-plated MWCNTs and composites was observed using a Hitachi S6700 scanning electron microscopy-energy dispersive spectrometer with an accelerating potential of 15 kV.

TGA measurement was performed using TGA-50H, Japan. A sample of 2 mg was heated under O₂ from room temperature to 950 °C at a heating rate of 10 °C/min. The residual content was estimated as a metal content on the Ni-MWCNT.

Electrical resistivity measurements were conducted using a Loresta GP resistivity meter (MCP-T610, Mitsubishi Chemical Co., Japan) connected with a 4-point-probe (MCP-TP03P, Mitsubishi Chemical Co., Japan). A 4-point-probe was used to eliminate the effect of contact resistance. For each formulation, at least ten specimens were tested.

The coaxial transmission line method according to ASTM D4935-89 was used to measure the EMI-SE of the HDPE/CF, HDPE/MWCNT/CF, and HDPE/Ni-MWCNT/CF samples. The SE was evaluated by measuring wave with the shield in the frequency range from 30 MHz-1.5 GHz; it was calculated and expressed in decibels (dB) using the following equation:

$$SE(\text{dB}) = 10 \log \frac{P_1}{P_2}, \quad (1)$$

where P_2 denotes the energy field strength, electric field strength, and magnetic field strength, respectively, of the transmitted wave, and P_1 denotes the above properties of the incident wave. The details of the theory of EMI-SE and the measurement methods can be found in the literature.^{29,30}

Results and Discussion

Morphologies of Electroless Nickel-plated Carbon Nano-

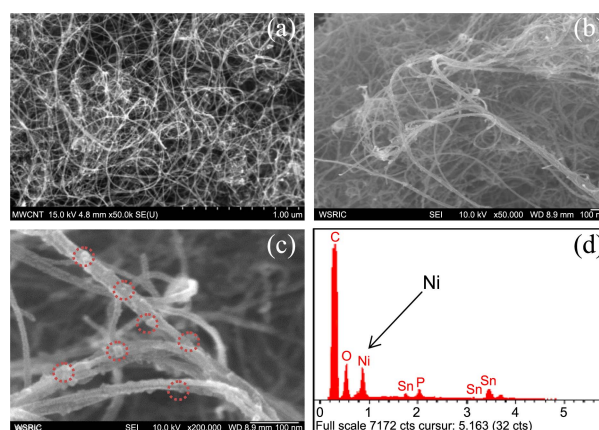


Figure 2. SEM micrographs of (a) as-received MWCNTs, (b) nickel-plated MWCNTs, (c) magnified image of (c), and (d) EDS result of nickel-plated MWCNTs.

tubes. Electroless nickel-plating, in contrast to nickel electroplating, does not use an external electric current to produce deposition. Deposition happens in an aqueous solution containing metal ions, a reducing agent, and a catalyst. Chemical reaction on the surface of the catalytic part being plated causes deposition of the metal or alloy.

Figure 2 shows SEM micrographs of the as-received MWCNTs and electroless nickel-plated MWCNTs. After the exposure time of 30 min, the nickel-particles on the MWCNTs surface increased significantly. Elemental analysis by EDS showed that the resulting products contain nickel, as seen in Figure 2(d). In Figure 2(c), the nickel particles on the MWCNTs surface showed increased distribution. The result-

Table 1. Residue contents of the as-received and Ni-plated MWCNTs measured by TGA under oxygen at 950 °C (initial sample weight: 2 mg)

Sample	Residue (mg)	Estimated Ni content (mg)	Ni (complex) content (wt %)
as-received	0.19	-	-
Ni-plated MWCNTs	1.07	0.88	44

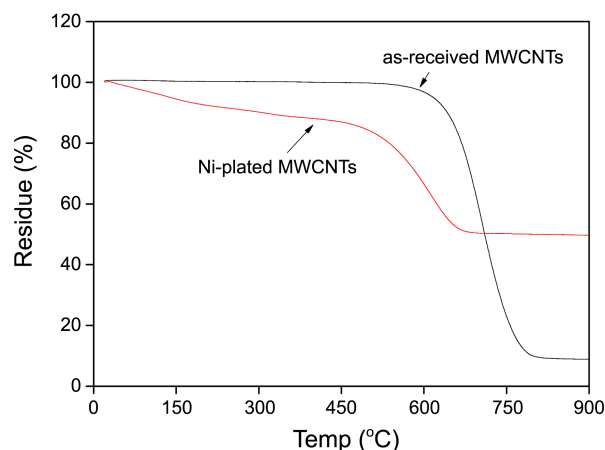


Figure 3. TGA curves of as-received and Ni-plated MWCNTs.

Table 2. Specific electric resistance of MWCNTs and HDPE/MWCNT/CF composites with various compositions

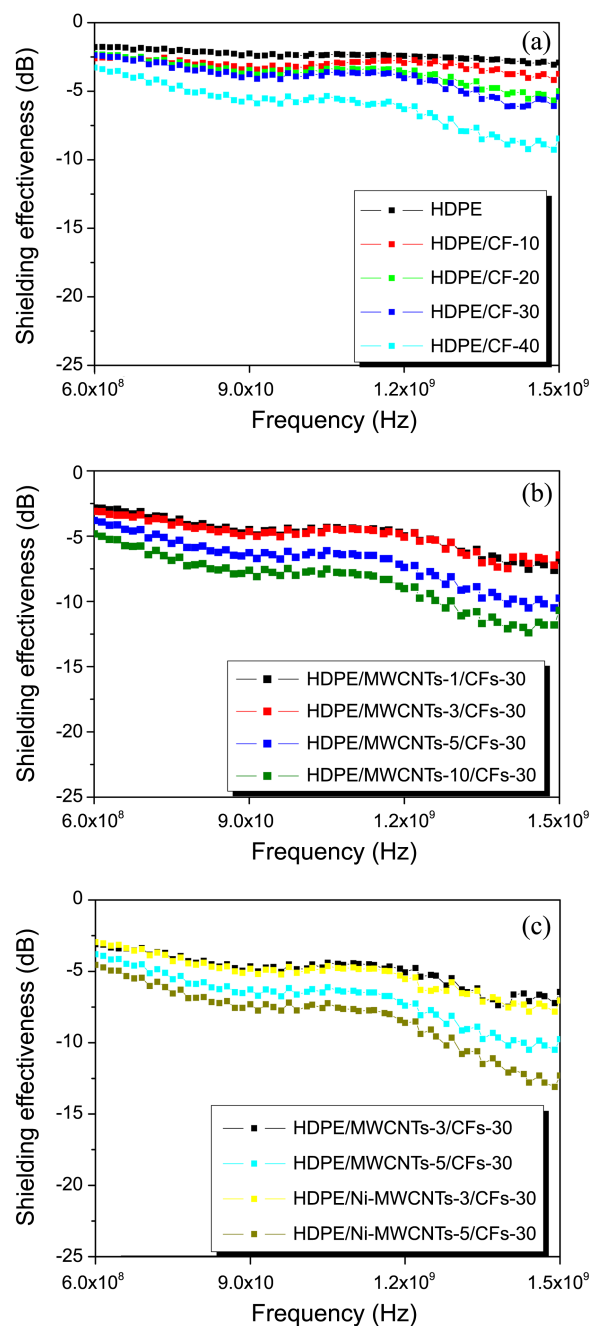
Sample	Specific Electric Resistance ($\Omega\cdot\text{cm}$)
HDPE/CFs-30	1.7×10^3
HDPE/MWCNTs-5	8.5×10^3
HDPE/MWCNTs-5/CFs-30	3.1×10^2
HDPE/Ni-MWCNT-5/CFs-30	1.4×10^2

ing plating nickel amounts of the MWCNTs measured by TGA are shown in Table 1 and Figure 3. In relation to the oxidation conditions of the experiment, each residue of the MWCNTs before and after Ni plating was measured by a high-resolution balance. Those of the as-received and Ni/MWCNTs were 0.19 mg and 1.07 mg, respectively, when the initial amount of each sample was 2.0 mg. This result indicates that the difference of the residue amount could be estimated as Ni complexes, such as metallic Ni, NiO, Ni(OH)₂ etc., corresponding to 0.88 mg of residue. This clearly indicates that the Ni/MWCNTs had around 44 wt % of Ni complex content.

Electrical Volume Resistivity. Table 2 shows the volume resistivity of the HDPE/CFs/MWCNTs composites with various compositions. As seen in Table 2, the average electrical conductivity of HDPE/CFs-30, HDPE/MWCNTs-5, HDPE/MWCNTs-5/CFs-30, and HDPE/Ni-MWCNT-5/CFs-30 composites were 1.7×10^3 , 8.5×10^3 , 3.1×10^2 , and $1.4 \times 10^2 \Omega\cdot\text{cm}$, respectively. These results simply means that a very high content of CF and CNT are permitted to flow through the composites due to the creation of an interconnecting conductive pathway. And Ni coating on CNT reduces the electric resistivity of the composites.

EMI Shielding Effectiveness. Figure 4 shows the EMI-SE of the HDPE/CFs/MWCNTs composites with various compositions. As seen in Figure 3(a), the EMI-SE of as-received HDPE was around -2 dB, indicating that this material does not have an EMI shielding feature. It is clearly shown that a large amount of CF content leads to good EMI-SE with high frequency. This result indicates that CFs can improve the electric conductivity of the composites, or CFs themselves are good EMI-absorbable fillers. The increase tendency of EMI-SE was not proportional. This means that CFs do not work only as conductive filler but also as an EMI absorber. Moreover, EMI-SE was dramatically strengthened with CF contents greater than 30 wt %, meaning that the electric networks in the composites were well-formed at higher levels.

Figure 4(b) shows very interesting results. We prepared composites with fixed CF 30 wt % as a function of CNT contents from 1 to 10 wt %. As seen in (a), the EMI SE of CF 30 wt % at 1.5 GHz of frequency is -6 dB. In (b) EMI-SE is shown as a function of CF contents, while (c) shows EMI-SE as a function of CNT contents (c) after Ni coating. With the addition of MWCNTs, the EMI-SE of the composites increased slightly up to 3 wt % of MWCNTs. It was found that the EMI-SE was dramatically enhanced with

**Figure 4.** Electromagnetic interference shielding properties of (a) HDPE/CFs composites (CFs: 10, 20, 30, and 40 wt %) (b) HDPE/MWCNTs/CFs composites (MWCNTs: 1, 3, 5, and 10 wt %), (c) HDPE/Ni-MWCNTs/CFs composites (Ni-MWCNTs: 1, 3, and 5 wt %).

MWCNTs contents greater than 5 wt %. This result indicates that good electric networks were formed with the addition of amounts of MWCNT 5 wt % or greater. In the case of MWCNT 10 wt %, the EMI-SE increased significantly, but the processability decreased due to the large volume fraction of MWCNTs.

To confirm the effects of metallic coating on the EMI-SE of the composites, Ni-coated MWCNTs were prepared, and the Ni content of the MWCNT was 4 wt %. To compare before and after Ni coating, HDPE/Ni-MWCNT-3/CF-30 and

HDPE/Ni-MWCNT-5/CF-30 samples were manufactured, and their EMI-SE results are shown in Figure 3(c).

As seen in (c), the EMI-SE of the HDPE/Ni-MWCNT-3/CF-30 sample was almost the same as that of the non-plated one, HDPE/MWCNT-3/CF-30. Meanwhile, the EMI-SE of the HDPE/Ni-MWCNT-5/CF-30 sample was significantly enhanced. This result indicates that the presence of metallic Ni can improve the EMI shielding characteristics of the composites.

Metallic coating on the MWNCTs by an electroless technique normally cause the agglomeration of MWCNTs, which can lead to poor dispersion of the MWCNTs in the matrix. Moreover, Ni-coated MWNCTs means a lower volume fraction in the composites with same amount of MWCNTs content in comparison with non-plated MWCNTs. This means that the amount of Ni-MWCNTs can be insufficient to form electric networks in the composite as seen in Figure 3(b). In (b), 3 wt % of CNTs could not improve the EMI-SE of the composites, so Ni coating cannot work in this low-content system. However, in the composites with high MWCNTs content, the presence of Ni coating clearly caused the synergistic EMI shielding characteristic of the HDPE/MWCNTs/CFs composites.

Conclusion

In this work, we prepared electroless Ni-plated MWCNTs/CFs-reinforced HDPE matrix composites for EMI shielding polymer composites. It was found that the EMI shielding features were not proportional to the content of CF filler, indicating that CF could help form electric networks in the composites and EMI absorbing, themselves. It was also found that the EMI shielding behavior could be dramatically enhanced by the addition of suitable amounts of CNT and metal coating in the presence of CF filler. However, large amount of fillers can cause severe formulation processability problems in composite preparation.

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