Carbon nanotubes materials and their application to guarantee safety from exposure to electromagnetic fields

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Abstract

Multi-walled carbon nanotubes (MWCNTs)-filled epoxy composites and poly(methyl methacrylate) (PMMA) coatings were prepared by mechanical grinding with the use of a planetary ball mill. Electromagnetic interference shielding effectiveness, electromagnetic absorption and reflection properties of the materials were investigated. With MWCNTs loadings higher than 20 wt%, epoxy/MWCNTs composites and PMMA/MWCNTs coatings also exhibited the full capability of shielding from more than 99% electromagnetic radiation at the 100 MHz–14 GHz frequency range.

Keywords: carbon nanotubes, electromagnetic shielding effectiveness, epoxy/MWCNTs composites, PMMA/MWCNTs coatings

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1. Introduction

Electromagnetic interference (EMI) is disturbance that affects a subject due to either electromagnetic induction or electromagnetic radiation emitted from an external source. As a consequence of the development of telecommunications and the electrical industry, EMI problem is becoming more and more serious; it not only causes operational malfunction of electronic instruments, but is also harmful to human health under certain circumstances [1]. Negative effects of electromagnetic field on human health are revealed as follows. Heating up is the first symptom when people are exposed to electromagnetic power. Energy absorption’s mechanism is quite complex. The heating of organisms can alter tissues, organs, impulse frequency and blood vessel response. Ultra-high frequency radiation can affect eyes, leading to cataracts. Low-intensity and short-wavelength radiation will cause the functional disorder of the central nervous system if it is repetitive [2–9]. The use of carbon nanotubes (CNTs) as a conductive additive for plastics in the electronics, automotive and aerospace sectors with potential uses as EMI shielding materials, coatings for enclosures, antistatic materials, conductive coatings, etc, is emerging as a major application area of CNTs in the plastics industry. Compared to conventional metal-based EMI shielding materials, CNT-based conductive polymer composites are becoming attractive because of their light weight, resistance to corrosion, flexibility and processing advantages. A major advantage of using CNTs is that conductive composites can be formed at low loading of CNTs due to low percolation thresholds [3–10]. The small diameter, high aspect ratio, high conductivity, and mechanical strength of CNTs make them an excellent option for creating conductive composites for high-performance EMI shielding materials at low loading.
In this study, CNTs-filled epoxy composites and PMMA coatings were fabricated. EMI shielding effectiveness (SE) was characterized by a network analyzer (HP E8363B) and tested by using a model of shielding electromagnetic wave in an electromagnetic chamber.

2. Experimental

2.1. Materials

Epoxy EPIKOTE 828 (Epon 828) and curing agent EPIKURE 3072 (Epicure 3072) used in this study were obtained from Hexion Specialty Chemicals, Inc. Pure polymethylmethacrylate (PMMA) resin was Acryrex, provided by Chimei Corporation. Solvents such as ethanol and xylene were from Sigma-Aldrich. MWCNTs from Institute of Materials Science, VAST, were prepared by CVD method using Fe as a main catalyst, the purity of MWCNTs was about 95%, the diameter was in the range of about 10–50 nm, length up to 1–10 µm [10–15].

2.2. Sample preparation

2.2.1. Preparation of epoxy/MWCNT composite materials. Epikote 828 was degassed at 80 °C for 2 h to eliminate air bubbles. CNTs were dispersed in ethanol in an ultrasonic bath for 1 h at room temperature then dried at 80 °C, pressure 100 mbar for 2 h to evaporate the solvent. After drying MWCNTs and adding them to epoxy resin, the mixture was ultrasonicated for 1 h. Epicure hardener was added into the mixture in the known weight ratios. The composite was molded into a flat plate and cured at 80 °C for 2 h.

2.2.2. Preparation of MWCNTs-filled PMMA paints. At first, the MWCNTs were dispersed in ethanol in an ultrasonic bath for 1 h at room temperature then dried at 80 °C, pressure 100 mbar for 2 h to evaporate the solvent. After drying, MWCNTs were ground in a planetary ball mill with PMMA resin, plasticizer and xylene.

2.3. Characterization

2.3.1. Testing by using network analyzer. Using a network analyzer (HP E8363B) to measure the reflection losses and transmission losses, vector network was connected to antennas. The test frequency was from 8 to 12 GHz. Dimensions of sample are 100 mm × 100 mm.

2.3.2. Testing by using electromagnetic wave shielding model in electromagnetic chamber. The frequency was in the range of 100 MHz–14 GHz, in an electromagnetic chamber (EMC). The sample was put in a closed wooden box (EUT) with the size 50 cm × 50 cm × 50 cm. The outside of the box was painted by a layer of PMMA/CNTs about 100 µm thick. The optical sensor was placed in the EUT and connected with an EMI test receiver. The EUT was put on a turntable, 0.8 m high from the floor and the distance from the antenna to the EUT is 1 m. The transmitting antenna was rotated vertically and horizontally (figures 1 and 2).

2.4. Results and discussion

2.4.1. Electromagnetic shielding effectiveness of MWCNTs-filled composite material. Effective EMI shielding materials must have electrical conductivity up to 10 S cm⁻¹ and more [10]. As we know, the ability of the material to achieve electrical percolation threshold and to become an electrical conductor is basically related to the nanotube–nanotube distances and polymer–nanotube interactions. In fact, direct connection and overlapping of the CNTs is not necessary, it means that CNTs do not need to touch each other physically. However, CNTs should be close enough to allow the electron tunneling effect. This mechanism requires the CNTs–CNTs distance to be less than their diameter [16]. For this reason, CNTs loading and dispersion in polymer matrix determine the electrical conductivity of the materials.

Electromagnetic interference shielding effectiveness (EMI SE) was obtained following ASTM D 4953–89 using a
Figure 3. Electrical conductivity of MWCNTs/epoxy composites materials.

Figure 4. EMI SE of MWCNTs/epoxy composites in 8–12 GHz.

EMI SE value expressed in dB was calculated from the ratio of incident power to transmitted power of the electromagnetic wave as follows:

$$\text{SE} = 10 \log \left| \frac{P_{\text{inc}}}{P_{\text{trans}}} \right| = 20 \log \left| \frac{E_{\text{inc}}^2}{E_{\text{trans}}^2} \right|,$$

where $P_{\text{inc}}$ ($E_{\text{inc}}$) and $P_{\text{trans}}$ ($E_{\text{trans}}$) are the power (electric field) of incident and transmitted electromagnetic waves, respectively, at a measuring point. The reflectance ($R_e$) and the transmittance ($T_r$) of the material were measured and the absorbance ($A_b$) was calculated by using the following equations:

$$R_e = \left| \frac{E_r}{E_i} \right|^2 = |S_{11}|^2 \quad \text{or} \quad R_e = \left| \frac{E_r}{E_i} \right|^2 = |S_{22}|^2,$$

$$T_r = \left| \frac{E_t}{E_i} \right|^2 = |S_{21}|^2 \quad \text{or} \quad T_r = \left| \frac{E_t}{E_i} \right|^2 = |S_{12}|^2,$$

where $R_e$ and $T_r$ were obtained by the measurement of S-parameters, $S_{11}$ (or $S_{22}$) and $S_{12}$ (or $S_{21}$) for the reflection and the transmission, respectively. In ideal conditions, without scattering, we have

$$R_e + T_r + A_b = 1.$$

Electrical conductivity measurements were performed by using a standard four-point probe method. The MWCNTs/epoxy composites material had conductivities of several orders of magnitude higher than conductivities of neat epoxy. As seen in figure 3, filling MWCNTs increases the electrical conductivity of pristine epoxy (10$^{-14}$ S m$^{-1}$) by ten orders of magnitude. To achieve the threshold of electromagnetic shielding, the electrical conductivity of the composites should reach about 10 S m$^{-1}$ when the concentration of MWCNTs filler was not less than 25 wt%.

Figure 4 shows the EMI SE of composites based on epoxy resin with 1–25 wt% MWCNTs loadings, thickness of 5 mm. We find that SE increases with increasing MWCNTs loading at a fixed frequency. At low loadings, the MWCNTs/epoxy composites exhibit an almost frequency-independent EMI SE performance. At higher loadings, the EMI SE values tend to fluctuate considerably. With 25 wt% CNTs, the SE effectiveness of epoxy/CNTs composite attained an average value 22 dB.

2.4.2. EMI SE of MWCNTs-filled PMMA paint. Figure 5 shows that PMMA coating is completely incapable of shielding electromagnetic waves while PMMA/CNTs coating with 25 wt% CNTs and thickness of 100 µm has the shielding effectiveness up to 30 dB in the frequency range 8–12 GHz; that is, more than 99.99% of electromagnetic energy was shielded over the tested frequency range.

Figure 6 shows the EMI shielding characteristics of PMMA coating in the frequency range of 8–12 GHz. It can be seen that the reflectance and absorbance can be considered as negligible. The electromagnetic wave almost 100% passes through this coating.

With a rising frequency, the reflectance of PMMA/CNTs coating decreases and the absorbance increases (figure 7). This is due to reflectance by mismatching impedance between materials and electromagnetic waves. Impedance of highly
Reflectance, Absorbance and Transmittance of PMMA/CNTs coating.

Table 1. The EMI SE of coated (PMMA/25 wt% CNTs) and uncoated samples in the 100 MHz–14 GHz frequency range.

| Transmitting antenna | Receiving antenna | Frequency (GHz) | No sample (dB) | Uncoated samples (dB) | Coated samples (dB) | Shielding effectiveness (dB) |
|----------------------|------------------|----------------|----------------|-----------------------|---------------------|-----------------------------|
| ETS 3142C (RF)       | TS-EMF           | 100            | −26.16         | −27.20                | −44.45              | 17.25                       |
|                      |                  | 200            | −45.86         | −47.29                | −67.13              | 19.84                       |
|                      |                  | 300            | −54.49         | −57.60                | −79.66              | 20.06                       |
|                      |                  | 400            | −42.14         | −41.15                | −59.71              | 18.66                       |
|                      |                  | 500            | −39.03         | −39.32                | −59.42              | 20.10                       |
|                      |                  | 600            | −33.70         | −33.87                | −54.69              | 20.82                       |
|                      |                  | 700            | −27.08         | −26.86                | −47.23              | 20.37                       |
|                      |                  | 800            | −20.70         | −20.64                | −41.87              | 21.23                       |
|                      |                  | 900            | −21.04         | −20.87                | −39.87              | 19.70                       |
|                      |                  | 1000           | −24.72         | −24.70                | −44.71              | 20.01                       |
|                      |                  | 1200           | −23.95         | −24.04                | −45.90              | 21.86                       |
|                      |                  | 1400           | −30.77         | −30.69                | −53.01              | 22.32                       |
|                      |                  | 1600           | −27.91         | −28.13                | −48.26              | 20.13                       |
|                      |                  | 1800           | −32.91         | −33.47                | −54.64              | 21.17                       |
|                      |                  | 2000           | −35.86         | −36.73                | −56.21              | 19.48                       |
| ETS 3115 (X-band)    | HL-050           | 4000           | −41.75         | −42.34                | −60.70              | 18.36                       |
|                      |                  | 6000           | −51.24         | −52.14                | −79.76              | 17.52                       |
|                      |                  | 7000           | −55.68         | −57.41                | −78.35              | 20.94                       |
|                      |                  | 8000           | −92.19         | −95.34                | −114.41             | 19.07                       |
|                      |                  | 10000          | −83.64         | −86.20                | −106.06             | 19.86                       |
|                      |                  | 11000          | −86.35         | −87.77                | −106.72             | 18.95                       |
|                      |                  | 12000          | −81.23         | −84.94                | −107.67             | 22.73                       |
|                      |                  | 14000          | −94.35         | −97.18                | −116.61             | 19.43                       |

Figure 7. Reflectance, absorbance and transmittance of PMMA/CNTs coating.

Conductive material is low and the impedance between PMMA/CNTs coating and PMMA coating is large, so that reflectance is great (average 0.3). However, characteristic absorbance is dominated (near to 0.7). Since EMI SE is the total outcome by reflectance and absorbance, it is nearly impossible for electromagnetic waves to pass through this coating.

2.4.3. Experimental models of shielding electromagnetic wave at frequency 100 MHz–14 GHz in electromagnetic chamber. The test was in the range of frequency from 100 MHz to 14 GHz and the sample was put in a closed wooden box sized 500 mm × 500 mm × 500 mm; the outside of the box was painted by PMMA/CNTs coating with the thickness of 100 μm.

The EMI SE of PMMA/CNTs coating determined by using a network analyzer is higher than the results in compliance with experimental models in EMC at X-band (8–12 GHz). It can be explained as follows: the first test shows the absolutely precise results in laboratory conditions, the sample dimensions are equal to those of transmitting and receiving speakers, the layer of PMMA/CNT coating is uniform. Meanwhile, the second test is more likely to be a practical model, EUT is bigger, and the PMMA/CNT layers are less homogeneous. In addition, EUT having slots (for electrical cables) permits the electromagnetic wave to go through partly. Nevertheless, it can be proved that by using PMMA coating with CNTs loading of 25 wt% for the purpose of electromagnetic field exposure protection, in practical conditions one can achieve an EMI SE of 20 dB in both X-band and RF (table 1).

3. Conclusions

The MWCNTs/epoxy composites materials had conductivities of several orders of magnitude higher than conductivities of neat epoxy. To achieve the threshold of electromagnetic shielding, the electrical conductivity of the composites should reach about 10 S m⁻¹ when the concentration of MWCNTs filler was not less than 25 wt%. Meanwhile, the EMI SE of the MWCNTs/epoxy composites materials achieved values higher than 20 dB at X-band frequency (8–12 GHz).

The electromagnetic wave shielding effectiveness of the MWCNTs-filled PMMA coating was investigated. The reflectance and absorbance of PMMA coating in the frequency range of 4–12 GHz are considered negligible. Electromagnetic waves almost 100% pass through this coating.

Meanwhile, the reflectance of 25 wt% MWCNT-filled PMMA coating is about 0.3, its absorbance is about 0.7 so the MWCNTs-filled PMMA coating can shield more than 99.9% electromagnetic wave power.
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