Wave-Absorbing Properties of Multi-Walled Carbon Nanotubes Reinforced Cement-Based Composites

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ABSTRACT

Multi-walled carbon nanotube (MWCNT)/Portland cement (PC) composites have been prepared to evaluate their electromagnetic wave absorbing properties. The effects of MWCNTs content and sample thickness were discussed in the frequency ranges of 2–18 GHz. Results show that the absorbing properties of cement-based composites are affected by the content of MWCNT and the thickness of the samples. When MWCNTs contents are 0, 0.25, 0.50, 0.75, and 1.00%, absorbing property of sample of 5 mm is unstable due to the resonance absorption. Samples of 10 mm and 15 mm thickness show stable microwave absorbing properties, and a sample of 15 mm thickness has better absorbing property than that of 10 mm. Optimum contents of carbon nanotube (CNT) of 0.75, 0.50, and 0.5% by mass are found in 5, 10, and 15 mm thick samples, respectively. A sample with thickness of 5 mm and 0.50% mass content of CNT has the best absorbing property and the peak is –15.3 dB.

1. INTRODUCTION

Electromagnetic interference (EMI) and electromagnetism pollution are becoming increasingly serious issues nowadays, which will harm the human body and decrease sensitivity of the equipment and even cause severe fault of data or accidents. Cement-based composite is commonly used in engineering constructions not only in civil fields but also in military fortifications. As one of the most commonly used building materials, cement-based composite exhibits excellent mechanical properties and durability, but its capacity for electromagnetic shielding and microwave absorption is unsatisfactory. Therefore, it is of great importance to develop special cementitious composite with excellent electromagnetic wave absorption property to prevent people from electromagnetic radiation.

In recent years, there are some researches on cement-based electromagnetic shielding and absorbing materials: traditional materials such as carbon fiber (Wang, Li, Li, Guo, & Jiao, 2008), expanded polystyrene (Guang, Liu, Duan, & Zhao, 2007), and ferrite (Lv, Chen, Wang, et al., 2010; Zhang & Sun, 2010), mixed with cement were used to improve the electromagnetic absorbing and shielding properties of building materials. However, these traditional absorbing materials usually have narrow absorption band, large density, and other disadvantages. As a result, studies and development of the new absorbing materials are very popular.

Carbon nanotubes (CNTs) are a kind of nano-scale material, which have been extensively investigated for their excellent mechanical, electrical, optical, and magnetic properties. Because of the special structure (which has radial dimension of nanometer, micrometer axial dimension, basically sealing the ends of the tube and the one-dimensional quantum materials), large specific surface area, and superior electric properties, multi-walled carbon nanotubes (MWCNTs) exhibit strong broadband microwave absorbing properties (Lin, Zhu, Guo, & Yu, 2007; Peng et al., 2008). Many researchers have studied the mechanical properties of MWCNTs-reinforced cement-based materials. They found that MWCNTs can increase the compressive and flexural strength of cement mortar, reduce the resistivity, and improve the pressure sensitive resistance (Li, Wang, & Zhao, 2005; Xu, Gao, & Pu, 2009). However, little research about using MWCNTs as absorbing agents to improve the electromagnetic properties of cement-based composites was conducted. Nam, Kim, and Lee (2012) investigated the EMI shielding effectiveness (SE) of MWCNT/cement composites. In their study, the most effective shielding performance at a frequency range from 0.1 to 18 GHz was attained with 1.5 wt.% MWCNTs. Moreover, they used silica fumes to disperse the MWCNTs and reported that the cement matrix with 0.6 wt.% MWCNTs and 20 wt.% silica fume exhibited the best EMI SE. Wang, Guo, Yu, and Zhang (2013) investigated the influence of the MWCNT content and sample thickness on the electromagnetic wave

reflectivity in the frequency ranges of 2–8 GHz and 8–18 GHz. They found that when the MWCNT content was 0.6 wt.%, the cement mortar sample with a thickness of 25 mm can remarkably absorb electromagnetic waves close to the absorbing peaks in the frequency range of 2–8 GHz. These obtained different conclusions could be due to the fact that different preparation and test methods were used.

In this study, the absorbing electromagnetic wave properties of MWCNTs-reinforced cement mortar were explored in the frequency ranges of 8–18 GHz using the radar cross-section (RCS) method. The thickness of the samples and MWCNTs content in mortar were discussed.

2. EXPERIMENTAL

2.1 Materials

MWCNTs were used in this work (Shenzhen Port of Nano Co., Ltd.). The physical properties are shown in Table 1. The cement with compressive 49.2 MPa at 28 days was used and its chemical compositions are shown in Table 2. ISO standard sand according to criterion of GSB08-1337-2001 was used as fine aggregate.

Table 1. Physical properties of the MWCNT.

Products	Diameter (nm)	Length (μm)	Purity (%)	Special Surface Area (m²/g)
MWCNTs	10–20	5–15	97	105

2.2 Sample preparation

For the mix proportion, the water-to-cement ratio was 0.5:1 and the sand-to-cement was 3:1, and 0.4 wt% polycarboxylate superplasticizer was used in the batching. MWCNTs were added proportional to the weight of the cement.

During the mixing, MWCNTs were uniformly dispersed in some water by ultrasonic dispersing for 10 min and the dispersant was also added to attain a stable homogeneous dispersion. Meanwhile, cement, sand, and the remaining water were mixed for 3 min by a rotary mortar mixer. Then, the pre-prepared CNT mixture was poured into the mortar and continually mixed for another 3 min. The compressive strength of the mortar was tested according to the Chinese national standard GB/T 17671-1999 "Method of testing cements-determination of strength".

After mixing, the mortar was poured into molds the size of 180 mm × 180 mm and thicknesses of 5, 10, 15 mm. The molds were vibrated for about 1 min and the surface was smoothed. The specimens were removed from their molds after 24 h and cured in 20 ± 2°C, relative humidity (RH) >95% condition for 28 days.

2.3 Testing Method

Space method was used to test the dielectric loss of the samples at the frequency 8.2–12.4 GHz. RCS method was used to test the reflectivity of the samples. Experimental apparatus used was PNA E8363B vector network analyzer produced by the Agilent Each group. Three specimens were tested and averaged as the representative value.

3. RESULTS AND DISCUSSIONS

3.1 Effect of MWCNTs content on dielectric loss

The complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) of EM wave absorber plays an important role in determining the reflection and transmission measurements. ε' is the real part of the complex permittivity, which stands for the ability of storing charge or energy; ε'' is the imaginary part of the complex permittivity and it stands for the wastage of the energy. According to the theory of electromagnetic wave (Hu, 2004), tan $\delta E = \varepsilon''/\varepsilon'$ stands for the electromagnetic loss due to electric loss mechanism and the higher the value, the greater the loss of material for electromagnetic waves. Figure 1 shows the effect of MWCNTs content on dielectric loss of cement-based materials within the frequency range of 8.2–12.4 GHz.
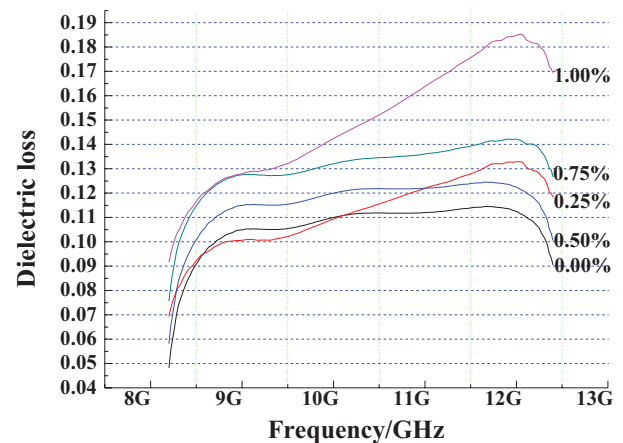
Figure 1. Effect of MWCNTs content on dielectric loss of cement-based materials.

Table 2. Chemical compositions of the cement (wt.%).

SiO$_2$	Fe$_2$O$_3$	Al$_2$O$_3$	CaO	MgO	SO$_3$	R$_2$O	Ignition Loss	Specific Surface Area (m²/kg)
23.63	2.85	8.00	54.75	4.75	2.38	0.94	3.27	350

It can be observed from Figure 1 that dielectric loss increases the mortar with MWCNTs content within 8.2–12.4 GHz. The dielectric loss presents the same change trend with the increase of frequency in this range. MWCNTs can act as electric dipoles to resonate with incident waves under an alternating electromagnetic field, producing electric polar current and transforming the electromagnetic energy into heat or other energy. When the frequency increases, electrons gain more energy and the tunneling effect of MWCNTs is also more obvious, and thus the conductivity can be influenced (Hou, Li, Zhao, Zhang, & Cheng, 2012).

3.2 Absorbing properties of cement-based composites

Electromagnetic wave absorption performance of materials is generally characterized by the reflectivity. The reflectivity of single-layer absorbing material can be expressed as Equations (1) and (2) (Hou et al., 2013):

$$R(dB) = 20\log_{10}\left|\frac{Z_{in} - 1}{Z_{in} + 1}\right| \tag{1}$$

$$Z_{in} = \left(\frac{\mu_r}{\varepsilon_r}\right)^{\frac{1}{2}} \tanh\left[j\left(\frac{2\pi f d}{c}\right)\left(\mu_r \varepsilon_r\right)^{\frac{1}{2}}\right] \tag{2}$$

where Z_{in} is the normalized input impedance at the free space and material interface; ε_r is the complex permittivity; μ_r is the complex permeability of absorber; f is the frequency of EM wave in free space; d is the thickness of the absorber, and c is the velocity of light in free space. The less the reflectivity of the material is, the better the absorbing electromagnetic wave properties it reaches.

It is known that permittivity and permeability can be expressed as: $\varepsilon_r = \varepsilon' - j\varepsilon''$ and $\mu_r = \mu' - j\mu''$, and the absorbing properties of materials are determined by the parameters $\varepsilon'\ \varepsilon''\ \mu'\ \mu''\ f$ and d (Lin, Zhu, Guo, & Yu, 2007). When $Z_{in} = 1$, electromagnetic wave is almost entirely absorbed by the absorber.

3.2.1 Effect of sample thickness on absorbing properties

Figure 2 presents the effect of thickness on absorbing proerties of cement mortar matrix within the frequency range of 8–18 GHz. It can be seen that cement-based mortar matrix also has a wave absorbing capability. With the increase of the thickness, the minimum reflectivity increases. It is indicated that the absorbing property decreases. Meanwhile, with the increase in thickness, the minimum peak of the reflectivity shifts to the lower frequency. When the thickness is 5 mm, samples show strong absorbing properties in the frequency range of 12–14 GHz and the minimum of the
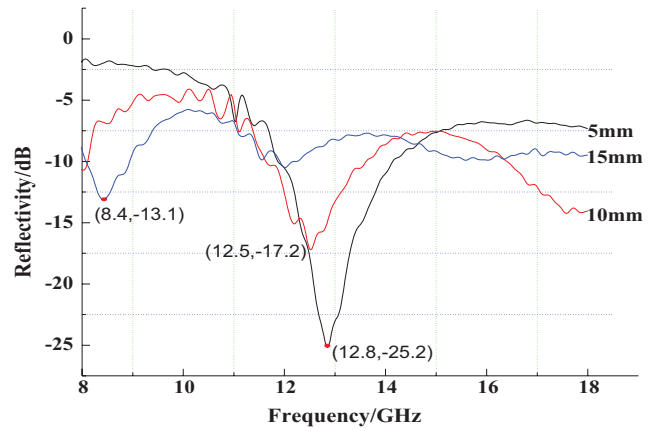

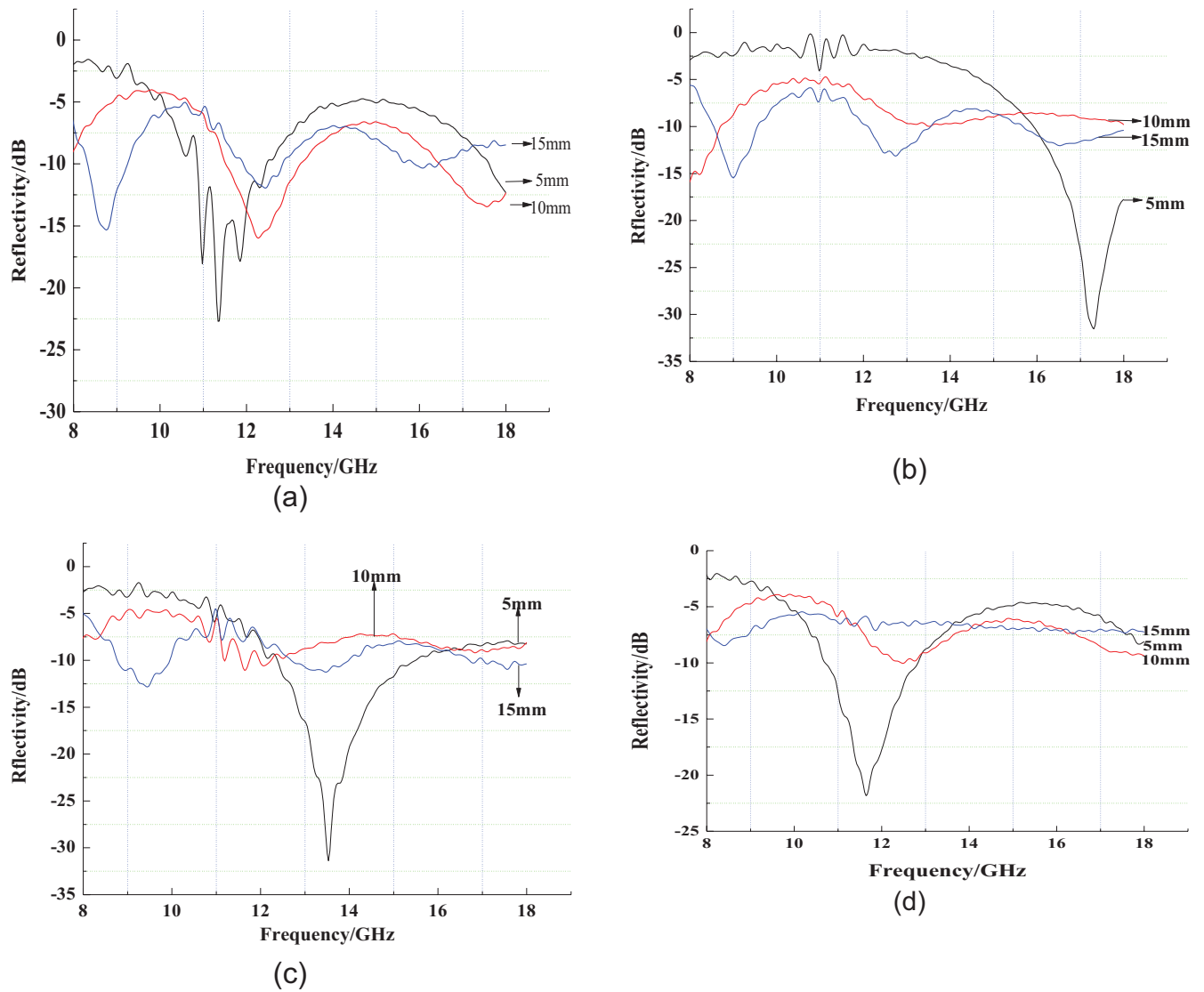**Figure 2.** Effect of thickness on absorbing properties of cement mortar matrix.

reflectivity is –25.2 dB at 12.8 GHz. When thickness is 10 and 15 mm, the peak is about 17 dB at 12.5 GHz, and 13.1 dB at 8.4 GHz, respectively.

Figure 3 shows the absorbing properties of samples with different thickness under different content of MWCNTs in 8–18 GHz range. It can be seen from Figure 3 that the thicker the sample, the lesser the cure fluctuates. The curve fluctuating cycle of the sample thickness of 15 mm is smaller than those of samples of thickness of 10 and 5 mm. For the volatility of the 15 mm samples, it is unobvious compared with 10 and 5 mm samples. In the frequency of 8–18 GHz, reflectivity of the 5 mm samples with different MWCNTs, the content owns a very obvious peak less than -20 dB.

In Figure 3(a), the content of MWCNTs is 0.25%. When thickness is 5 mm, the wave absorbing performance is weak in 8–10 GHz, while wave absorption performance is good in 10.5–13 GHz (the reflectivity is smaller than -7 dB); When thickness is 10 mm, reflectivity is smaller than -5 dB except for the small range around 10 GHz; When thickness is 15 mm, samples show stable absorbing properties and the reflectivity is smaller than -5 dB in 8–18 GHz.

Figure 3(b) shows the absorbing properties of samples with various thicknesses with 0.50% wt MWCNTs in the 8–18 GHz range. When thickness is 5 mm, reflectivity is smaller than -10 dB only within the 16–18 GHz range and reaches the peak value of -31.5 dB at 17.31 GHz; when thickness is 10 or 15 mm, their absorbing properties are stable and absorbing properties of samples with thickness of 15 mm are more stable and reflectivity is below -5 dB at the 8–18 GHz range.

Figure 3(c) shows the absorbing properties of samples of various thicknesses with 0.75% wt MWCNTs in the 8–18 GHz range. When thickness is 5 mm, samples show strong absorbing properties only in the 12.5–15.5 GHz range; when thickness is 10 mm, reflectivity

Figure 3. Effect of the thickness of the samples on the absorbing properties. (a) Samples with 0.25% wt MWCNTs. (b) Samples with 0.50% wt MWCNTs. (c) Samples with 0.75% wt MWCNTs. (d) Samples with 1.0% wt MWCNTs.

reaches the peak value of -16.5 dB at 7.20 GHz. It also shows that the absorbing property of samples with thickness of 15 mm is more stable and the peak is -12.8 dB at 9.48 GHz.

Figure 3(d) shows the absorbing properties of different thicknesses of the samples with 1.00% wt MWCNTs in the 8–18 GHz range. When thickness is 5 mm, samples show strong absorbing properties within the 11–12.5 GHz range and the peak is -21.3 dB at 11.7 GHz; when thickness is 10 mm, reflectivity reaches the peak of -17.0 dB at 7.23 GHz and reflectivity is below -5 dB in 8–18 GHz when thickness is 15 mm.

In general, it can be observed from Figure 3 that the curves tend to be smoother with the increase of the thickness d and the number of peaks also increases as the sample thickness increases. This is due to the resonance absorption (Bao, Zhao, Su, & Duan, 2011).

When the sample thickness d meets the formula resonance absorption will occur.

$$d = (2n + 1)\frac{\lambda}{4} = (2n + 1)\frac{\lambda_0}{4\sqrt{\mu_r \varepsilon_r}} \quad (n=0, 1, 2…) \quad (3)$$

Where λ and λ_0 are the wavelengths in the absorbing materials and free space, respectively and n is a whole number.

From Equations (1)–(3), the relationship between thickness and incident wave frequency can be found when resonance absorption occurs.

By transforming (3), k_0 can be expressed as:

$$\lambda_0 = \frac{4d\sqrt{\mu_r \varepsilon_r}}{(2n + 1)} \quad (4)$$

It can be seen from Equation (4) that the number of peaks could increase with the thickness d. When the thickness increases, electromagnetic wave entering into materials decreases. So resonance absorption weakens and the curves tend to be smoother.

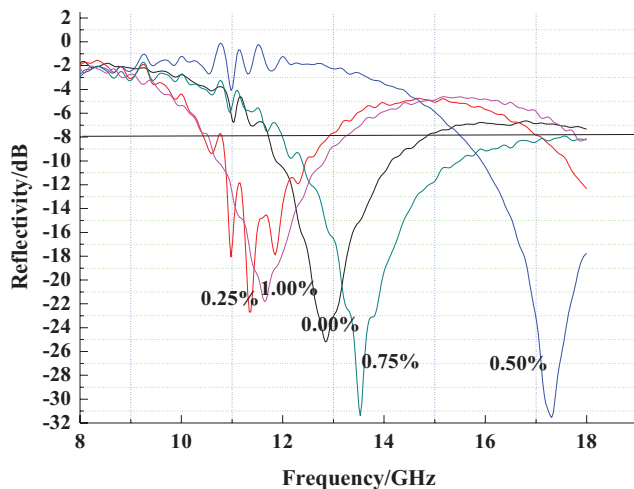### 3.2.2 Effect of MWCNTs content thickness on absorbing properties

Figure 4(a)–(c) show the influence of MWCNTs content on absorbing properties in the 8–18 GHz range.

Figure 4(a) shows the effect of MWCNTs content on absorbing properties of the samples with 5 mm thickness in the range of 8–18 GHz. When MWCNTs content increased from 0 to 1.00%, absorbing properties of samples have no significant change in 8–10 GHz range. Samples with 0.25 and 0.10% wt MWCNTs have good absorbing properties in the low frequency range, while samples with 0.50 and 0.75% wt MWCNTs have good absorbing properties in the high frequency range. By comparison, samples with 0.75% wt MWCNTs have the best absorbing properties and the peak is –31.4 dB at 13.5 GHz.

Figure 4(b) shows effect of MWCNTs content on absorbing properties of the samples with 10 mm thickness. When CNT content increased from 0 to 1.00%, the absorbing properties of samples change slightly within the 8–11 GHz range. However absorbing properties of samples with 0–0.25% wt MWCNTs are better than the other two groups in the 11–18 GHz range. Absorbing properties of samples with 0.50% wt MWCNTs are better than other groups within the 8–10 GHz range. In general, the optimal dosage of MWCNTs at 10 mm thickness is 0.50%.
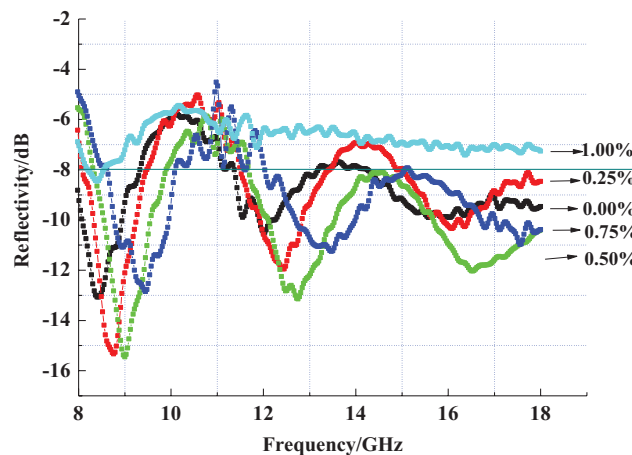
Figure 4(c) shows the effect of MWCNTs content on absorbing properties of the samples with 15 mm thickness. Reflectivity of the samples are close to each other except for samples with 1.00% wt MWCNTs.

(a)
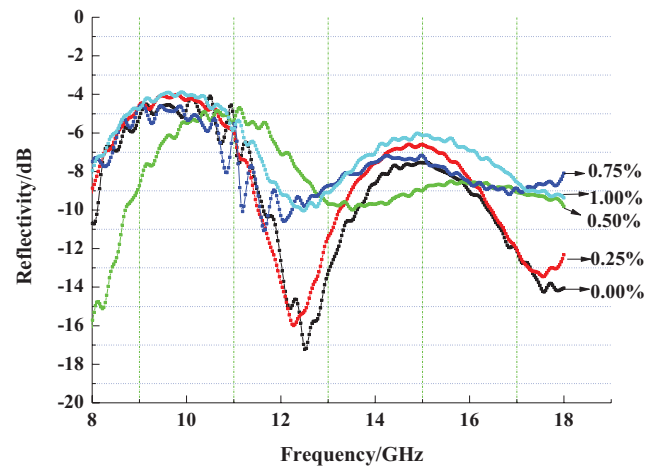
(b)

(c)

Figure 4. Effect of MWCNTs content on absorbing properties of the samples with different thickness. (a) 5 mm thickness. (b) 10 mm thickness. (c) 15 mm thickness.

However, absorbing properties of samples with 0.50% wt MWCNTs are the best in general and the peak is –15.3 dB at 8.76 GHz. With the increase of MWCNTs, the peak shifts to the higher frequency.

In general, it can be observed from Figure 4 that absorbing properties of samples are not directly proportional to MWCNTs content. Disperse state of MWCNTs will be affected when content reaches a certain value and high content always lead to aggregation and conductivity increase. CNTs have good electrical conductivity (conductivity is 1000´ of copper). Aggregation increases the conductivity of cement-based materials so that shielding of materials will increase and absorbing properties will be reduced (Nam et al., 2012).

According to the experiments, samples with 15 mm thickness and 0.5% wt MWCNTs have the best wave absorption performance and reflectivity is <-8 dB in 11–18 GHz range.

3.3 Mechanism of microwave absorption of CNTs reinforced cement-based composites

Trace amounts of MWCNTs was added to a moderate amount of alcohol for ultrasonic dispersion for 15 min and then dropped in aluminum foil (20 mm × 20 mm). After alcohol evaporated, MWCNTs could be observed by SEM.

Figure 5 shows the microstructure of a single CNT. The diameter is about 50 nm and the length is about 15 mm. The structure is just like a tube with many small fluffs internal on the wall. MWCNTs exhibits excellent microwave absorbing properties because of their microstructure and dielectric properties. Owing to their small size, MWCNTs have considerably larger specific surface area than normal particulate; therefore, there will be more particles that can be polarized to cause electromagnetic energy loss when the electromagnetic waves are applied, which leads to a better wave absorbing performance. Moreover, a hopping conduction can occur between MWCNTs if they are sufficiently close as the electrons or holes transit through a tunneling effect (Zhao, Zou, Shi, Li, & Guo, 2006).

Hardened cement-based mortar contains several kinds of cement hydration products such as ettringite, calcium hydroxide, calcium silicate hydrate, and unhydrated cement particles; interfaces exists between the hardened cement paste and silica sand, also among different particles and different size pores. When the electromagnetic wave gets into the cement mortar, the part energy will be absorbed owing to the multiple reflections. When MWCNTs were added, they connected with cement hydration products or even covered them, which formed a network structure as shown in Figure 6. Conductive network formed inside the mortar increases the dielectric loss of
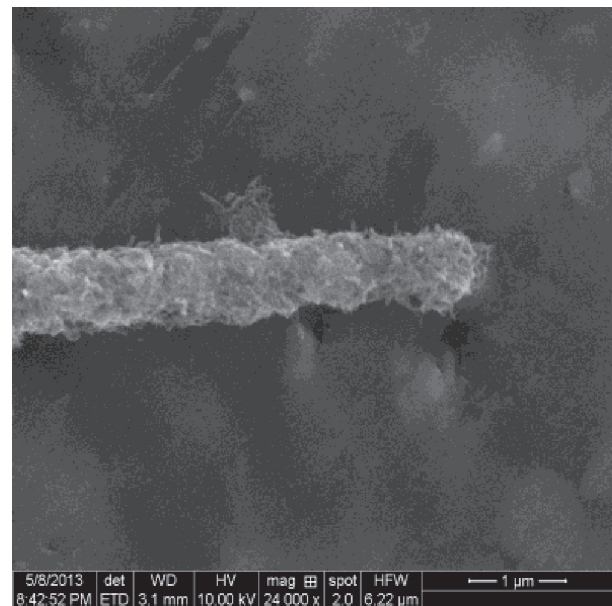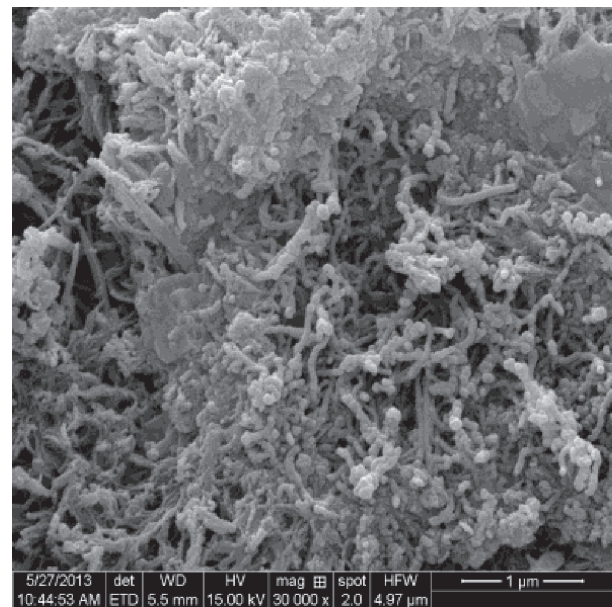

Figure 5. Single CNT.

Figure 6. MWCNTs reinforced cement-based material.

the mortar. In addition, the structure and dielectric properties of MWCNTs will also lead to the increase of electromagnetic energy.

4.   CONCLUSIONS

Cement-based mortars with different MWCNTs contents were prepared and their reflectivities of the microwave were explored. Based on the experiments, the following conclusions can be drawn.

(1) Absorbing properties of MWCNTs-reinforced cement-based composites are affected by CNT content and thickness.

(2)   The curves tend to be smoother with an increase of the thickness, and the number of peaks increases as the sample thickness increases.

(3)   Samples with 15 mm thickness and 0.5% wt MWCNTs have the best wave absorption performance, and reflectivity is <–8 dB in the 11–18 GHz range.

ACKNOWLEDGMENTS

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