Mild functionalization of carbon nanotubes filled epoxy composites: Effect on electromagnetic interferences shielding effectiveness

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ABSTRACT: The effect of nitric acid mild functionalized multiwalled carbon nanotubes (MWCNTs) on electromagnetic interference (EMI) shielding effectiveness (SE) of epoxy composites was examined. MWCNTs were oxidized by concentrated nitric acid under reflux conditions, with different reaction times. The dispersion of MWCNTs after functionalization was improved due to the presence of oxygen functional groups on the nanotubes surface. Functionalization at 2 h exhibits the highest EMI SE and electrical conductivity of MWCNTs filled epoxy composites. However, EMI shielding performance of MWCNTs filled epoxy composite declined when the functionalization reaction time was prolonged. This was due to extensive damage on the MWCNT structure, as verified by a Raman spectroscope. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42557.

INTRODUCTION

Nowadays, the wide use of electronic devices and instruments in the commercial, industrial, healthcare, and defense sectors has brought about a serious new pollution problem, known as electromagnetic interference (EMI). The high power of EMI can cause the disturbance or malfunction of electronic devices or instruments in power systems, communications, healthcare etc., which induces significant losses in time, energy, resources, and money.[1] Therefore, an effective method for shielding against unwanted electromagnetic waves is in great demand.

The potential of carbon nanotubes (CNTs), used as a conductive additive for EMI shielding polymer composite, has been studied extensively in recent years. Compared with metal EMI-shielding materials, CNT-based polymer composites have advantages such as being lightweight, corrosion-resistance, flexible, and easy to process.[2] Yang *et al.* introduced multiwalled CNTs (MWCNTs) into polystyrene foam, to form an EMI shielding composite.[3] An EMI shielding effectiveness (SE) around 20 dB was achieved, with 7 wt % MWCNT loading, at a frequency range of 7–12 GHz. In addition, the correlation between SE and electrical conductivity of the composites was reported, and they concluded that composites with higher conductivity are efficient in shielding EMIs.

Despite the potential of CNTs in EMI shielding applications, the main limitation of CNTs is their poor dispersion in organic matrices in their pristine state. The nanotubes tend to agglomerate, due to strong intertube Van der Waals forces, and high surface energy in nature.[4] To improve dispersion, and promote interfacial bonding between CNTs and polymer matrix, the functionalization of CNTs is needed.[5] Acid oxidation is one popular route in chemical modification for CNTs. Oxygen-containing functional groups such as hydroxyl, carbonyl, and carboxylic functional group can be introduced on CNTs through acid oxidation.[5] These functional groups facilitate the dispersiveness of CNTs' aqueous solutions and organic solvents, thus improving their dispersion and adhesion when added to the polymer matrix. However, these acid oxidation methods have some drawbacks: that is, the occurrence of CNT fragmentation (shortening); defect-generation in the graphitic network; accumulation of carbonaceous impurities; disappearance of small diameter nanotubes; and overall loss of material.[6] This structural damage may affect the unique properties of CNTs, especially for EMI shielding performance. Intensive studies of EMI shielding performance using MWCNT composites have been done by many researchers over the past few years.[3,7,8] However, work on the effect of MWCNTs' functionalization on EMI shielding performance is rarely reported. The performance of EMI shielding is commonly measured based on the effectiveness of the shielding materials to block the incoming electromagnetic wave.

Therefore, the aim of this study is to identify sufficiently mild conditions that can provide successful CNT functionalization
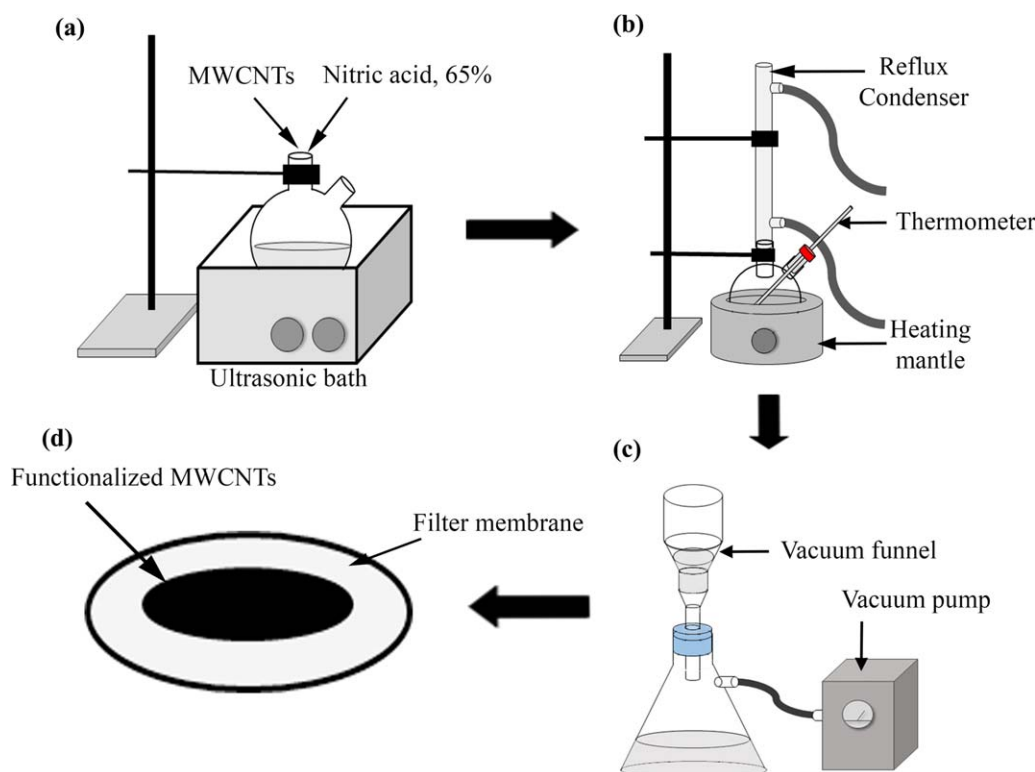
Figure 1. Schematic illustration of functionalization steps: (a) sonication, (b) heating under reflux, (c) vacuum filtering, and (d) functionalized MWCNTs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

without significant CNT damage. This functionalized CNT filled polymer might improve the EMI SE. Nitric acid treatment is implemented since this treatment is preferred for the controlled formation of functional groups, with minimal damage to the CNTs' structure.[9] In this study, the EMI SE of MWCNT composites was measured using a vector network analyzer, with a frequency range of 7.0–12.0 GHz. Moreover, the effect of functionalization duration on the surface chemical composition, dispersion stability, electrical properties, and EMI shielding performance of functionalized MWCNTs was examined.

EXPERIMENTAL

Materials

MWCNTs were purchased from USAINS Holding, Universiti Sains, Malaysia. These MWCNTs were produced via a catalytic chemical vapor deposition process, with carbon purity of more than 80%.[10] Average diameter and average length of MWCNTs are 10 ± 1 nm and 1–5 μm, respectively. Residuals of the MWCNTs may include molybdenum and cobalt. Epoxy resin used in this research is D.E.R 332 Epoxy Resin, a bisphenol A diglycidylether (DGEBA), with epoxide equivalent weight of 171–175 g eq^{-1}. Epoxy resin was supplied by Penchem Technologies Sdn. Bhd. Polyetheramine, D230 M was used as a hardener in this study. Here, the mixing ratio was set to 100 epoxy resin:32 hardener. Nitric acid 65% for analysis (maximum 0.005ppm Hg) EMSURE ISO was purchased from Merck Millipore.

Functionalization of MWCNTs

The functionalization of MWCNTs was conducted at various reaction times (1, 2, 3, 4, 6, 12, and 24 h). Here, the functionalization process used was based on previous works.[5–9] However, modifications on process parameters and pre-sonication step before reflux were considered in the study. In this study, 0.3 grams of pristine MWCNTs were added to a 250-ml Pyrex round-bottom flask, containing nitric acid aqueous solution (65%). The mixture of MWCNTs and nitric acid was sonicated in a conventional ultrasonic bath (Sono Swiss SW12H) for an hour, to promote MWCNTs disentanglement within the acid solution. Next, the mixture was heated by a heating mantle under reflux, at a temperature of 120°C, according to the designated reaction time. After reflux, the mixture was filtered using vacuum filtration, with a 0.45-μm polytetrafluoroethylene membrane (Merck Milipore), and the filtration residue was rinsed with deionized water until all the nitric acid was neutralized. The functionalized MWNCTs (F-MWCNTs) were dried in a vacuum oven for 24 h, at 80°C. Figure 1 shows the schematic illustration of MWCNTs' functionalization steps.

Sample Preparation

The EMI shielding composites were fabricated by conventional casting method, and classified according to treatment time, as shown in Table I. Functionalized MWCNTs (F-MWNCTs) were added into epoxy resin (D.E.R 332). The mixture was sonicated with a sonicator (Hielscher—Ultrasound Technology, UP200S) at room temperature, for 10 min, with 50% amplitude, and 0.5

Table I. Composites Preparation Based on MWCNTs Functionalization Reaction Time

Sample name	Functionalization reaction time (h)
EWMCNT-0H	Pristine MWCNTs
EWMCNT-1H	1
EWMCNT-2H	2
EWMCNT-3H	3
EWMCNT-4H	4
EWMCNT-6H	6
EWMCNT-12H	12
EWMCNT-24H	24

sonication cycle. Once the sonication process was completed, the curing agent (Polyetheramine, D230 M) was added into the mixture, at a ratio of 100 : 32 by weight (epoxy:curing agent). Immediately, the mixture was sonicated for another 10 min, in the presence of an ice-water bath, to slow down the curing process. After sonication, the mixture was placed into a vacuum oven (National Appliance Model 5831) for 45 min, for the degassing process, to remove the air entrapped during sonication. In the meantime, soup water was applied to the glass mold as a releasing agent. Once the degassing process was finished, the mixture was poured into a glass mold, and dried at room temperature for 12 h. Finally, the composite sheet was cured at 80°C for 2 h.

Characterizations

The surface chemical composition of F-MWCNTs was analyzed using Perkin Elmer Spectrum One Fourier transform infrared spectroscopy (FTIR), in transmission mode. The wavelength range used was 700–4000 cm^{-1} with eight scanning times. The effect of functionalization on MWCNTs' structure was examined with a Renishaw inVia Raman microscope. In this testing, 633 nm of He-Ne laser with 20 nW power was used for excitation, and focused with the magnification of 50×. The scanning range used was 1200–1900 cm^{-1}, with three scanning time. The homogeneity of the MWCNTs' dispersion in the epoxy matrix was observed with field emission scanning electrons microscopy (FESEM, Zeiss Supra 35VP), on the fracture surface of the composite, with 10.0 kV under 5 and 10 K magnification. The composite was fabricated by introducing 1.0 vol % of F-MWNCTs into the epoxy matrix and the thickness for all the composites was set to 1 cm.

The direct current (DC) volume resistivity of composites was measured by Advantest R8340 Digital Ultra-High Resistance Meter at room temperature. Silver paste was applied onto the contact surface of the composite, to minimize the contact resistant. The EMI SE measurement method used in this study was a waveguide system. This setup was according to a previous work.[11] The composite was located in between two adapters during the measurement. The vector network analyzer was calibrated by using electronic calibration (ECal) modules before the measurement. After calibration, the waveguide adapters were connected to the vector network analyzer via a coaxial cable.

The composites were placed in between the adapters, and the S parameters were measured from 7 to 12 GHz.

RESULTS AND DISCUSSION

Surface Chemical Composition

Based on FTIR spectra of pristine MWCNTs, shown in Figure 2, there are some obvious peaks found at 880, 1040, 1400, and 2360 cm^{-1}. These peaks could be assigned to the isolated aromatic C—H out-of-plane bending mode, stretching vibration of C—O in ethers, H—O bending vibration in water, and CO_2, respectively, that were absorbed during sample preparation of FTIR.[5,12,13] Furthermore, the presence of these O—H functional groups on the pristine MWCNTs might be due to ambient atmospheric moisture absorbed by MWCNTs, or potassium bromide, KBr.[5] By comparing the FTIR spectra of pristine MWCNTs and functionalized MWCNTs (F-MWCNTs), except 1 h functionalized MWCNTs, some new peaks appeared on all the functionalized MWCNTs spectra, at 1630, 1720, and 3410 cm^{-1}. The spectra peaks at 1630 and 1720 cm^{-1} refer to the C=O stretching vibration in carboxylic, and the broad transmission band at 3410 cm^{-1} refers to the O—H stretching vibration in phenols, and carboxylic functional groups.[5,14,15] No extra peaks that represented the oxygenic functional groups are found in FTIR spectrum of 1 h functionalized MWCNTs, since 1 h treatment is only sufficient to remove the residue of amorphous carbon that present after synthesis process.

From the spectra in Figure 2, the broad transmission band at 3410 cm^{-1}, which indicates the formation of O—H functional group, was introduced onto the surface of MWCNTs after 2 h reaction, even though the intensity of the peak was relatively low. The low peak intensity for the short reaction indicates that the oxidation process was not completed.[5] The intensity of this peak increased with the reaction, which indicated that the amount of the O—H functional group on the surface of MWCNTs increased as well. When the reaction reached 12 h (Figure 2(e)), the carboxylic group was introduced onto the surface of the MWCNTs, which is represented by peaks 1630 and 1720 cm^{-1}. This finding is consistent with the outcome reported by previous works.[9,14] According to these findings, the functionalization reaction starts with the formation of the carbonyl group on the surface defects of the MWCNTs. After an hour, the phenol group is generated, and finally, lactones, anhydrides, and carboxylic functional groups are formed accordingly. The formation rate of the carboxylic functional group is relatively slower than other oxygen-containing functional groups.[9] In short, based on the FTIR spectra, it is observed that the MWCNTs were functionalized successfully via chemical oxidation. This is shown by the increase of surface oxygen-containing functional groups with functionalization reaction times from 2 to 24 h.

Effect of Functionalization on MWCNTs Structure

Acid oxidation of MWCNTs is often attributed to surface defects on the MWCNTs' structure. The Raman spectra of pristine MWCNTs and F-MWNCTs with different reaction times are shown in Figure 3. There are three characteristic bands observed in the Raman spectra, namely: D-band at approximately 1330cm^{-1}; G-band at approximately 1580 cm^{-1}; and D' band at 1610 cm^{-1}. The D-band is commonly associated with
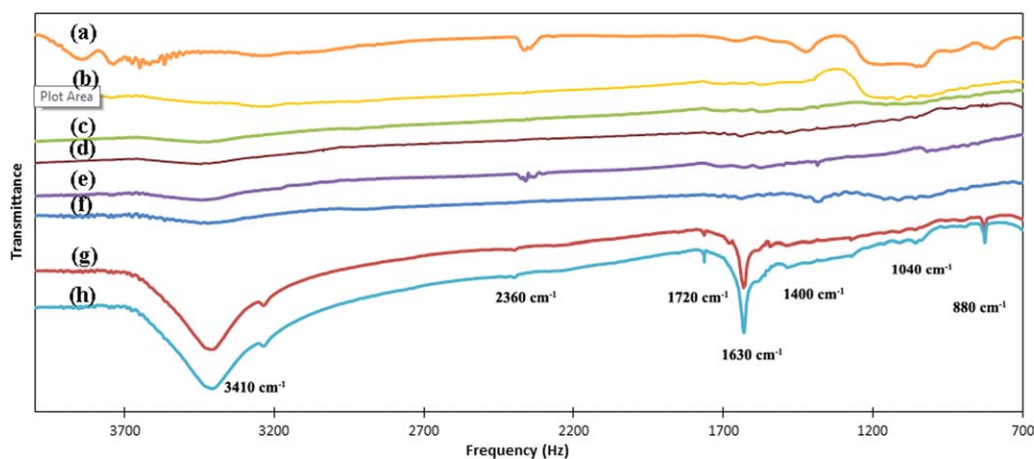
Figure 2. FTIR spectra of (a) Pristine MWCNTs, (b) F-MWCNTs with 1 h reaction, (c) F-MWCNTs with 2 h reaction, (d) F-MWCNTs with 3 h reaction, (e) F-MWCNTs with 4 h reaction, (f) F-MWNCTs with 6 h reaction, (g) F- MWCNTs with 12 h reaction, and (h) F-MWCNTs with 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the disordered sp³ carbon atoms, or amorphous carbon.[16] The disorder of carbon structure is due to defects on the nanotubes' sidewalls, vacancies, heptagon-pentagon pairs, kinks and heteroatoms.[17] The G-band represents the sp² carbon atoms in graphene sidewalls, with well-ordered structure.[16] The D′ band at higher frequencies is also associated with double resonance feature caused by disorder and defects.[17] The intensity ratio of I_D/I_G is often used as the indicator to quantify the degree of disorder of the nanotubes.

In Figure 3, it is obvious that an increment of D-band intensity was observed after nitric acid functionalization, and intensity increased with the reaction times. After spectrum normalization, the intensity ratio I_D/I_G was estimated, and is summarized in Table II. Based on Table II, the intensity ratio I_D/I_G increased sharply right after 2 h functionalization, from 1.42 to 2.04, and kept increasing until it reached 2.89 at 24 h functionalization. The increases in the intensity ratio I_D/I_G clearly indicated that the acid oxidation of MWCNTs etches the surface of the nanotubes by breaking some of their bonds, and forming the functional groups.[15]
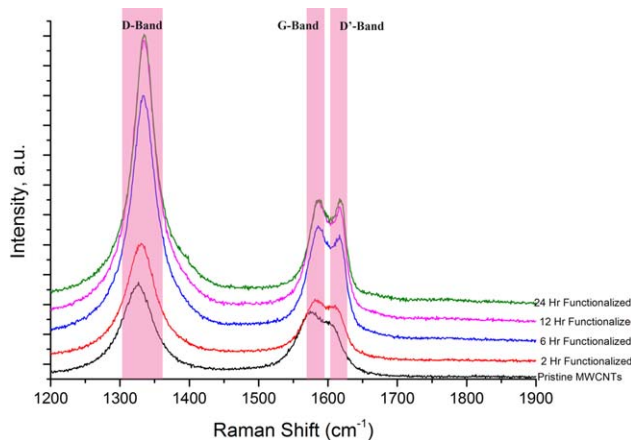

Figure 3. Raman spectra of MWCNTs samples after functionalization with different reaction times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Homogeneity of the MWCNTs Dispersion

The homogeneity of the MWCNTs' dispersion in the epoxy matrix was observed using field emission scanning electrons microscopy (FESEM) on the fracture surface of the composite, as shown in Figure 4. Figure 4(a,b) shows the FESEM micrographs of the fracture surfaces of composites, with the pristine MWCNTs and 2 h F-MWCNTs fillers, respectively. It can be clearly observed from Figure 4(a) that the dispersion of pristine MWCNTs was poor in an epoxy matrix, and large MWCNTs agglomerates were observed. In addition, MWCNTs are also seen protruding from the facture surface, suggesting a large occurrence of MWCNT pullout, which is indicated by weak interfacial bonding between the pristine MWCNTs and the epoxy matrix. In contrast, the 2-h functionalized MWCNTs were dispersed homogeneously in an epoxy matrix, as shown in Figure 4(b). Composites with F-MWCNTs do not show bare nanotube pullout, and have a good contact with matrix, which may contribute to a good interfacial interaction between F-MWNCTs and the surrounding matrix.

After being functionalized with nitric acid, the surface of the MWCNTs were damaged due to oxidation, and followed by the formation of oxygenic functional groups, as observed in FTIR result (Figure 2). These oxygenic functional groups facilitated the dispersion of MWCNTs in the polymer matrix, and inhibited agglomeration among MWCNTs. In addition, these functional groups interacted with epoxy groups and formed the ester linkages between nanotubes and the matrix to enhance bonding.

Electrical Conductivity of F-MWCNTs/Epoxy Composites

The effect of the reaction time of MWCNTs that were functionalized with nitric acid on DC electrical conductivity was studied, and the results are shown in Figure 5. Based on the figure, the electrical conductivity of 1-h acid-treated MWCNT epoxy composite was slightly higher than untreated MWCNT epoxy composites, where the electrical conductivities were 4.0×10^{-3} s cm^{-1} and 3.7×10^{-3} s cm^{-1}, respectively. The electrical conductivity reached to maximum value, 5.7×10^{-3} s cm^{-1}, when under 2 h

Table II. Intensity Ratio I_D/I_G of F-MWCNTs with Different Reaction Times

Samples	Pristine MWCNTs	F-MWCNTs 2H	F-MWCNTs 6H	F-MWCNTs 12H	F-MWCNTs 24H
RATIO I_D/I_G	1.42	2.04	2.33	2.52	2.89

functionalization. However, the electrical conductivity dropped rapidly once it reached 4 h reaction, 3.2×10^{-3} s cm^{-1}, and continued to decrease as the reaction time increased.

The enhancement of electrical conductivity after the functionalization process—i.e., 1 h functionalization time—might be due to an increase in interaction between MWCNTs and the epoxy matrix. Based on the result of the FTIR spectrum, oxygenic species were found on the surface of MWCNTs after acid functionalization, and these oxygenic species minimized the agglomeration effect of MWCNTs, by electrostatic repulsion force. As according to Bose et al., this electrostatic repulsion force will greatly enhance the solubility of MWCNTs in the solvent, and help to disperse them in epoxy matrix.[18]

The decrease in electrical conductivity after 2 h functionalization is due to the reduction of the MWCNTs' diameter after acid oxidation, and an increase in carrier scattering, as a result of intensified defects density, as shown in the Raman spectra (Figure 3). The decrease in electrical conductivity can be further explained by increased defect density at the interfaces between the MWCNTs and the epoxy matrix, which causes the distance between the individual MWCNTs to be much longer. Hence, the charges carriers, such as electrons and holes, travelling between the MWCNTs and the epoxy matrix would be more difficult.[14] Furthermore, Li et al. reported that acid treatment on MWNCTs shortened the length of nanotubes, and conductive network paths are difficult to form in the acid F-MWCNTs/epoxy composite.[19] Luo et al. have suggested that when SWCNT length is less than the critical length, the distance of charge carrier localization in SWCNT decreases rapidly with reducing the length of nanotubes. Besides, the charge transport behavior of SWCNT is intra-tube/bundle transport when the length of nanotubes is greater than critical length while the dominated by inter-tube/bundle when less than critical length.[20] Hence, it is found that the functionalization of MWCNTs should be carried out in relatively mild conditions (2 h functionalization reaction time), to achieve higher electrical conductivity in the MWCNTs/epoxy composite.
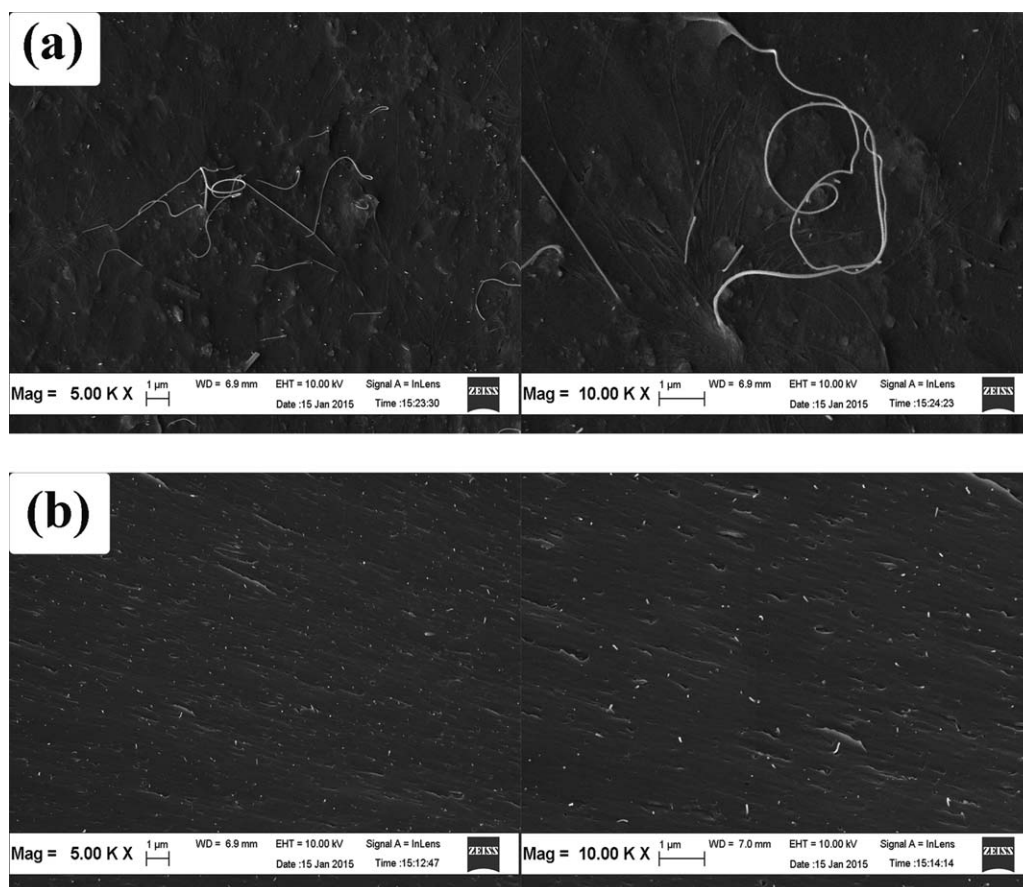

Figure 4. FESEM micrographs of the fracture surface of (a) pristine MWCNTs and (b) 2 h F-MWCNTs-filled epoxy matrix at the magnification of 5000× (left) and 10,000× (right).
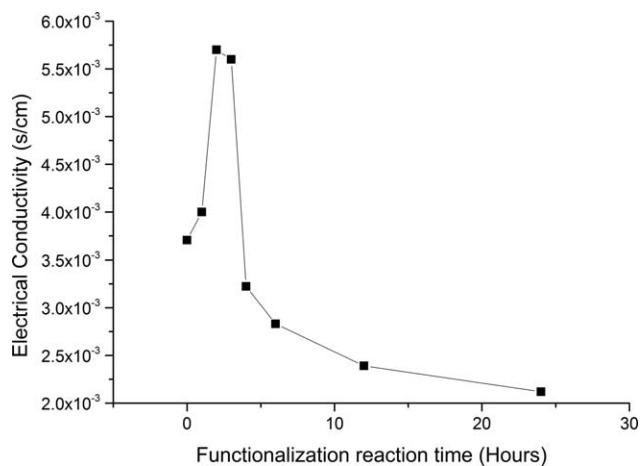
Figure 5. Effect of MWNCTs functionalization reaction time on electrical conductivity of MWCNTs-filled epoxy composite.

EMI SE of F-MWCNTs/Epoxy Composites

Figure 6 shows the effect of MWCNTs functionalization reaction time on EMI SE of MWCNTs/epoxy composite. Based on the figure, the EMI SE for all composite samples fluctuated with the frequency, and shows a gradual decreasing trend. Composite with MWCNTs of 2 h functionalization reaction time performs slightly higher in overall EMI SE than others in the frequency range of 7–12 GHz. This result is found to be consistent with that of DC electrical conductivity result.

According to Xu and Hao, the fluctuation of EMI SE value with frequency is due to two fluctuation factors, which are wave-current interaction and microstructure defects.[21] When incident EMI hits the surface of the composites, some incident waves will be reflected, because of an impedance mismatch between the incident wave and the surface of the shield. These reflected waves may intervene with the incident wave at the same spot, which causes a fluctuation in the EMI SE. Nevertheless, the
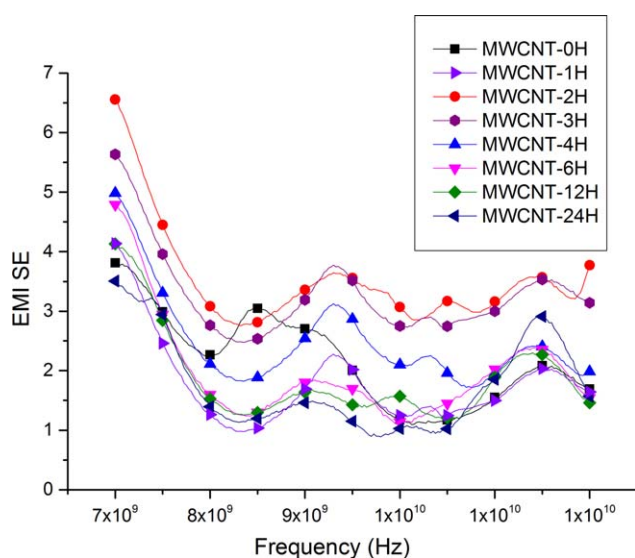

Figure 6. Effect of MWNCTs functionalization reaction time on EMI SE of MWCNTs/epoxy composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
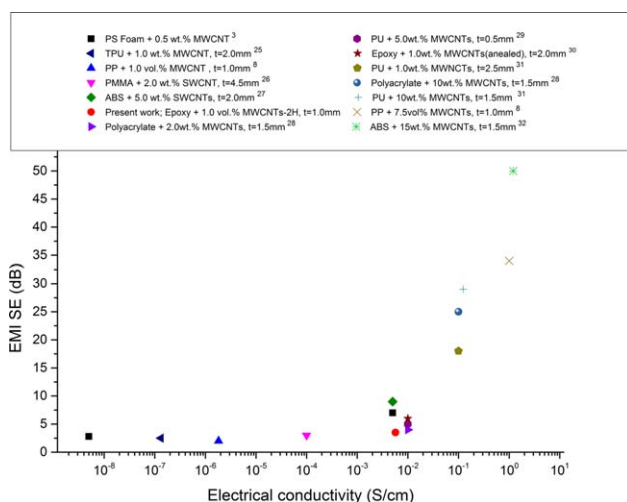

Figure 7. Comparison of EMI SE at 10 GHz versus electrical conductivity between this work and data reported in the literature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presence of microcracks or pores within the complex structure of the epoxy composite may affect the performance of EMI shielding, and lead to fluctuation. Based on the review, the mechanism of EMI shielding of a material depends on two major parameters: reflection loss and absorption loss. The reflection loss decreases with the increase in electromagnetic wave frequency, while absorption loss increases with the increase in frequency. Therefore, the slight decline in the overall EMI SE curve with the increase of frequency is governed by decreases in reflection loss, although the absorption loss tries to prevent it.[22]

The shielding mechanism of EMI is governed mainly by reflection loss, absorption loss, and multiple reflection. Multiple reflection is not relevant in the current study, since this mechanism is only considered in porous or foam materials.[23] Reflection loss increases with the increase in electrical conductivity, while absorption loss increases with the increase in dielectric constant.[24] Therefore, 2-h F-MWCNTs, with the highest electrical conductivity, contributed to the highest overall EMI SE, when compared with others. The reduction EMI SE of composites with functionalization reaction duration of more than 2 h was due to extensive damage on the surface of the MWCNTs, and caused a decrease in electrical conductivity.

Comparison of EMI SE and Electrical Conductivity

Figure 7 displays the comparison of EMI SE and the electrical conductivity of composites samples reported in previous work, and in this work. It should be stressed that two different CNTs (MWCNTs and SWCNTs) were used as filler, and various polymer matrices (i.e., polyurethane, polypropylene, etc.) were used in the previous works.[3,8,25–32] Based on Figure 7, it is observed that the result from this work falls in between data reported in the previous works. It is interesting to observe that all the data falls into an exponential distribution, and describe the correlation between the EMI SE and electrical conductivity of CNT polymer composites. It is clearly shown in Figure 7 that a minor increase in SE occurred at low electrical conductivity. However,

the performance of shielding became more efficient, and the SE increased dramatically once electrical conductivity was higher than 10^{-3} S cm^{-1}. The dramatic enhancement in SE is due to the conductive filler (MWCNTs) reaching the critical concentration (percolation threshold), when conductive networks path were formed. According to electromagnetic theory, the EMI SE should increase significantly once percolation is achieved.[30] However, factors such as filler homogeneity, filler loading, composite thickness, and interaction between fillers and matrix should be considered, since all these factors might contribute to electrical conductivity, and EMI SE of the composite.

CONCLUSIONS

Based on the results and analysis, the following conclusions can be drawn:

1. Multiwalled CNTs were functionalized successfully with nitric acid oxidation. Mild functionalization with nitric acid for 2 h under reflux enhanced the dispersion of MWCNTs, by the addition of a small number of oxygen functional groups.
2. Positive results on dispersion, electrical conductivity, and EMI SE for 2-h functionalized MWCNTs were observed, as compared with pristine MWCNTs. The overall EMI SE curve in the frequency range 7–12 GHz for MWCNTs with 2-h functionalization was improved, and reached the maximum value 6.6 dB at 7 GHz.
3. Electrical conductivity and EMI shielding performance for functionalized MWCNTs with more than 2 h treatment were declined, due to extensive damage of the MWCNTs' structure, as verified by Raman spectroscope.
4. It can be concluded that, to improve the EMI shielding performance of MWCNTs epoxy composites, mild functionalization must be carried out without extensity damage on the MWCNTs' structure by controlling the treatment time.

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