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

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ABSTRACT

Multiwalled carbon nanotubes (MWCNTs) were homogeneously dispersed in pure acrylic emulsion by ultrasonication to prepare MWCNT/polyacrylate composites applied on building interior wall for electromagnetic interference (EMI) shielding applications. The structure and surface morphology of the MWCNTs and MWCNT/polyacrylate composites were studied by field emission scanning microscopy (FESEM) and transmission electron microscopy (TEM). The electrical conductivity at room temperature and EMI shielding effectiveness (SE) of the composite films on concrete substrate with different MWCNT loadings were investigated and the measurement of EMI SE was carried out in two different frequency ranges of 100–1000 MHz (radio frequency range) and 8.2–12.4 GHz (X-band). The experimental results show that a low mass concentration of MWCNTs could achieve a high conductivity and the EMI SE of the MWCNT/polyacrylate composite films has a strong dependence on MWCNTs content in both two frequency ranges. The SE is higher in X-band than that in radio frequency range. For the composite films with 10 wt.% MWCNTs, the EMI SE of experiment agrees well with that of theoretical prediction in far field.

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1. Introduction

With the rapid development of electrical industry, electromagnetic interference (EMI) has become a serious problem in modern society. EMI not only causes operational malfunction of electronic instruments, but also is harmful to human health under certain circumstances. Many diseases such as leukemia, miscarriages, breast cancer, are correlated to 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 the buildings containing power transformers and other electronic facilities which will radiate electromagnetic wave to the environment.

Using conductive paint is a very popular shielding method because it can be easily processed, remolded and cost-effective [2]. Most of conductive paints are produced by incorporating conductive pigments into a polymeric system that has desirable physical/chemical properties [3]. Water borne paints are widely used in the field of the architectural paints to decrease the amount of volatile organic compounds [4]. Common metal powders (like Ag, nickel) possessing high conductivity are considered to be the most common conductive pigments [2], but the dispersed metal particles are easily oxidized in water-based system. Thus, there is a growing need for new conductive fillers that are lightweight, chemical stable and more easily adapted to a wider range of environments.

At present, multiwalled carbon nanotubes (MWCNTs) have been intensively investigated for their excellent electrical, mechanical properties and unique structure (large aspect ratio, tube-shape form) [5], which make them an excellent option to create overlapping conductive network for high-performance EMI shielding at very low loading [6–8]. They can be produced today in a large amount and at lower cost by using natural gas or coal as a stock catalyst [9]. Many MWCNT–polymer composites have been developed as EMI shielding materials due to easy processes, excellent mechanical properties and good conductivity. Park et al. [10] predicted the EMI shielding effectiveness (SE) of MWCNT-added glass fabric/epoxy composites used as structural materials.
Xiang et al. [11] studied the SE of MWCNT-reinforced fused silica composites between X-band and Ka-band. Jou et al. [12] have synthesized MWCNT-LCPs and MWCNT-MF composites whose highest SE reaches 60 dB, indicating a possible realistic use for an industrial application.

Pure acrylic emulsion is known to be a very important emulsion with many prominent properties such as high weather-resistance and stabilities of water dilution and Ca²⁺, etc. It is a universal choice for making alkali resistant paints for internal decoration. However, polycrlylate alone is inherently non-conductive and provides no shielding against electromagnetic radiation. Percolation theory indicates that the electrical conductivity of a composite is determined by the ability to form a conducting network [13]. It seems reasonable to prepare conductive polycrlylate films for building shielding materials used on concrete substrate by incorporating a low MWCNT loadings with all the remarkable structural, mechanical and electrical properties mentioned above.

In the present paper, we reported the direct current (dc) conductivity (σ_{dc}) and EMI SE of the composite films on concrete substrate in order to explore the possibility for its EMI shielding applications. The EMI SE of the composite films was assessed over 100–1000 MHz (radio frequency range) and 8.2–12.4 GHz (X-band).

2. Experimental details

2.1. Materials

Pure acrylic emulsion used in this paper was YS-08 provided by Beijing Huyi Co., Ltd., whose solid content was 48 ± 2%. The purified MWCNTs were obtained from Shanghai Jiaotong University (Shanghai, China), which were prepared by an arc discharge method using Fe as the main catalyst. They were purified according to procedures described by Chen et al. in Ref. [14,15]. The diameter of the MWCNTs was 5–10 nm, the length was 5–10 μm, and the purity was 95%. Anionic surfactant sodium dodecylbenzene sulfonate (SBDS) was introduced to prevent the agglomeration of the MWCNTs and to obtain better dispersion. The dispersion of MWCNTs in the composites was observed by means of field emission scanning microscopy (FESEM) in our experiment. Small quantity of the samples with non-homogeneous distribution of MWCNTs were removed. The concrete specimens for substrate were prepared in our laboratory with ordinary cement, coarse aggregate with maximum size of 19 mm and natural sand by following steps: first, cement, water, aggregate and sand were mixed in a rotary mixer for 30 min. The cement:sand:aggregate ratio is 1:2:4. Second, they were poured into oiled molds and cured for 28 days in a laboratory environment (100% relative humidity) at room temperature.

2.2. Preparation of the MWCNT/polyacrylate composite films

The MWCNT/polyacrylate composites were prepared as follows. At first, the MWCNTs were dispersed in de-ionized water with 2.0 wt.% SBDS in an ultrasonic bath with oscillation frequency of 42 kHz for 1 h at room temperature. The pure acrylic emulsion was gradually poured into the MWCNTs suspension with designed weight ratios. The mixture was further sonicated for more than 1.5 h to increase the compatibility of MWCNTs with the pure acrylic emulsion and was coated on the prepared concrete panels of dimension 60 cm × 60 cm × 5 cm (to fit the aperture for EMI measurement). The wet films were consolidated at 50 °C for 15 min and further cured at room temperature overnight for further testing. The thickness of the composite films was 1.5 mm. A serious of MWCNT/polyacrylate composite films were prepared with different mass concentrations of MWCNTs.

2.3. Conductivity and morphology characterization

The dc conductivity of the composite films was measured with ESCORT apparatus of resistance Model 3146A coupled with a four-point cylindrical probe on rectangular concrete slabs at room temperature in our lab. Data were taken as averages of at least three measurements. The morphology of MWCNTs and composites was examined by FESEM and transmission electron microscopy (TEM).

2.4. Measurement of shielding effectiveness

There are several methods to characterize the shielding performance of flat, thin samples, and the coaxial cable line test method based on ASTM D4935-99 is probably most used and cost-effective [10]. The test setup mainly consists of a network analyzer and coaxial cable line with a sample holder and provides SE of a material against the plane wave. The shortcoming of this measurement method is that it seldom reflects the real electromagnetic field conditions, which is usually different from that in standardized test method. The MWCNT/polyacrylate composite films were used on concrete substrate for building shielding, therefore, the SE of the composite films was tested in an anechoic shielded room to simulate the actual conditions. There are absorbers on the inside walls to minimize the reflection [16] and an aperture in one wall of the anechoic shielded room, where the samples can be placed. The transmitting antenna (signal generator) and the receiving antenna (signal detector) are located on separate sides of the aperture. The distance between two antennas was 2.0 m and the sample was placed midway perpendicular to the both antennas. The experimental configuration is sketched in Fig. 1. The samples were pressed against the brass plate as a means for preventing radiation leakage. The setup of SE measurement is composed by a vector network analyzer (Hewlett-Packard HP 8563E), a sweep oscillator (Hewlett-Packard HP83640A), transmitting and receiving antennas. This system can be able to measure from 30 MHz to 40 GHz. Dipole and horn antennas were used for both the transmitting and the receiving antennas. The SE in the frequency range 100–1000 MHz was measured utilizing dipole antennas and the SE in the frequency range 8.2–12.4 GHz was measured utilizing horn antennas. The lower frequency limit is determined by the aperture size, which acts as a wave guide and attenuates electromagnetic wave under a specific cut-off frequency [16]. The aperture size is 60 cm × 60 cm to ensure that the cut-off frequency is sufficiently low and the lower frequency dynamic range is increased. Different samples were measured to check the repeatability of the results.

![Fig. 1. Schematic configuration of the measurement setup for the SE of MWCNT/polyacrylate composites on concrete substrate.]
3. Experimental results and discussion

3.1. Morphological properties

Fig. 2(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 [17], like those produced by chemical vaporization deposit method (CVD) [12]. Further TEM observation (Fig. 2(b)) illustrates that the MWCNTs are hollow and cylindrical, which are carbon nanotubes instead of nanofibers and the aspect ratio of these MWCNTs is up to 1000, which can assist the construction of conductive network. As we can see, many impurities such as Fe catalyst were enclosed within the MWCNTs, which still remained after purification and can induce charge tunneling in the conductive network [18]. Fig. 2(c) shows a FESEM microphotograph of fractured cross-section of MWCNT/polyacrylate composites with 2 wt.% filler loading. The high resolution FESEM reveals that MWCNTs were mostly embedded inside the polyacrylate matrix (as indicated by arrows) and part of MWCNTs clusters could be seen. The MWCNTs were homogeneously dispersed and some of the MWCNTs were aggregated. This uniform microstructure is ascribed to the good wetting of the purified MWCNTs and polyacrylate matrix because of carboxyl groups on the external walls and the end caps of MWCNTs formed by acid treatment in purification [17].

3.2. DC conductivity

Fig. 3 illustrates dc conductivity at room temperature ($\sigma_{dc}$) of MWCNT/polyacrylate composites as a function of MWCNTs mass concentrations ($p$) in log–log scale. The inset of Fig. 3 is plot of $\sigma_{dc}$ as a function of $p$ in linear scale. As can be seen in Fig. 3, the $\sigma_{dc}$ of the composites exhibits a dramatic increase of 10 orders of magnitude as the MWCNTs concentrations increased up to 10 wt.%, indicating a percolating phenomenon. In the classical percolation theory, the conductivity of a conductor–insulator composite obeys the power law relationship around the percolation threshold [19] as follows:

$$\sigma(p) \propto |p - p_c|^t$$

where $\sigma(p)$ is the composites conductivity, $p_c$ is the percolation threshold, $t$ is the critical exponent. As shown in Fig. 3, the $\sigma(p)$ of MWCNT/polyacrylate composite films agrees well with the
The slope, i.e., the critical exponent $t$ in Fig. 3 varied from 10.29 to 2.29 at $p/C_{24}^{0.58}$ wt.% of MWCNT concentration, implying a percolation threshold at $p/C_{24}^{0.0058}$. For a three-dimensional system of ideal hard spheres randomly dispersed in a continuous matrix, the percolation threshold is $f_c = 0.16$ by volume fraction [19–20]. In the current case, the mass fraction of the WMCNTs ($p$) is preferred instead of the volume fraction ($f$) due to the similar densities of both the polyacrylate and WMCNTs. The relatively low value of the percolation threshold found in the WMCNT/polyacrylate system is accounted for the one-dimensional large aspect ratio and efficient dispersion of WMCNTs. Our value for the percolation threshold is in the same magnitude with the investigation by H.M. Kim et al. for their WMCNT-PMMA system [19]. Concerning the critical exponent, it is well consistent with the value predicted from the percolation theory ($t = 1.87$) [20].

### 3.3. Electromagnetic shielding effectiveness

According to [11], the shielding effectiveness test procedure is to quantitatively measure the insertion loss (IL) of the test sample. The SE (IL) is defined as [10]

$$\text{SE} (\text{dB}) = 20 \log \left(\frac{Z_0 \delta \sigma}{2 \sqrt{2}}\right) + 8.68 \frac{t}{\delta}$$

(5)

For ‘electrically thick’ films, in the far field case, the SE is expressed as follows:

$$\text{SE} (\text{dB}) = 20 \log \left(1 + \frac{Z_0 \sigma r}{2}ight)$$

(6)

In the near field case, the SE is given by [24]:

$$\text{SE} (\text{dB}) = 20 \log \left(\frac{Z_0 \sigma r}{2\pi}\right)$$

(7)

![Fig. 3. dc conductivity at room temperature ($\sigma_{dc}$) of WMCNT/polyacrylate composites as a function of the WMCNT mass concentrations ($p$) in log-log scale. Inset: plot $\sigma_{dc}$ of as a function of $p$ in linear scale.](image)

![Fig. 4. EMI shielding effectiveness of MWCNT (0–10.0 wt.%)/polyacrylate composites as a function of frequency measured in (a) 100–1000 MHz, (b) X-band.](image)
where \( c = 2.998 \times 10^8 \) m/s is the velocity of light, \( Z_0 = 120\pi \) is the impedance of the free space, \( \omega = 2\pi f \) is the angular frequency.

Fig. 4(a) and (b) show the EMI SE variation of MWCNT/polyacrylate composite films containing different carbon nanotubes loadings over two frequency ranges, namely 100–1000 MHz and 8.2–12.4 GHz. It can be observed that the SE of blank concrete panel is about 1–2 dB, which is primarily attributed to the slight conductivity (mainly ionic conduction) of cement-based concrete panel. The results show that the SE of composite films is almost independent of frequency in the two measured frequency ranges, and increases with MWCNTs loadings. It is interesting to note that the SE of all the composite films appreciably increases when the frequency changes from radio frequency range to X-band. For example, the MWCNT/polyacrylate composite film with 10 wt.% loading exhibits shielding level of 25.1–25.8 dB in X-band, which is much higher than the 20.1–20.6 dB in radio frequency range at the same MWCNTs loading.

Fig. 5 shows the variation of SE with MWCNTs loadings at fixed frequencies of 500 MHz and 10 GHz. It is evident that the shielding effectiveness increases progressively with the increase of filler loading, but the rate is much faster for 10 GHz compared to that of 450 MHz. The higher EMI SE for MWCNT/polyacrylate composite films in X-band is mainly ascribed to the smaller skin depth (as shown in Eq. (4)) which results in a high multiple reflection. The high performance of SE in our work is mainly due to the high conductivity and large number density of MWCNTs, which helps a lot in forming good conductive networks in the insulating polyacrylate matrix. The conductive network formed due to the dispersion of MWCNTs behaves like a conductive mesh, as shown in Fig. 2(c), which intercepts electromagnetic radiation [25]. The small mesh size generally increases the SE.

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%) incident signal is blocked. For MWCNT/polyacrylate composite films containing 10 wt.% of MWCNT with 1.5 mm thickness, the SE shows more than 99% shielding of electromagnetic energy over the measured frequency ranges. The highest SE of the composite films was 25.1–25.8 dB with 10 wt.% MWCNTs. This indicates that the composite film with 10 wt.% MWCNT can meet the commercial application SE requirement (more than 20 dB). It is evident that MWCNT/polyacrylate nanocomposites are excellent shielding materials for EMI, especially in X-band.
results and the predicted ones, the difference in radio frequency range is 1 dB in far field and about 7 dB close to near field. This difference may be contributed to the transition form the far field to near field. In X-band, there is no obvious difference and a good correlation is observed.

4. Conclusions

MWCNT/polyacrylate composites were successfully prepared for EMI shielding applications and the properties were investigated. FESEM microphotographs showed that the MWCNTs were well dispersed in polyacrylate matrix. We observed that a low weight fraction of MWCNTs could achieve a high level of conductivity and a low percolation threshold ($p_c \approx 0.58$ wt.% for MWCNTs content was confirmed. The EMI SE of the composite films has a strong dependence on MWCNTs content in two different frequency ranges 100–1000 MHz (radio frequency range) and 8–12 GHz (X-band). The SE is higher in X-band than that in radio frequency range. The theoretical prediction for EMI SE is analyzed. For the composite film with 10 wt.% MWCNTs, the EMI SE of the experiment agrees well with that of theoretical prediction in far field. We suggest that MWCNT/polyacrylate composites are promising building shielding materials, especially in X-band.

References