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RESEARCH ARTICLE

Impact of Polymer Matrix on the Electromagnetic Interference Shielding Performance for Single-Walled Carbon Nanotubes-Based Composites

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Composites of acrylonitrile butadiene styrene (ABS), epoxy and soluble cross-linked polyurethane (SCPU) with various loadings of single-walled carbon nanotubes (SWCNTs) were prepared. Their electromagnetic interference (EMI) shielding effectiveness (SE) in the frequency range of 8.2–12.4 GHz (*X* band) was studied. Well-dispersed SWCNT composites were created in these three representative polymer matrixes. The choice of polymer matrix greatly affects the conductivity, percolation threshold, and EMI shielding properties of the SWCNT/polymer composites. Enhanced EMI SE performances were observed for the composites with better dispersed SWCNTs. Moreover, the EMI SE performances strongly correlated with SWCNT loading in the polymer matrix. The best SWCNT dispersion was achieved in the epoxy matrix: 20–30 dB EMI SE was obtained with 15 wt% SWCNTs.

Keywords: Electromagnetic Interference Shielding, Single-Walled Carbon Nanotubes, Composite.

1. INTRODUCTION

Materials with electromagnetic interference (EMI) shielding effectiveness (SE) are in high demand for both commercial and military applications. Conventionally, inorganic magnetic or metallic particles are used as EMI materials. However, their high specific gravity and poor processibility have limited their practical applications. Thus, the urgent need remains for EMI materials that are relatively lightweight, structurally sound and flexible and efficient in wide band-range shielding or absorption. Recently, nano-structured materials have generated significant attention for these applications due to their many unique chemical and physical properties.[1–4] With a low specific mass and excellent thermal, electrical and mechanical properties, carbon nanotubes (CNTs), including both single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes, have been studied for potential engineering applications in electronics, electrostatic dissipation, multilayer printed circuits, and conductive coatings.[5–11] Their excellent electrical properties, small diameters and high aspect ratios,[12–14] have made them an excellent option for high performance EMI shielding.[2, 12, 13, 15–22]

While most reports point out that the structure and properties of CNTs strongly influence the EMI shielding performance of CNT/polymer composites,[1, 15–17, 19, 23, 24] few reports focus on the influence of polymer matrix.[20] Recently, we reported the impact of SWCNT structure (i.e., diameter, aspect ratio and wall integrity) on the EMI performance of epoxy composites.[23, 24] In this work, we studied the influence of different polymer matrices on the EMI SE performance of SWCNT/polymer composites in the microwave band. SWCNT/polymer composites with varying SWCNT loading and three sets of representative matrix polymers (thermoplastic acrylonitrile butadiene styrene (ABS), thermosetting epoxy and soluble cross-linked polyurethane (SCPU)) were prepared in this work. The results indicated that the polymer matrix, which strongly affects the dispersion state of SWCNTs, has great impact on the conductivity, percolation threshold, and EMI

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SE properties of the composites. The epoxy composites displayed the best SWCNT dispersion and resulted in 20–30 dB of EMI SE with 15 wt% SWCNT loading.

2. EXPERIMENTAL DETAILS

2.1. Preparation of SWCNT/Polymer Composites

SWCNTs were prepared in our laboratory with a modified arcing method at large scale using a Ni/Y catalyst.[25] The SWCNT/SCPU composites, SWCNT/ABS composites and SWCNT/Epoxy composites were prepared according to our previously works.[23,24,26]

2.2. Instruments and Measurements

Scanning electron microscopy (SEM) was performed on a Hitachi S-3500N scanning electron microscope. Direct-current (DC) conductivity of the SWCNT/polymer composites was determined using the standard four-point contact method on rectangular sample slabs to eliminate the contact-resistance effect. The data were collected with a Keithley SCS 4200. The EMI SE and permittivity data of the SWCNT composites were measured using 22.86 mm × 10.16 mm × 2 mm slabs (to fit waveguide sample holder), by an HP vector network analyzer (HP E8363B) in the 8.2–12.4 GHz (*X* band) range. All ultrasonication processing was performed with a sonicator (Gongyi Yuhua Instrument Co., LTD., Model: KQ400B, 400 W).

3. RESULTS AND DISCUSSION

The EMI SE properties of composites are highly related to the filler's intrinsic conductivity, dielectric constant, aspect ratio[12,13] and dispersion state. And it is well known that the conductivity of conductor-insulator composites follows the critical phenomena around threshold. Figure 1 shows the dc conductivity (σ) of our SWCNT/SCPU, SWCNT/ABS and SWCNT/epoxy composites as a function of the SWCNT mass fraction (p). All composites exhibited a change of over 10 orders of magnitude at different SWCNT loadings, indicating the formation of the percolating network.

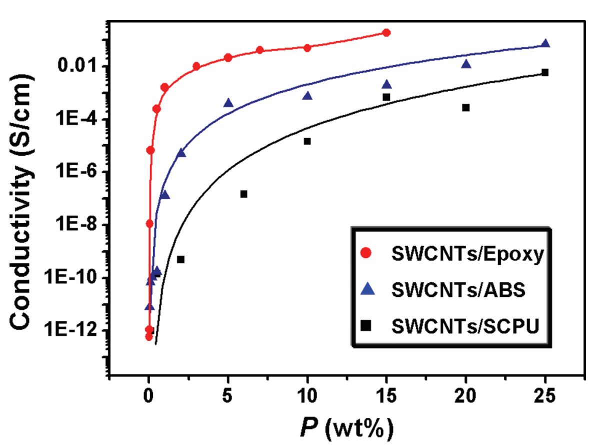

Fig. 1. log10 DC conductivity (σ) versus mass fraction (p) of SWCNT/polymer composites (Red circle: SWCNT/SCPU, Blue triangle: SWCNT/ABS, Black square: SWCNT/epoxy) measured at room temperature.

To date, different thresholds have been found for the conductivity of SWCNT/polymer composites. Since lower filling fractions imply lower cost and smaller perturbation of bulk physical properties, it is crucial to have a low filling threshold for practical applications. It is well known that the conductivity of a conductor-insulator composite follows the critical phenomena around the percolation threshold (Eq. (1)):[27]

$$\sigma \propto (\nu - \nu_c)^{\beta} \tag{1}$$

where σ is the composite conductivity, ν is the SWCNT volume fraction, ν_c is the percolation threshold and β is the critical exponent. Because the densities of the polymer and SWCNT are similar, we assume that the mass fraction, p, and the volume faction, ν, of the SWCNTs in the polymer are similar. log–log plots (σ vs. $(p - p_c)/p_c$) were generated using Eq. (1) and least-square fit to the data near the threshold. The fit shows that the threshold volume p_c for each set of composites was strongly bounded by the regions between the highest insulating and lowest conducting points. The conductivity of SWCNT/polymer composites agreed very well with the percolation behaviour predicted by Eq. (1).

In previous works, both theoretical and experimental results for the percolation threshold (p_c) of composites depended primarily on the filler's aspect ratio, processing methods and matrix.[13,23,28] Table I summarizes the percolation thresholds and critical exponents obtained using Eq. (1) for the three composites. The percolation threshold of SWCNT/epoxy composites was found to be quite low (0.062 wt%) and in good agreement with previous studies of SWCNT/polymer systems.[29,30] This indicated that our processing method distributed the SWCNTs well in the epoxy matrix. Higher values for the percolation threshold were obtained for the SWCNT/ABS (0.599 wt%) and SWCNT/SCPU composites (3.34 wt%). Thus, the best dispersion of SWCNTs was achieved in the epoxy matrix. The values of the critical exponent β were also in good agreement with the theoretical results for a percolating rod network system.[28,31] The conductivity of the SWCNT/polymer composites all dramatically increased at

Table I. Percolation thresholds, critical exponents, and correlation factors for the three SWCNT/polymer composites.

SWCNTs used	Percolation threshold (wt%), p_c	Critical exponent B	Correlation factor R
SWCNT/SCPU	3.39	4.7	0.97
SWCNT/ABS	0.599	2.95	0.99
SWCNT/epoxy	0.062	2.68	0.98

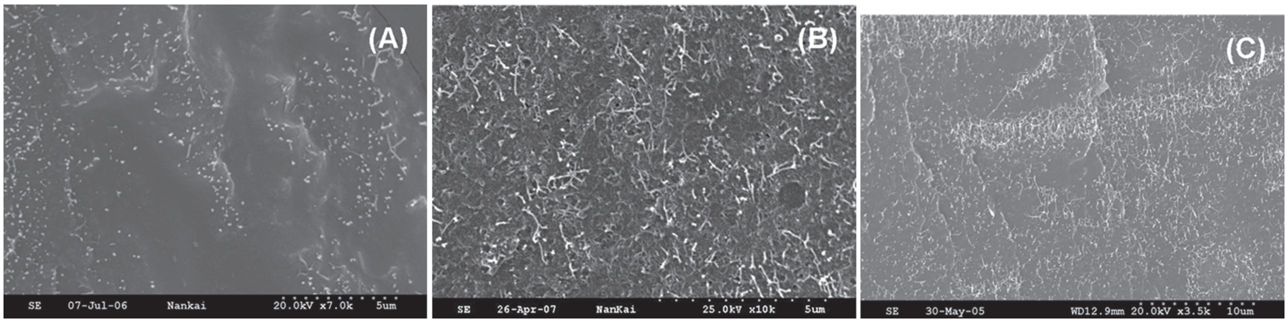

Fig. 2. Representative SEM images of the cross section of SWCNT/polymer composites. (A) SCPU with 20 wt% SWCNTs, (B) ABS with 20 wt% SWCNTs, (C) epoxy with 10 wt% SWCNTs. All the samples freeze-fractured in liquid nitrogen and gold coated.

low SWCNT loadings. Figure 1 shows that the conductivity of SWCNT/epoxy composites exhibited a remarkable increase of over 10 orders of magnitude below 0.6 wt%. At 15 wt% loading, the conductivity reached 0.2 S/cm. Compared with SWCNT/epoxy composites, the SCPU and ABS composites showed slower conductivity increases, resulting in higher values of the percolation threshold for SWCNT/ABS (0.599 wt%) and SWCNT/SCPU composites (3.34 wt%). The percolation threshold in SWCNT composites is highly coupled to the properties of polymer matrix and the dispersion state of SWCNTs in the polymer matrix, as discussed below.

The dispersion state of SWCNTs in the polymer matrices were studied by SEM. Figure 2 displays representative

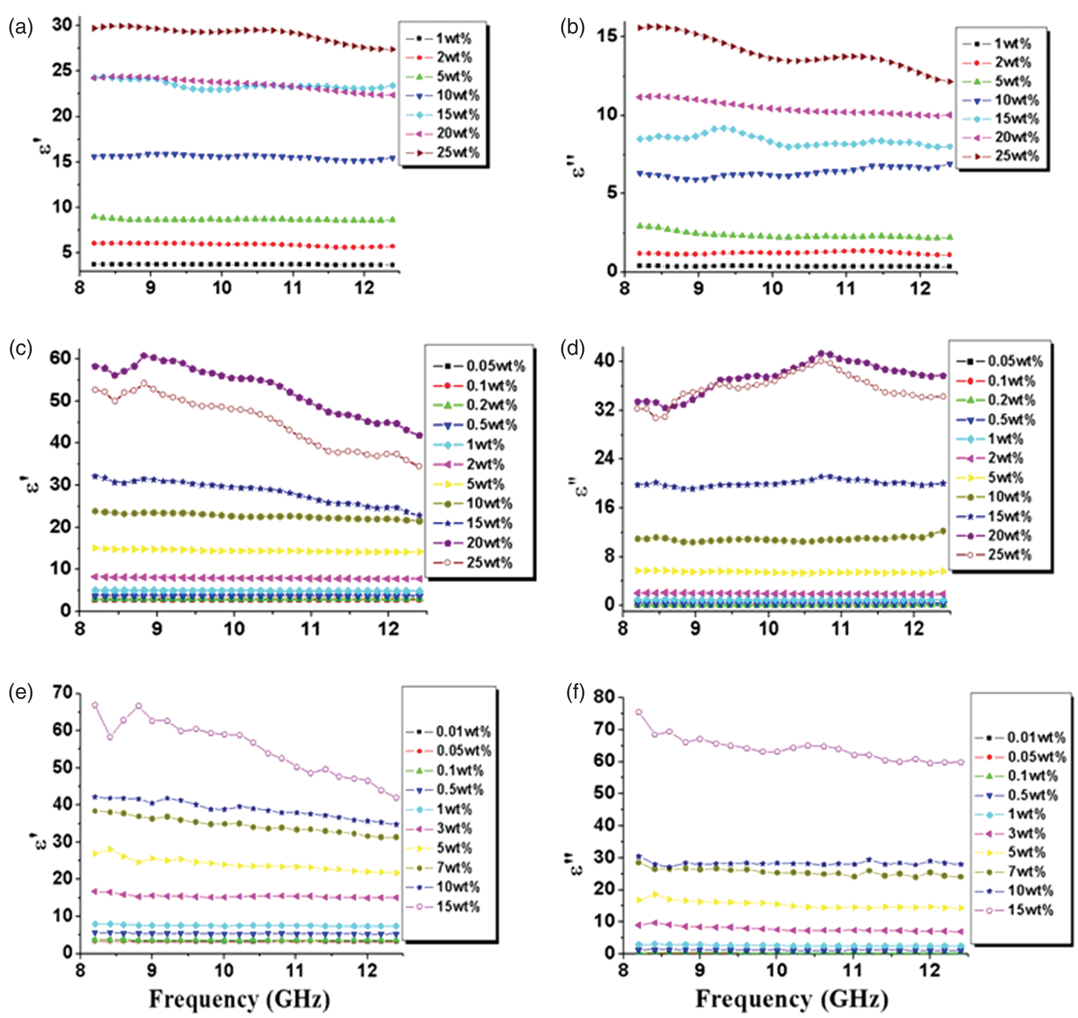

Fig. 3. Complex permittivity spectra of the SWCNT/SCPU (a), (b), SWCNT/ABS (c), (d) and SWCNT/epoxy (e), (f) composites with various SWCNT loading.

cross-sectional SEM images of SWCNT/SCPU (20 wt%), SWCNT/ABS (20 wt%) and SWCNT/epoxy (10 wt%) composites. Compared to SWCNT/SCPU composites (Fig. 2(A)), SWCNTs were better dispersed and embedded throughout the polymer matrix in ABS and epoxy matrices (Figs. 2(B) and (C), respectively). Conductivity is a consequence of conducting path formation in the insulating polymer matrix. The conducting path from interconnected SWCNT network also contributes to the EMI SE. Because of their better conducting networks, SWCNT/epoxy composites have better conductivity than both SWCNT/ABS and SWCNT/SCPU composites with similar SWCNT loadings. Unlike the thermoplastic ABS and SCPU composites, SWCNT/epoxy composites were prepared by dispersing SWCNTs in the epoxy precursor 618-epoxy before curing with the amine-type hardener. Thus, SWCNTs could be dispersed much better due to the low viscosity of the 618-epoxy solution, leading to the formation of a better conducting network. As a result, the best conductivity, EMI performance (discussed below) was obtained with SWCNT/epoxy composites. Moreover, SCPU have a lower solubility than ABS due to SCPU partly cross-linking and it was harder to obtain a well-dispersed SWCNT composite. Therefore, with the same SWCNT loadings, SWCNT/ABS composites had better conductivity than SWCNT/SCPU composites due to the better dispersion of SWCNTs in ABS matrix. Therefore, SWCNT/SCPU composites had the highest percolation threshold among the SWCNT/polymer composites evaluated here.

To evaluate the EMI shielding performance of SWCNT/polymer composites, we measured the complex permittivity of the composites in the frequency range of 8.2–12.4 GHz (X band). Figure 3 shows the complex permittivity spectra of the SWCNT/SCPU, SWCNT/ABS and SWCNT/epoxy composites containing various SWCNT loadings. Both the real (ε') and imaginary (ε'') permittivity increased dramatically with increasing SWCNT loading. Furthermore, at low loadings, both the real and imaginary parts of permittivity were almost independent of frequency in X band. At higher loadings, the values fluctuated, perhaps because of the high electrical conductivity in the composites with high SWCNT loading.[2] For a given loading, the SWCNT/epoxy composites had the highest real and imaginary permittivity and the SWCNT/SCPU composites had the lowest. The permittivity data pattern corresponded well with the composite conductivity shown in Figure 1.

The much-enhanced imaginary and real parts of permittivity in these SWCNT composites indicated that they are suitable for use as EMI materials in the measured frequency region. Figure 4(a) shows the EMI SE SWCNT/ABS composites with various loadings of SWCNTs. It can be seen that the EMI SE was almost independent of frequency. Furthermore, the EMI SE increased with increasing of the concentration of SWCNTs. The EMI SE performance of SWCNT/SCPU and SWCNT/epoxy composites also had similar results. As can be found in Figure 4(b), the EMI SE of SWCNT/epoxy composites was higher than that of SWCNT/ABS and SWCNT/SCPU composites. For example, with 15 wt% loading, the EMI SE value for the SWCNT/epoxy composite reached 28 dB at 12.4 GHz, while the SWCNT/ABS and SWCNT/SCPU composites exhibited 12 dB and 9 dB, respectively. This trend agreed well with the conductivity (Fig. 1) and permittivity data (Fig. 3). The results and discussion above confirm that the composites with better dispersion of SWCNTs exhibited higher electrical conductivity, permittivity and better EMI shielding.

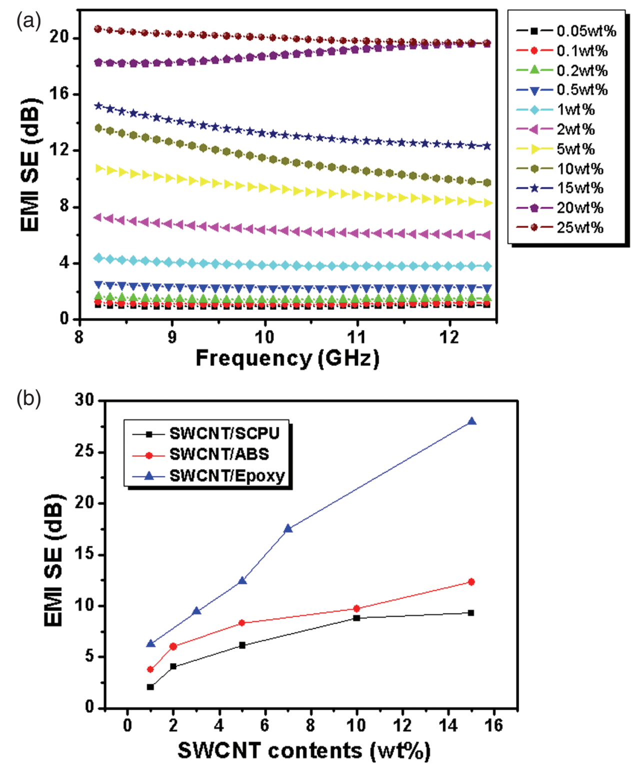

Fig. 4. (a) EMI SE in the range of 8.2–12.4 GHz for SWCNT/ABS (B) and composites with various SWCNT loadings. (b) Comparison of the EMI SE at frequency of 12.4 GHz among the SWCNT/SUPU (Black square), SWCNT/ABS (Red circle), SWCNT/Epoxy (Blue triangle) with SCWNT loadings from 1 to 15 wt%.

4. CONCLUSIONS

The EMI SE in the X band properties had been studied for SWCNT/polymer composites with three representative types of polymer matrices: SCPU, ABS and epoxy. The results demonstrated that the polymer matrix had great impact on the conductivity, percolation threshold, EMI SE performance. The EMI SE of the composites was highly correlated with the dispersion state of the SWCNTs. With the best dispersion of SWCNTs in the epoxy matrix, epoxy/SWCNT composites, 28 dB EMI SE was obtained for the composite with 15 wt% loading of SWCNTs at

12.4 GHz. The EMI shielding performance was strongly related to the degree of SWCNT loading and with increasing SWCNT loading, the EMI SE of SWCNT/polymer composites increased.

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