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The influence of single-walled carbon nanotube structure on the electromagnetic interference shielding efficiency of its epoxy composites

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Abstract

Three types of single-walled carbon nanotube (SWCNT) homogeneous epoxy composites with different SWCNT loadings (0.01–15%) have been evaluated for electromagnetic interference (EMI) shielding effectiveness (SE) in the X-band range (8.2–12.4 GHz). The effect of the SWCNT structure including both the SWCNT aspect ratio and wall integrity, on the EMI SE have been studied and are found to correlate well with the conductivity and percolation results for these composites. The composites show very low conductivity thresholds (e.g. 0.062%). A 20–30 dB EMI SE has been obtained in the X-band range for 15% SWCNT loading, indicating that the composites can be used as effective lightweight EMI shielding materials. Furthermore, their EMI performance to radio frequencies is found to correspond well with their permittivity data.

1. Introduction

The unique structure and excellent properties of carbon nanotubes (CNTs), (both single-walled and multi-walled (SWCNTs and MWCNTs)) has prompted intensive study for potential engineering applications [1–6], for example for CNT conductive composites, in the electronics, automotive and aerospace sectors with uses such as electrostatic dissipation, electromagnetic interference (EMI) shielding, multilayer printed circuits, and conductive coatings. The EMI shielding of radio frequency radiation has become a serious concern in modern society. Light weight and effective EMI shielding is needed to protect the workspace and environment from radiation coming from computers and telecommunication equipment as well as for protection of sensitive circuits. Electrically conducting polymer composites have received much attention recently compared to conventional metal-based EMI shielding materials [7–10], because of their light weight, resistance to corrosion, flexibility and processing advantages. In our recent communication [11], we found that SWCNT–epoxy composites had excellent EMI shielding performance in the frequency range of 10 MHz to 1.5 GHz. However, shielding in the range of 8.2–12.4 GHz (the so-called X-band)is more important for many military and commercial applications. For example, Doppler, weather radar, TV picture transmission, and telephone microwave relay systems lie in X-band [12]. Here we report the first detailed studies of the EMI shielding effect and performance of SWCNT–polymer composites in this band. The results show that the conductivity, percolation threshold, and EMI shielding effectiveness of these composites are strongly correlated to the structure of the SWCNTs. These homogeneous composites should find various applications as effective and

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light weight electrostatic dissipation and EMI shielding materials.

The EMI shielding effectiveness of a composite material depends mainly on the filler's intrinsic conductivity, dielectric constant, and aspect ratio [7,13]. The small diameter, high aspect ratio, high conductivity and mechanical strength of CNTs make them an excellent option to create conductive composites for high-performance EMI shielding materials at very low filling. Despite several studies on the EMI of MWCNT composites [14–17], EMI studies for SWCNT composites are few [11]. The electrical properties of small diameter SWCNTs are distinctly different from their larger diameter MWCNT counterparts. Small diameter (i.e., $1 < d < 2$ nm) SWCNTs can be either metallic or semiconducting depending on their chirality integers (n,m). In addition, small diameter metallic SWCNTs have been found to be exceptional metals, even exhibiting ballistic transport at low temperature [18]. On the other hand, MWCNTs, because of the larger inherent diameter of SWCNTs present in the concentric tube shells (i.e., $d > 5$ nm), should be $\sim$ zero gap semiconductors or exhibit very weak band overlap leading to weak semi-metallic behavior. Thus, per unit wt% added to the polymer host, the nature of the EMI shielding properties of MWCNT- and SWCNT–polymer composites are expected to be altogether different.

Three types of SWCNTs with different aspect ratios and/or wall structures have been used for the fabrication of the SWCNT composites in this study with which we have studied the relationship of EMI shielding effectiveness to the SWCNT structure (i.e., aspect ratio and wall integrity) in X-band.

2. Experimental

2.1. Materials

The SWCNTs used in this study were produced using our modified arc-discharge method [19,20] and have diameters mainly in the range of 1.3–1.8 nm. Three types with different aspect ratios and/or wall structures were then used for the fabrication of the SWCNT composites. These were made by [11,19]: (1) arc vaporization, using He as the carrier gas in the arc chamber; this material exhibited the largest bundle length/diameter aspect ratio (i.e., referred to here as "long-SWCNTs"); (2) arc vaporization using He/10% CO_2 as the carrier gas; these materials exhibited a smaller aspect ratio (referred to here as "short-SWCNTs"); and (3) material obtained after annealing the "short-SWCNTs" at 1100 °C for 3 h in a tube furnace under N_2 (referred to here as "annealed-SWCNTs").

The SWCNT–polymer composites for EMI shielding studies were fabricated as below. A commercially available bisphenol A-type epoxy resin (618 type, Tianjin Resin Company) and an amine-type hardener ($[C_{17}H_{31}CONH(C_2H_4NH)_2H]_2$, Tianjin Ningping Chemical Co., LTD, Model: A022-2) were used to prepare the polymer matrix. The resin/curing agent ratio was 2/1. The following example gives the process to prepare the composite with 1 wt% of "long-SWCNTs" loading. The "long-SWCNTs" (0.15 g) were first dispersed in acetone (200–300 mL) in an ultrasonic bath (Gongyi Yuhua Instrument Co., LTD, Model: KQ400B, 400 W) at room temperature for 1 h and then an epoxy resin/acetone solution (10 g epoxy in 50 mL) was added to the suspension of the SWCNTs. The mixture was then again sonicated for 1.5 h, and the hardener (5 g) was added with mechanical stirring. The mixture was further sonicated for 15 min, and then most of the acetone was evaporated. The mixture was poured into suitable molds to allow any remaining acetone to evaporate completely at room temperature in air. The composite was then further cured at room temperature overnight. Other composites with different loadings and SWCNTs were prepared similarly. The samples were cut to slabs of the desired sizes and the surfaces of the slabs were polished if necessary.

2.2. Measurements

The dc electrical conductivity of the SWCNT–epoxy composites was determined using the standard four-point contact method on rectangular sample slabs in order to eliminate contact-resistance effects at room temperature. Data were collected with a Keithley SCS 4200. The EMI shielding effectiveness and permittivity data of the SWCNT–epoxy composites were measured using slabs of dimension 22.86 mm × 10.16 mm × 2 mm (to fit waveguide sample holder), by an HP vector network analyzer (HP E8363B) in 8.2–12.4 GHz (X-band) range. DSC was obtained using a NETZSCH STA 409 PC, with a heating rate of 2 °C/min from room temperature to 800 °C in a mixture of N_2:O_2 (4:1). An XRD analysis was carried out on a Rigaku D/Max-2500, using standard Ni-filtered CuKα radiation ($k = 1.5418$ Å).

3. Results

The EMI performance for a composite is related to the filler's intrinsic conductivity, dielectric constant, and aspect ratio [7,13], and the conductivity of conductor–insulator composites follows the critical phenomena around threshold. Fig. 1 shows the dc conductivity (σ) of our SWCNT–epoxy composites as a function of the SWCNT mass fraction (p) and all exhibit an increase of 10 orders at low loadings, indicating the formation of percolating network. For example, below 0.6 wt%, the conductivity of the "long-SWCNTs" composites displays a dramatic increase of over 10 orders of magnitude and the conductivity reaches 0.20 S/cm at 15 wt% loading of "long-SWCNTs". This value is 12 orders of magnitude higher than that of the pure epoxy resin (i.e., 2.44×10^{-13} S/cm).

Thus far, studies on the conductivity of SWCNT–polymer composites have shown low thresholds at various volume fractions with different fabrication methods and different SWCNT aspect ratios [21–23]. For practical applications, it is critical to have a low filling threshold, since lower filling fractions imply smaller perturbations of bulk physical properties as well as lower cost. It is well known that the conductivity of a conductor–insulator composite follows the critical phenomena around the percolation threshold (Eq. (1)) [24]:

$$\sigma \propto (v - v_c)^{\beta}, \tag{1}$$

where σ is the composite conductivity, v is the SWCNT volume fraction, v_c is the percolation threshold and β is the critical exponent. Because the densities of both the epoxy resin and the SWCNTs are similar (1.2–1.4 vs 1.3–1.4 g/cm^3), we assume that the mass fraction, p, and the volume faction, v, of the SWCNTs in the polymer are almost the same. As shown in the inset to Fig. 1, for the log (σ) vs log $((p - p_c)/p_c)$ plot, a least-squares analysis of the fits using Eq. (1) showed that the threshold volume p_c for each

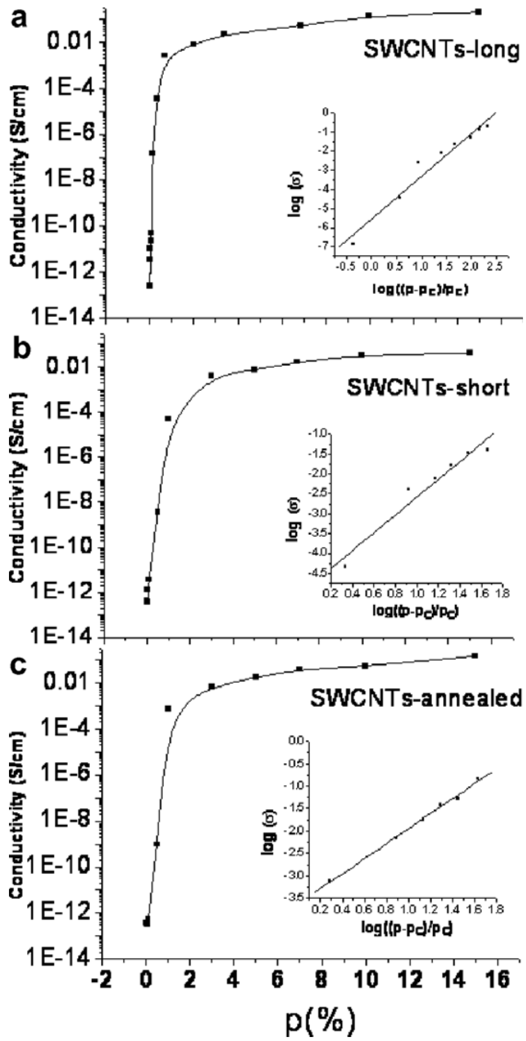

Fig. 1. log10 DC conductivity (σ) vs mass fraction (p) of SWCNT–epoxy composites ((a), (b) and (c) for "long-SWCNTs", "short-SWCNTs" and "annealed-SWCNTs" composites, respectively) measured at room temperature. Inset: log–log plots (σ vs $(p - p_c)/p_c$) were generated using Eq. (1) and a least-squares fit to the data near the threshold.

set of composites was strongly bounded by the regions between the highest insulating and lowest conducting points and the SWCNT–epoxy composite conductivity agrees very well with the percolation behavior predicted by Eq. (1).

Table 1 summarizes the percolation thresholds and critical exponents of the three sets of composites in Fig. 1 (found using Eq. (1)). The percolation thresholds are found to be quite low, that is, 0.062 wt% of "long-SWCNTs" and in good agreement with previous studies for SWCNT–polymer systems [22,23]. This indicates that the SWCNTs were well distributed in the polymer matrix using our processing method. Good values of percolation threshold were also obtained for the other two sets of composites containing "short-SWCNTs" and "annealed-SWCNTs" (0.318% and 0.342%). Because "short-SWCNTs" and "annealed-SWCNTs" composites have similar aspect ratio and percolation threshold values and the composites with

Table 1
Percolation thresholds, critical exponents, and correlation factors for the three sets of composites

SWCNTs used	Percolation threshold (%), p_c	Critical exponent β	Correlation factor R
"Long-SWCNTs"	0.062	2.68	0.980
"Short-SWCNTs"	0.318	2.22	0.975
"Annealed-SWCNTs"	0.342	1.67	0.997

"long-SWCNTs" have much lower percolation threshold, we believe that aspect ratio have stronger impact on the percolation threshold using the same processing method. The values of the critical exponent β were also found to be in good agreement with the theoretical results for a percolating rod network system [21,25].

Recent studies have shown that SWCNT–polymer composites possess high real permittivity (polarization, ε') as well as imaginary permittivity (adsorption or electric loss, ε'') in the 0.5–2 GHz range [26], indicating that such composites could be used as the electromagnetic shielding material for cell-phone electronic protection [11]. However, operation of EMI or/and RAM at higher frequencies would be highly desirable. To evaluate the EMI performance of SWCNT–polymer composites, we thus measured the complex permittivity of our composites in the frequency range of 8.2–12.4 GHz (X-band). Fig. 2 shows the complex permittivity spectra of the composites containing 0.01–15% of "long-SWCNTs". As can be seen, the real (ε') and imaginary (ε'') permittivity increase dramatically as the concentration of the SWCNTs increases from 0.01 to 15 wt%. The highest values of the real and imaginary permittivity parts for the composite with 15% SWCNT loading reach 67 and 76, respectively. Overall the real and imaginary parts of permittivity for the composites with 15 wt% of SWCNTs range from 67–42 and 76–60 in the frequency of 8.2–12.4 GHz. These are much higher than those of 15 wt% carbon nanofibers in polystyrene (ε': 38–29, ε'': 24–19) [10], and are close to or better than those of the MWCNT–polymer composites in the X-band with similar loadings [12,14,16,26,27]. Furthermore, at low loadings, both the real and imaginary parts of permittivity are almost independent of the frequencies in the range we measured. At higher (e.g. 15%) loading, these values tend to decrease with increasing of frequency. The absolute values of the measured permittivity are of the same order of magnitude as those reported by Grimes et al for SWCNT–polymer composites in the 0.5–2 GHz range [26]. The permittivity of the "short-SWCNTs" and "annealed-SWCNTs" epoxy composites (not shown) gave similar patterns.

The EMI shielding effectiveness (SE) of a material is defined as SE (dB) = $-10\ \log_{10}(P_t/P_0)$, where P_t and P_0 are the transmitted and incident electromagnetic power, respectively,. For example, an attenuation of the incident beam by a factor of 100 (i.e., 1% transmission) is equivalent

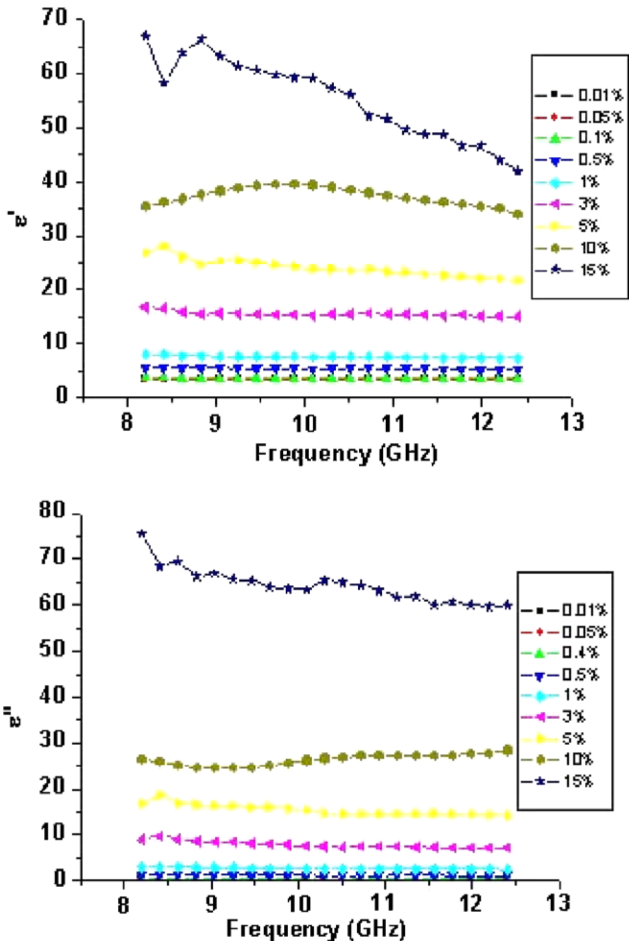

Fig. 2. Complex permittivity spectra of the composites using "long-SWCNTs" with loading from 0.01 to 15 wt%.

to 20 decibels (dB) of attenuation. The much enhanced imaginary and real parts of permittivity of these SWCNT composites indicate that they are suitable for use as EMI materials in the measured frequency region. Fig. 3 shows the EMI shielding effectiveness for the three sets of composites, "long-SWCNTs", "short-SWCNTs" and "annealed-SWCNTs" with 0.01–15 wt% SWCNT loadings. We find that SE increases with increasing wt% SWCNTs at a fixed frequency. At low loadings, the SWCNT–epoxy composites exhibit an almost frequency independent EMI SE performance. At higher loadings, the EMI SE values tend to fluctuate more. This pattern is also found for the permittivity data, shown above in Fig. 2. It is evident that the main contribution to the EMI shielding comes from the addition of the SWCNTs.

The target value of the EMI shielding effectiveness for commercial applications is around 20 dB. As shown in Fig. 3, the composites made from both the "long-SWCNTs" and the "annealed-SWCNTs", exhibited SE ~ 20 dB in the X-band for both 10 and 15 wt% loadings. This indicates that SWCNT/epoxy composites with 10–15 wt% of SWCNTs can meet the commercial SE application requirement. The EMI SE of composite with 15 wt%

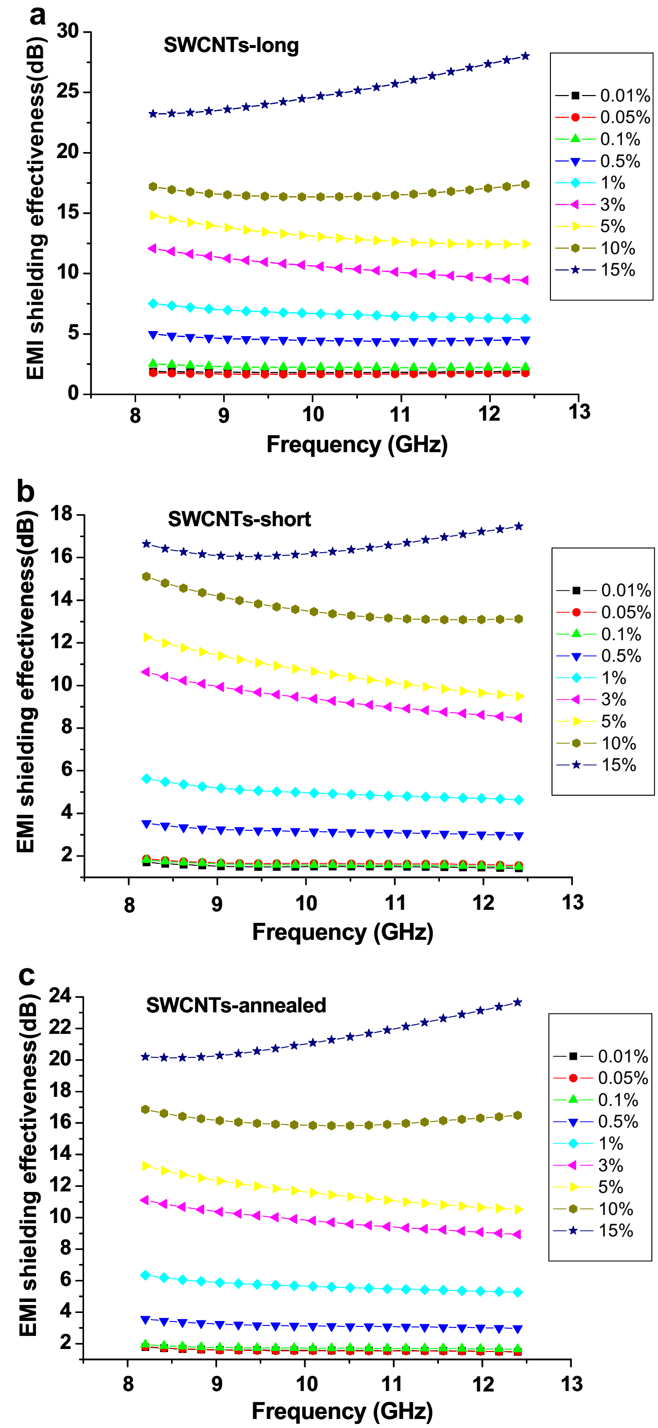

Fig. 3. EMI shielding effectiveness for SWCNT(0.01–15 wt%)-epoxy composites studied in 8–12 GHz. (a) "long-SWCNTs", (b) "short-SWCNTs", (c) "annealed-SWCNTs".

of "long-SWCNTs" is in the range of 23–28 dB in 8.2–12.4 GHz, which is higher than that of 15 wt% carbon nanofibers [28] in polystyrene (18–19 dB) but very close to the results of 40 wt% MWCNTs [15] in PMMA (23–26 dB) in the same frequency range. Overall, these results are comparable with those observed for the MWCNT–polymer composites with different matrices [14–17].

The conductivity, and permittivity of the three SWCNT composites with the same loadings all show considerable differences. We were thus motivated to study and compare in more detail the changes in the EMI performance of the composites and their structure–property relationship for the three different types of SWCNTs. Fig. 4a shows the EMI SE results for the three sets of composites with 0.01–15 wt% of SWCNTs at 10 GHz. It can be seen that the values of SE increase with increasing wt% of the SWCNTs. But more interestingly, while the SE values have smaller differences at low loadings for the three sets of SWCNT composites, with increasing loading of SWCNTs, the SE values increase fastest for the SWCNTs-long composites and slowest for the "short-SWCNTs" composites. This trend is particularly evident after the percolation threshold point.

Fig. 4b gives the SE of these composites with 15 wt% of SWCNTs at 8.2–12.4 GHz. It can be seen that the SE of the "long-SWCNTs" composites is significantly higher than that of the "short-SWCNTs" composites at all frequencies. After the "short-SWCNTs" were annealed at high temperature, the SE for their composites increased significantly, but was still lower than that of the "long-SWCNTs" composites. For example, the EMI SE of the composites with 15 wt% of "long-SWCNTs", of "annealed-SWCNTs" and of "short-SWCNTs" were 25, 21 and 16 dB at 10 GHz, respectively. These results are similar to those in the 10 MHz to 1.5 GHz frequency range [11].

Although it is expected that wall defects and the aspect ratio will affect EMI SE values, their impact on EMI shielding has not yet been explored in either MWCNT- or SWCNT–polymer composites [12]. According to percolation theory, if the conductive filler in the matrix has a high aspect ratio, then the filler should form a conductive network at a lower wt%. For example, Yodh et al. reported detailed dc conductivity studies for composites with different SWCNTs and they have found that the SWCNT bundle aspect ratio significantly impacts the threshold concentration and the composite conductivity [21]. Once percolation is achieved, EM theory indicates that the EMI SE should increase dramatically [7]. We therefore decided to study how the SWCNT aspect ratio and its surface structure/morphology affect the SWCNT–epoxy EMI performance as well as other properties.

To study the impact of annealing on the wall structure, we compared the XRD and DSC for the three types of SWCNTs.

Fig. 5 shows the DSC curves of the "long-SWCNTs", "short-SWCNTs" and "annealed-SWCNTs". Line A for the "long-SWCNTs" in Fig. 5 shows two peaks in the vicinity of 337 °C and 403 °C. The first peak is usually associated with the oxidation of amorphous carbon and the second peak with the SWCNTs [29,30]. From the DSC of the "short-SWCNTs" (curve B), it can be seen that the peak near 340 °C was much weaker, implying that the "short-SWCNTs" have less amorphous carbon [19]. However, weak oxidation by CO_2 in the arcing process might also introduce more defects in the wall of SWCNTs. This is consistent with the downward movement of the peak

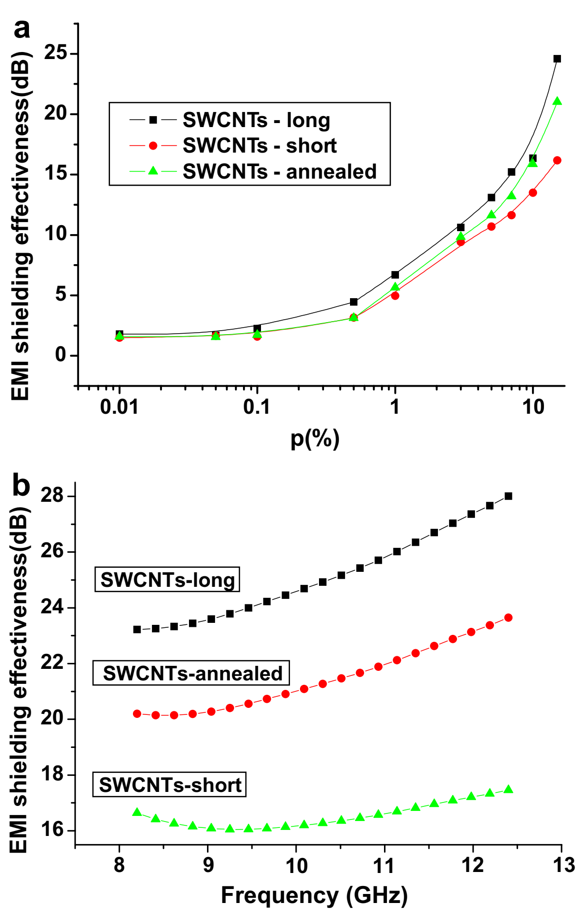

Fig. 4. EMI shielding effectiveness (SE) for SWCNT–epoxy composites. (a) SE of SWCNT (0.01–15 wt%)-epoxy composites at 10 GHz; (b) SE of SWCNT (15 wt %)-epoxy composites in the range of 8.2–12.4 GHz.

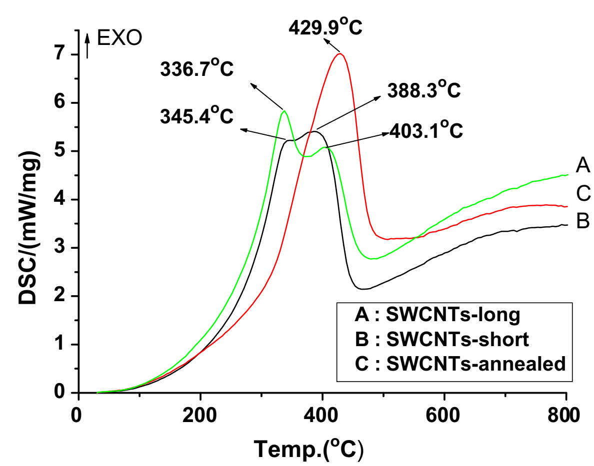

Fig. 5. The DSC curves of "long-SWCNTs", "short-SWCNTs" and "annealed-SWCNTs". Heated at a rate of 2 °C/min from room temperature to 800 °C in a mixture of N_2:O_2 = 4:1.

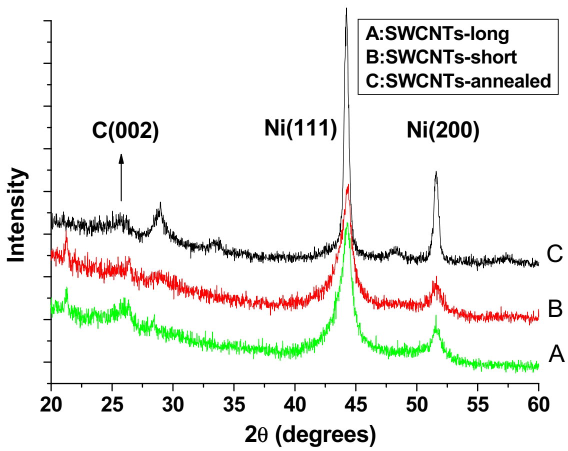

Fig. 6. XRD of different SWCNTs. FWHM and Intensities were obtained from XRD data analysis program (search peak) directly.

associated with SWCNTs at ~400 °C. The oxidation peak of the SWCNTs shifts from around 403 °C for the "long-SWCNTs" varieties to 388 °C for the "short-SWCNTs" varieties. After annealing, both the defects and amorphous carbon could be partially removed and the wall structure integrity was improved. Then the DSC curve shows only the peak mainly associated with SWCNTs, and the degradation temperature (430 °C) increased for the "annealed-SWCNTs" tubes (curve C). Similar results were observed from the XRD data (Fig. 6). The full width at half maximum (FWHM: 0.447, from XRD data analysis program using the search peak function) of the C(002) (typically $2\theta = 26.42$ °) peak of the "short-SWCNTs" was much larger than that of the "long-SWCNTs" (0.141). But the peak intensity of the "short-SWCNTs" was much lower than that of the "long-SWCNTs" (1616 vs 1929). High temperature annealing of the CNTs has been shown to be a good way to increase the graphitic perfection of the carbon nanotubes [31]. From curve C in Fig. 6, we can see the FWHM of C(002) peak of the SWCNTs-annealed is 0.188, much smaller than that of the "short-SWCNTs" (0.447). The intensity also reaches 1949, much higher than that of the "short-SWCNTs" (1616). It is known that narrower FWHM and higher intensities of C(002) peaks are indicative of a more developed graphitic structure [31]. These results clearly show that "short-SWCNTs" produced using CO_2 have more defects than those produced without CO_2. The defects however, are mostly removed after annealing. All the DSC and XRD results indicate that the wall structure of the "short-SWCNTs" is improved after annealing.

4. Discussion

4.1. Conductivity and percolation threshold

It is worth noting that "long-SWCNTs" composites have the best conductivity and lowest threshold volume. Filler conductivity and aspect ratio are two keys to affect the conductivity and percolation behavior of composites [21]. It is important to find out how after fabrication, the SWCNT structure, including its aspect ratio and wall integrity (defect), affect the threshold values for the three sets of SWCNT–polymer composites. Using AFM, we previously found [19] that the average aspect ratio of bundles of "short-SWCNTs" ($L/D = 740/5.32 = 139$, ±8% error) was significantly lower than that ($1430/5.95 = 240$) of "long-SWCNTs". From the simplified percolation and EMI theories for the isotropic dispersion of a random rod network [21], the SWCNT composites with higher SWCNT bundle aspect ratio are predicted to have lower percolation threshold concentration, higher conductivity and better EMI shielding performance under the same wt% loading. Indeed, this is what we observed above. For example, the conductivities and percolation thresholds for the composite with 15% loading were 0.20 S/cm and 0.062%, respectively, for the "long-SWCNTs" composite and 0.04 S/cm and 0.318% for the "short-SWCNTs" composite.

As we mentioned above, high temperature annealing of the CNTs has been shown to increase the graphitic perfection of the carbon nanotubes [31]. This annealing should therefore be expected to improve the dc conductivity of the SWCNTs. While more detailed work is needed to study the impact of the surface chemistry of "annealed-SWCNTs" in the composites, we believe the improved conductivity for "annealed-SWCNTs" composites is because the high temperature annealing in inert gas or vacuum could have removed wall defects and amorphous carbon and thus improved the composite conductivity. Indeed, this is supported by the DSC and XRD data above. While the "annealed-SWCNTs" have similar aspect ratio and therefore similar threshold value as "short-SWCNTs" composites, the former composites are expected to have better conductivity due to their improved wall integrity caused by the annealing process. We have observed this, as is shown in Fig. 1. For example, the conductivity (0.15 S/cm) for the composite with 15% loading of "annealed-SWCNTs" is better than that (0.04 S/cm) for the composite using "short-SWCNTs" (same loading). Both, however, have lower conductivity than that (0.20 S/cm) for the composite with 15% "long-SWCNTs" loading.

These results clearly indicate that both the SWCNT aspect ratio and wall integrity have a strong affect on the composite conductivity and are in agreement with the expectations of simple models for percolation in random rod networks [21].

4.2. EMI shielding effectiveness

As was observed for the conductivity and threshold values for the three sets of composites, the "long-SWCNTs" composites show the best EMI shielding, while the "annealed-SWCNTs" composites are better than that of the "short-SWCNTs" ones. For example, the EMI SE of the composites with 15 wt% of "long-

SWCNTs" and "annealed-SWCNTs" were 25 and 21 dB at 10 GHz, respectively; both are better than that (16 dB) for corresponding "short-SWCNTs" composite. According to EMI theory, the filler with a high aspect ratio should have better EMI shielding performance for the same composites. The improved wall integrity of SWNTs after high temperature annealing and thus the better conductivity of their composites are expected to improve their EMI shielding. It is worth noting that although the EMI shielding effectiveness increases significantly after annealing, but the composites using "annealed-SWCNTs" still exhibited lower EMI SE than the composites with the same loading based on "long-SWCNTs". This should be because of the higher aspect ratio of "long-SWCNTs" than that of "annealed-SWCNTs" and is also consistent with the higher observed conductivity (0.20 S/cm for 15% loading) of the composite with "long-SWCNTs" than that (0.15 S/cm for 15% loading) of "annealed-SWCNTs". But to draw a quantitative conclusion for which parameter between aspect ratio and wall integrity is more sensitive for better EMI SE, more detailed studies need to be done.

5. Conclusion

In summary, we have fabricated three sets of SWCNT–epoxy composites using three different SWCNTs: long, short and annealed, with different aspect ratios and wall integrities. Very low percolation volumes and 20–30 dB EMI shielding effectiveness in the X-band were obtained for their epoxy composites. The results from conductivity, EMI SE and morphology studies show that the percolation threshold and EMI shielding performance of composites using these SWCNTs are highly correlated with the aspect ratio and wall integrity of the SWCNTs. That is, high aspect ratio and better surface integrity of the SWCNTs gave better conductivity, lower threshold and higher EMI performance. With controllable synthesis of SWCNTs [19], a new approach to effectively tune the conductivity and EMI performance for SWCNT composites is now possible. These composites are thus very promising for use in both civil and military electrical applications as effective light-weight EMI shielding materials.

Acknowledgements

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