Electrical conductivity and electromagnetic interference shielding characteristics of multiwalled carbon nanotube filled polyurethane composite films

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Abstract

Multiwalled carbon nanotubes (MWCNTs) were homogeneously dispersed in a pure polyurethane resin by grinding in a planetary ball mill. The structure and surface morphology of the MWCNTs and MWCNT/polyurethane composites were studied by filed emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) methods. The electrical conductivity at room temperature and electromagnetic interference (EMI) shielding effectiveness (SE) of the composite films with different MWCNT loadings were investigated and the measurement of EMI SE was carried out in a frequency range of 8–12 GHz (X-band). The experimental results show that with a low MWCNT concentration the composite films could achieve a high conductivity and their EMI SE has a strong dependence on MWCNT content. For the composite films with 22 wt% of MWCNTs, the EMI SE attained an average value of 20 dB, so that the shielding effect reduced the penetrating power to 1%.

Keywords: multiwalled carbon nanotube, polyurethane, composite films, electromagnetic interference shielding

Classification numbers: 5.11, 5.14

1. Introduction

With the rapid development of the telecommunications and electrical industries, electromagnetic interference (EMI) has become a serious problem. It not only causes operational malfunction of electronic instruments but is also harmful to human health under certain circumstances. Many diseases, such as leukaemia, miscarriages and breast cancer, are correlated with continuous exposure to EM fields and pulses [1]. Effective shielding is in critical demand to protect the environment and workplace from EMI due to unwanted electromagnetic waves. It is particularly needed for buildings containing power transformers and other electronic facilities that radiate electromagnetic waves to the environment.

Using conductive paint is a very popular shielding method because it can be easily processed and remoulded, and it is cost-effective [2]. Most conductive paints are produced by incorporating conductive pigments into a polymeric system that has desirable physical/chemical properties [3]. Common metal powders (e.g. silver and nickel) possessing high conductivity are considered to be the most common conductive pigments [2], but the dispersed metal particles could easily be oxidized in an air-based system. Thus, there is a growing need for new conductive fillers that are lightweight, chemically stable and more easily adapted to a wide range of environmental conditions. At present, multiwalled carbon nanotubes (MWCNTs) have been intensively investigated for their excellent electrical and mechanical properties. With...
a tensile strength that is eight times greater than that of stainless steel and a thermal conductivity five times greater than that of copper, CNTs are an obvious choice for creating a new class of composite materials [4–11]. Their inclusion in a polymer or ceramic matrix holds the potential to boost the host material’s electrical, mechanical, electromagnetic interference (EMI) shielding or thermal values by orders of magnitude in comparison with traditional fillers, such as black carbon or ultra fine metal powders. Although CNTs have exceptional physical properties when they are incorporated into other materials, these properties could be inhibited by the surface chemistry of carbon. Many MWCNT/polymer composites have been developed as EMI shielding materials due to their easy processing, excellent mechanical properties and good conductivity. Park et al [12] predicted the EMI shielding effectiveness of MWCNTs—added glass fabric/epoxy composites used as structural materials.

Here, we report on the direct current conductivity and EMI SE of the composite films based on the MWCNT/polyurethane system in order to explore the possibilities for its EMI shielding applications at a frequency range of X-band (8–12 GHz).

2. Experimental

CNTs in all their forms are difficult to disperse and dissolve in any organic and aqueous medium. Due to the strong attractive long-range van der Waals interaction, nanotubes tend to aggregate and form bundles or ropes, usually with highly entangled network structures. This attraction is fundamental for many body particles and well known for colloids dispersed in polymers [13]. When suspended in a polymer, an attractive force between fillers also arises due to the entropic effects [14]. Polymer chains in the region of the colloidal filler suffer an entropic penalty since roughly half of their configurations are precluded.

Therefore, there is a depletion of the polymer in this region, resulting in an osmotic pressure forcing the filler particles to come together [12, 15–17]. Homogenous dispersion of CNTs within a supporting medium is crucial for the fabrication of composites with improved properties, well defined and uniform structures. This issue stimulates intensive studies of the exfoliation of carbon nanotubes. There are two categories of methods: mechanical/physical and chemical. The chemical methods often use surfactant or chemical treatment of the tube surface. However, certain types of aggressive chemical treatment can lead to the key nanotube properties being compromised.

In general, the functionalization of CNTs requires chemical modifications of their surface supported by mechanical agitation methods, such as ultrasonication and shear mixing [18–21]. Several functionalization strategies have been reported recently. They are mainly based on the covalent (‘grafting-to’ and ‘grafting-from’) [22–24], and non-covalent (polymer wrapping [25, 26], π–π stacking interaction [27], adsorption of surfactants [28]) coupling of surfactants and functionalities to CNTs.

However, composite materials filled with modified or functionalized carbon nanotubes are generally not a good electrical conductor. This is because bond breaking across the surface of the CNTs (e.g. by oxidation), which disrupts the delocalized π-electron systems and fracture of σ-bonds leads to incorporation of other species across the CNTs’ surface. Introducing defects to a CNT’s shell significantly alters the optical, mechanical and electrical properties of the nanotubes, leads to inferior performance of the composites and consequently reduces their electromagnetic shielding effectiveness [29].

As we know, to achieve electrical percolation threshold and thus become electrically conductive, which is basically related to the nanotube–nanotube distances and polymer–nanotube interactions, direct connection and overlapping of the CNTs is not necessary—nanotubes do not need to touch each other. Nanotubes can just be close enough to allow for a hopping/tunneling electron effect. These mechanisms require the CNT–CNT distance to be less than 5 nm [30]. However, CNTs are often functionalized with different surfactants, polymers and bio-species; in a composite system, CNTs are also coated with a layer of an insulating polymer. All of this reduces the quality and quantity of electrical contacts between the nanotubes, and also diminishes the tunneling effect. It must be noted that in the batch of synthesized carbon nanotubes, there are always CNTs with various electrical properties, including semiconductors and nanotubes with surface defects (e.g. caused by functionalization). Such CNTs do not contribute significantly to the electrical conductivity.

Therefore, we have chosen a method of manufacturing nano-polymer compositions using not really new but suitable equipment and materials that are available and efficient. It is a method of mechanical grinding with a planetary ball mill and some solvents to increase the swelling of the CNTs.

2.1. Materials

The pure polyurethane resin used was Copon polyurethane provided by Nippon Co. Ltd with solid content of 49%. The purified MWCNTs were obtained from the Institute of Materials Science, VAST, and these were prepared by the arc discharge method using Fe as the main catalyst. The MWCNTs have a diameter of about 10–50 nm, a length of 1–10 μm and a purity of 95%. Dispersion of the MWCNTs in the composites was observed by means of FESEM.

2.2. Preparation of MWCNT/polyurethane composite films

MWCNT/polyurethane composites were prepared as follows. At first, the MWCNTs were dispersed in ethanol in an ultrasonic bath for 1 h at room temperature. The pure polyurethane resin was gradually poured into the MWCNT suspension with designed weight ratios. The mixture was further ground in a planetary ball mill for more than 1.5 h to increase the compatibility of the MWCNTs with the polyurethane resin. Then a hardener was added and the mixture was poured onto the prepared concrete panels of dimension 10 cm × 10 cm × 5 cm (to fit the aperture for EMI measurement). The thickness of the composite films was 100 μm. A set of MWCNT/polyurethane composite films was prepared with different mass concentrations of MWCNTs.
Table 1. Relationship between shielding effectiveness and power transmission.

| dB  | Power transmission in % | dB  | Power transmission in % |
|-----|-------------------------|-----|-------------------------|
| 0   | 100                     | 20  | 1.00                    |
| 1   | 91.00                   | 19  | 0.99                    |
| 2   | 82.80                   | 18  | 0.98                    |
| 3   | 75.00                   | 17  | 0.97                    |
| 4   | 68.00                   | 16  | 0.96                    |
| 5   | 62.00                   | 15  | 0.95                    |
| 6   | 59.30                   | 14  | 0.94                    |
| 7   | 57.00                   | 13  | 0.93                    |
| 8   | 54.00                   | 12  | 0.92                    |
| 9   | 51.00                   | 11  | 0.91                    |
| 10  | 49.00                   | 10  | 0.90                    |
| 11  | 47.00                   | 9   | 0.89                    |
| 12  | 45.00                   | 8   | 0.88                    |
| 13  | 43.00                   | 7   | 0.87                    |
| 14  | 41.00                   | 6   | 0.86                    |
| 15  | 39.00                   | 5   | 0.85                    |
| 16  | 37.00                   | 4   | 0.84                    |
| 17  | 35.00                   | 3   | 0.83                    |
| 18  | 33.00                   | 2   | 0.82                    |
| 19  | 31.00                   | 1   | 0.81                    |
| 20  | 29.00                   | 0   | 0.80                    |

2.3. Conductivity and morphology characterization

The dc conductivity of the composite films was measured with ESCORT apparatus Model 3146A coupled with a four-point cylindrical probe on rectangular concrete slabs at room temperature. Data were taken as an average of at least three measurements. The morphology of the MWCNTs and composites was examined by means of FESEM and TEM.

2.4. Measurement of shielding effectiveness

The network analyzer (HP E8363B) in the frequency range 8-12 GHz presents the results of the shielding measurements in decibels (dB). The mode of measurement is a typical transmission measurement (scalar $S_{21}$—measurement). The dB value describes how much the level of an incident power or power-flux density has decreased, passing the device under test.

This describes the values of field strengths as well. The calculation of the per cent-values presented in table 1 refers to power relationships. It tells us that 20 dB shielding reduced the penetrating power to 1%.

To calculate the dB value from the incident power $P_1$, respectively, from the arriving electrical field strength $E_1$ and the transmitted power $P_2$ or field strength $E_2$, one has to use the following equation:

$$
\alpha_{\text{Shield}} = 10 \log \frac{P_2}{P_1} = 20 \log \frac{E_2}{E_1} .
$$

3. Results and discussion

3.1. Morphological properties

Figure 1(a) shows the FESEM image of the MWCNTs. It can be observed that MWCNTs are curvy and tangled with each other because of van der Waals interactions [31], like those produced by the chemical vaporization deposit method (CVD) [32]. Further TEM observation (figure 1(b)) shows that the MWCNTs are hollow and cylindrical, indicating carbon nanotubes instead of nanofibers. As we can see, many impurities, such as Fe catalyst, were enclosed within the MWCNTs, and this remained after purification and can induce charge tunneling in the conductive network [33].

Figure 2 shows an FESEM microphotograph of a fractured cross-section of MWCNT/polyurethane composites with 15 wt% (figure 2(a)) and 25 wt% (figure 2(b)) filler loading. The high resolution FESEM reveals that MWCNTs were mostly embedded inside the polyurethane matrix (as indicated by arrows) and part of the MWCNT clusters could be seen. The MWCNTs were homogeneously dispersed and some of them were aggregated.

3.2. Dc conductivity

Electrical conductivity measurements were performed using a standard four-point probe method. The MWCNT/polyurethane composite films had conductivities of several orders of magnitude higher than the conductivities of neat polyurethane. As seen in figure 3, filling MWCNTs increases the electrical conductivity of pristine polyurethane (10$^{-14}$ S m$^{-1}$) by ten orders of magnitude. Previous
experiments with CNTs have required loadings at up to 5–10 wt% to obtain similar conductivity values. To achieve the threshold of shielding electromagnetic waves, the electrical conductivity of the composites films should reach about 10 S m\(^{-1}\) when the concentration of MWCNT filler was not less than 20 wt%.

3.3. Electromagnetic shielding effectiveness

According to [34], the shielding effectiveness test procedure involves measuring quantitatively the insertion loss (IL) of the test sample. The SE (IL) is defined as [35]

\[
\text{SE} = 10 \log \left| \frac{P_{\text{inc}}}{P_{\text{trans}}} \right| = 10 \log \left| \frac{E_{\text{inc}}^2}{E_{\text{trans}}^2} \right| \text{ (dB)},
\]

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 at a measuring point, respectively. The EMI shielding is the result of the reflection loss \( R \), transmission or absorption loss \( A \) and internal multiple reflection loss \( I \) of the incident electromagnetic waves in the samples. These three losses are inter-related by [36]

\[
S = R + A + I \text{ (dB)}.
\]

Figure 4 shows the EMI SE variation of MWCNT/polyurethane composite films containing different carbon nanotube loadings over a frequency range of 8–12 GHz. It can be seen that the SE of a blank concrete panel is about 1–2 dB, which is primarily attributed to the slight conductivity (mainly ionic conduction) of the cement-based concrete panel. The results show that the SE of composite films is almost independent of frequency in the measured frequency range, and it increases with MWCNT loadings.

The value of EMI SE indicates how much incident signal is blocked by the shielding medium: 10 dB (or 20 dB) EMI SE means 90% (or 99%) of the incident signal is blocked. For MWCNT/polyurethane composite films containing 25 wt% of MWCNT with 100 \( \mu \)m thickness, the highest SE was \( \sim 25 \) dB, that is, more than 99.69% of electromagnetic energy was shielded over the tested frequency range. This indicates that composite films with 22 wt% of MWCNTs can meet their commercial application, which requires a SE value more than 20 dB.

4. Conclusions

MWCNT/polyurethane composites were successfully prepared for EMI shielding applications and their properties
were investigated. FESEM microphotographs showed that the MWCNTs were well dispersed in polyurethane. We observed that a low weight fraction of MWCNTs was able to achieve a high level of conductivity. This is important because low loadings are necessary to achieve the conductivity levels required for various industrial applications without compromising the preferred host polymer’s physical properties and lower cost. The EMI SE of the composite films demonstrates a strong dependence upon the MWCNT content in the frequency range 8–12 GHz (X-band). For the composite film with 22 wt% of MWCNTs, its EMI SE was 20 dB with a shielding effect of 90%, and the product is capable of meeting the commercial application electromagnetic shielding requirements. We suggest that MWCNT/polyurethane composites are promising building shielding materials, especially in the X-band.

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