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Electromagnetic interference shielding effectiveness of multiwalled carbon nanotube reinforced fused silica composites

Changshu Xiang [a,b], Yubai Pan [a,*], Jingkun Guo [a]

[a] *State Key Laboratory of High Performance Ceramics and Superfine Structure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China*
[b] *Graduate School of the Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100039, People's Republic of China*

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Abstract

Electromagnetic interference (EMI) shielding properties of multiwalled carbon nanotube (MWCNT) reinforced fused silica composites were investigated in the frequency region of 26.5–40 GHz (Ka band). The experimental results indicate that the EMI shielding effectiveness (SE) of MWCNT-fused silica composites is sensitive to the MWCNT volume fraction and increases with the increase of the MWCNT content. The average value of EMI SE reaches 68 dB for 10 vol.% MWCNT-fused silica composites at 36–37 GHz, indicating a possible use for commercial application at high frequency. At the same filler loading, MWCNT-fused silica composites show higher EMI SE compared to that of carbon black (CB)-fused silica composites. In particular, the EMI SE of the CB-fused silica composites is easy to be saturated in high frequency. Moreover, the experimental data reveal that the improvement of EMI SE of the MWCNT-fused silica composites is primarily ascribed to the enhancement of conductivity, which leads to dramatic increase of complex permittivity by adding conducting MWCNTs.

Keywords: A: Hot pressing; A: Sol–gel processes; B: Composites; C: Dielectric properties

1. Introduction

In recent years, EMI shielding and absorbing materials, which can effectively prevent the leakage of harmful EM wave, have attracted considerable attention with the increasing application of electronic devices such as television, computers, mobile telephones and automobile communication apparatuses, etc., that emit electromagnetic (EM) energy resulting in electromagnetic wave pollution. Typical metals (like copper, aluminum) and their composites possessing high conductivity and dielectric constant are considered to be the best conventional EM shielding materials with high EM shielding effectiveness. But their disadvantages such as heavy weight and easy corrosion restrict their wide use for shielding materials [1,2]. Now considerable research work focuses on the development of lightweight, chemical stable and high broadband EM shielding effectiveness composite materials. Actually doping conducting carbon materials, including carbon black, carbon fiber, carbon filaments and carbon nanotubes (CNTs), into lightweight matrix is an effective way to obtain advanced shielding materials and some successful results have been reported [3–5].

Recently, single walled and multiwalled carbon nanotubes (SWCNTs and MWCNTs) have been widely investigated for possible applications such as mechanically reinforcing fillers in composites, nanoelectronic devices and field emitter, etc., for their remarkable properties (especially, excellent electrical and mechanical properties) and unique structure [6–8]. One of the important applications is the development of CNTs bulk composites, including CNT–metal [9,10], CNT–polymer [11,12] and CNT–ceramic [13,14] matrix composites. It has been reported that a combination of dramatic improvement of mechanical and electrical properties has been achieved in CNT composites [15]. Recently, due to easy processing and good flexibility, some CNT–polymer composites with high conductivity have been employed for application as promising EMI shielding materials. For example, Joo and co-workers [16] have synthesized MWCNT–PMMA composites whose highest EMI shielding effectiveness reaches 27 dB at 50 MHz to 13.5 GHz, indicating the possible use for commercial

* Corresponding author. Tel.: +86 21 52412820; fax: +86 21 52413903.
E-mail address: ybpan@mail.sic.ac.cn (Y. Pan).

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application. Gupta and co-workers [17] have prepared MWCNT–polystyrene composites. The experimental results show that the EMI shielding effectiveness is high to 26 dB at 10 GHz.

Ceramic matrix materials are very important materials and have wide applications, especially in some harsh environments, like high temperature, strong acid and base, etc. So it is reasonable to prepare conductive ceramic tile for shielding materials used in harsh conditions by incorporating CNTs. Fused silica is an essential ceramic material with many prominent properties such as low density ($2.16\ g/cm^3$), excellent chemical inertness and high softening temperature [18]. However, its application is restricted by the intrinsic brittleness. Our group, therefore, has dispersed MWCNTs into fused silica matrix and successfully prepared dense MWCNT-fused silica composites [19]. We have found that enhanced mechanical properties and improved EMI shielding effectiveness (8–12 GHz, X band) have been achieved simultaneously in MWCNT-fused silica composites [19,20]. The average SE of 10 vol.% MWCNT-fused silica composite reaches 33 dB at 11–12 GHz. In this paper, we report the EMI shielding effectiveness and complex permittivity of MWCNT-fused silica composites in Ka band in order to investigate the possibility for application in high frequency.

2. Experimental procedure

2.1. Sample preparation

Purified MWCNTs (provided by Shenzhen Nanotech Port Co. Ltd., China), 20–40 nm in diameter and 5–15 μm in length, were dispersed in de-ionized water with cetyltrimethylammonium bromide (CTAB) cationic surfactant. Tetraethylorthosilicate was used as raw material of fused silica and the MWCNT-fused silica composite powders were synthesized by a rapid sol–gel method. The as-prepared MWCNT-fused silica composite powders were packed in graphite die and then hot pressed at 1300 °C under 25 MPa in argon atmosphere for 30 min to obtain bulk MWCNT-fused silica composites. The detailed fabrication procedure has been described previously [19]. In order to compare the EMI shielding properties, CB filled fused silica composites were prepared by the same method. The CB is a kind of commercial powders with average particle size of 24 nm and specific surface area of $112\ m^2/g$.

2.2. Morphology observation

The cross-section morphology of the composites was observed by field emission scanning electron microscopy (FESEM, JSM-6700F, 15 kV, Japan).

2.3. Microwave measurements

At present, the EMI shielding effectiveness test procedure is to quantitatively measure the insertion loss (IL) that results from introducing the test sample. The IL is expressed as follows:

$$\mathrm{SE} = \mathrm{IL} = 10\log\frac{P_\mathrm{T}}{P_\mathrm{I}} = 20\log\frac{E_\mathrm{T}}{E_\mathrm{I}}$$

where P_I (E_I) and P_T (E_T) are the power (electric field) of incident and transmitted EM waves, respectively. The IL typically expressed in decibel (dB). The higher the SE absolute value in dB, the less energy passes through the materials [21].

In this study, the as-prepared samples were precisely cut into 22.86 mm × 10.16 mm × 5.0 mm and 7.12 mm × 3.56 mm × 5.0 mm to fit waveguide for insertion loss measurement (WILTRON 54169A Scalar Measurement System) at 8–12 and 26.5–40 GHz, respectively.

The samples were also made with the size of 7.12 mm × 3.56 mm × 1.5 mm and used for complex dielectric permittivity measurement in Ka band (Hewlett-Packard 8722ES network analyzer).

3. Results and discussion

MWCNTs are effectively dispersed and well embedded in the fused silica matrix by powerful ultrasonic in surfactant aqueous solution. Fig. 1(a) shows the representative image of the fracture surface of the sample with 10 vol.% MWCNTs. From the figure, the fused silica matrix forms high dense continuous phase with only a few pores. In addition, CNT pull-out denoted by white arrows is depicted in Fig. 1(a). The MWCNT pull-out not only implies good compatibility between MWCNTs and fused silica matrix but also improves the mechanical properties of MWCNT-fused silica composites. Our previous experimental results revealed that there is 88 and 146% increase in bending strength and fracture toughness, respectively, over fused silica by incorporating 5 vol.% MWCNTs [19]. Fig. 1(b) shows the morphology of the cross-section of 10 vol.% CB-fused silica composite. While the average primary particle size of CB is 24 nm, there are also some CB aggregates of approximate size of 100 nm.

It is well known that pure fused silica is an electromagnetic wave transparent material. However, in our previous study, EMI shielding effectiveness of MWCNT-fused silica composites in X band increases with the increase of MWCNT volume fraction. The average magnitude of SE reaches 33 dB at 11–12 GHz when the volume fraction of MWCNTs increases to 10 vol.% [20]. The EMI shielding effectiveness of MWCNT-fused silica composites with different MWCNT content in Ka band is presented in Fig. 2. The results show that the SE of all the composites is also sensitive to the MWCNT volume fraction and increases with the MWCNT content, similar to that in X band. From Fig. 2, the value of SE in Ka band is equal to that in X band when the content of MWCNTs is 2.5 vol.%. But it is noteworthy that the value of SE in Ka band is noticeably higher than that in X band as the MWCNT content is up to 5 vol.%. Especially, when the MWCNT volume concentration gets to 10%, the average magnitude of SE in Ka band increases to 65 dB, almost two times than that in X band, which is suitable for commercial application. Nevertheless, for CB-fused silica

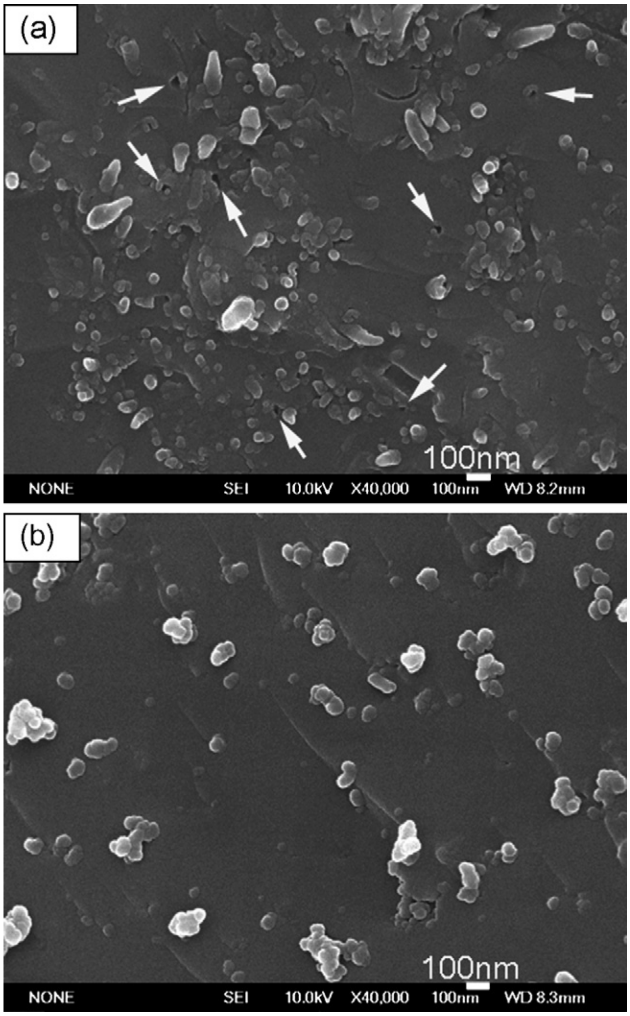

Fig. 1. FESEM images of the cross-section of fused silica composites: (a) 10 vol.% MWCNT-fused silica composites and (b) 10 vol.% CB-fused silica composites. The white arrows indicate the pull-out of the MWCNTs.

composites, the EMI SE is hardly enhanced between X band and Ka band. Fig. 3 shows the comparative spectra of EMI SE between MWCNT and CB composites as a function of frequency. As the figures show, the EMI SE of CB composites is lower to that of the same volume amount MWCNT composites

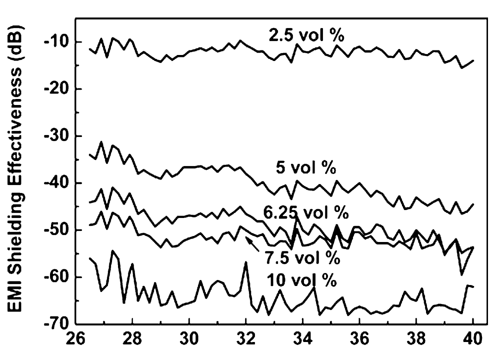

Fig. 2. EMI shielding effectiveness of MWCNT-fused silica composites with different MWCNT content as a function of frequency measured in the range of 26.5–40 GHz.

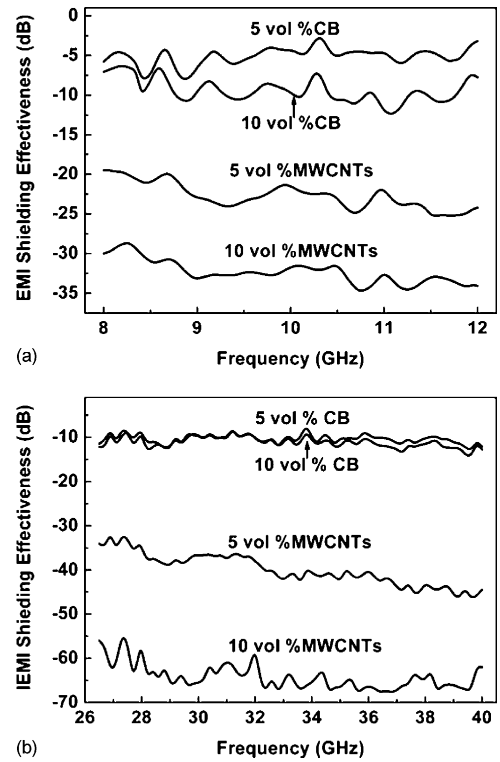

Fig. 3. Comparison of EMI shielding effectiveness between MWCNT and CB composites as a function of the frequency: (a) 8–12 GHz and (b) 26.5–40 GHz.

in all measured frequency region, and the EMI SE of 10 vol.% CB-fused silica composite seems to be saturated and the SE maintains approximate 10 dB even the frequency changes from X band to Ka band. The results clearly show that MWCNTs are most promising EMI shielding additive compared to CB.

As we all know, the improvement of shielding effectiveness is primarily ascribed to the improvement of conductivity. Pure fused silica is an insulator with high electrical resistivity. MWCNTs with excellent electrical properties and high aspect ratio (about 500) are easy to form conducting networks, which can effectively improve the electrical properties of silica matrix. The conducting networks in the composite may interact with EM wave radiation to attenuate EM wave. Table 1 presents the data of direct current conductivity and shielding effectiveness of the fused silica composites at 10 and 34 GHz. As can be seen, there is an increase in conductivity of about twelve orders of magnitude when increasing the volume fractions of MWCNTs from 2.5 to 5 vol.%, where the conductivity changes from 6.49×10^{-14} to 0.04 S/m, thereby the value of EMI SE increases nearly three times from 7 to 22 dB at 10 GHz and from 12 to 41 dB at 34 GHz. The conductivity of MWCNT-fused silica composites further increases to 0.574 S/m, then the highest SE value reaches 66 dB. However, the conducing mechanism of CB-fused silica composites is hopping transfer, which results in lower conductivity. So the SE of CB-fused silica composites is lower compared to the same volume fraction MWCNT-fused silica composites.

The complex permittivity of MWCNT-fused silica composites with different MWCNT content has been performed in Ka band. The complex permittivity spectra, including real,

Table 1
The conductivity and EMI shielding effectiveness of the fused silica composites

MWCNTs or CB content (vol.%)	Conductivity (S/cm)		SE at 10 GHz (dB)		SE at 34 GHz (dB)	
	MWCNT composites	CB composites	MWCNT composites	CB composites	MWCNT composites	CB composites
2.5	6.49×10^{-14}		7		12	
5	0.04	3.17×10^{-14}	22	4	41	10
7.5	0.218		26		53	
10	0.574	8.77×10^{-5}	32	10	66	11

imaginary permittivity and loss tangent, are presented in Fig. 4. As we know, pure fused silica has excellent dielectric properties, for example, its dielectric constant is about 3.3 and the loss tangent is approximately 4×10^{-4} at 8–10 GHz [22]. However, the real and imaginary permittivities (ε', ε'') are all sensitive to the MWCNT volume fraction and increase with the MWCNT volume fraction. Small volume fraction addition of MWCNTs to the fused silica matrix has a dramatic effect on the complex permittivity spectra. As seen from Fig. 4(a), by only adding 2.5 vol.% MWCNTs, the magnitude of real permittivity is over two times that of pure fused silica. When the MWCNT volume fraction increases to 10%, the measured value of ε' reaches 21 at 26.5 GHz. The spectra of ε'' have similar features of ε'. From Fig. 4(b), the values of ε'' are all over 1. Especially, when the CNT content increases to 10 vol.%, the value of ε'' is higher to 28 at 26.5 GHz. It is noteworthy that the loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$), as seen in Fig. 4(c), increases nearly three orders over pure fused silica with small MWCNT content addition. In particular, the magnitude of $\tan\delta$ for 10 vol.% MWCNT composite is as high as 1.3 at 26.5 GHz. The dramatic enhancement of complex permittivity is primarily also ascribed to the addition of MWCNTs. The high electrical conductivity and large aspect ratio of MWCNTs can impart the electrical properties, eventually controlling the electrical properties of the MWCNT-fused silica composites. The improved conductivity of the composites gives rise to high electric loss ($\varepsilon'' > 1$), i.e., there exists considerable conduction current. The high electric loss is the main element leading to high EM attenuation. In addition, factors influencing the complex permittivity and EMI SE may also include the aggregation state, distribution, orientation after hot-pressing and the characteristic properties (length, diameter, specific surface area, defects and chirality, etc.) of MWCNTs in the composite.

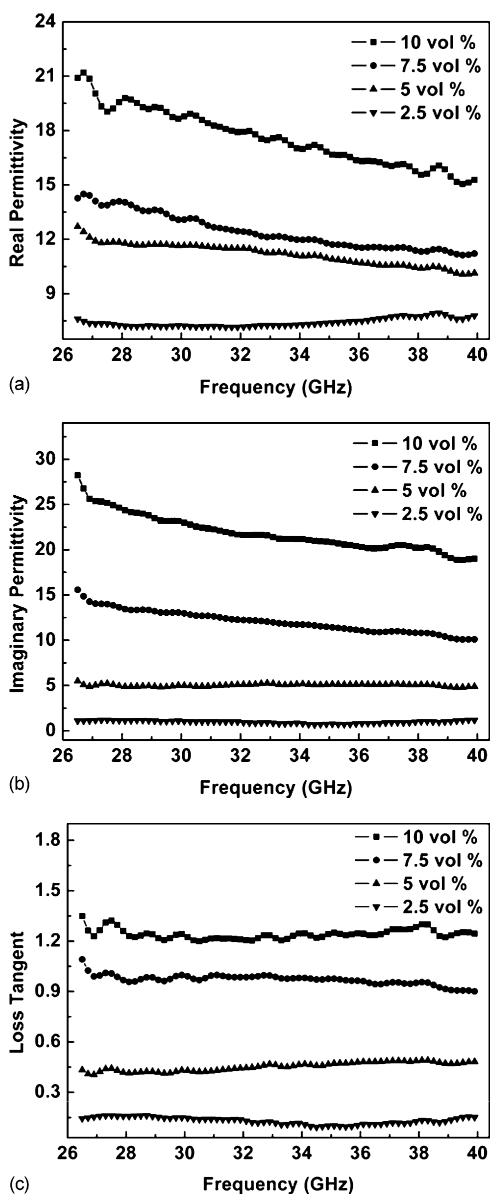

Fig. 4. Complex permittivity spectra of the MWCNT-fused silica composites as a function of the measured frequency from 26.5 to 40 GHz: (a) real permittivity; (b) imaginary permittivity; (c) loss tangent.

4. Conclusions

MWCNT-fused silica composites were successfully prepared by hot-pressed sintering. EMI SE and complex permittivity were measured in the frequency range from 26.5 to 40 GHz. The results show that MWCNT-fused silica composites exhibit excellent EMI shielding ability with SE reaching 68 dB for 10 vol.% MWCNT-fused silica composite. MWCNT-fused silica composites were found to be more effective in providing EMI SE compared to that of CB-fused silica composites in broad-band frequency. The SE of 10 vol.% MWCNT composites increases approximately two times, while the SE of 10 vol.% CB-fused silica composites is unchanged from X band to Ka band. Furthermore, the addition of MWCNTs dramatically improves the conductivity and complex permittivity of the composites, which contribute high EMI SE. These results imply that MWCNT-fused silica composites may present potential application as shielding materials in broad-band microwave frequency.

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