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Electromagnetic and microwave absorbing properties of Co-filled carbon nanotubes

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ABSTRACT

Microwave absorbing property, complex permittivity and permeability of the Co-filled carbon nanotubes (CNTs) have been investigated. CNTs were filled with Co nanoparticles via a wet-chemical method. Compared with the CNTs, the real part (ε') and imaginary part (ε'') of the complex permittivity as well as the dielectric dissipation factor ($\tan\delta_\varepsilon = \varepsilon''/\varepsilon'$) of the Co-filled CNTs were much smaller, while the real part (μ') and imaginary part (μ'') of the complex permeability and the magnetic dissipation factor ($\tan\delta_\mu = \mu''/\mu'$) were greater. The Co-filled CNT/epoxy composites achieved a reflection loss below −10 dB (90% absorption) at 10.8–14.2 GHz, and the minimum value was −21.84 dB at 12.2 GHz. The microwave enhancement absorption of the Co-filled CNT/epoxy composites was attributed to both dielectric and magnetic losses. The microwave absorbing peak of the CNT/epoxy composites moved to the higher frequency by filling the Co nanoparticles into the CNTs. Compared with the CNTs, there are more interfaces between the Co nanoparticles and CNT inner surfaces in the Co-filled CNTs. Therefore, interfacial multipoles contributed to the absorption of the Co-filled CNT/epoxy composites.

1. Introduction

Carbon nanotubes (CNTs) have many practical and potential applications due to their outstanding physical and electrical properties [1,2]. The unique mechanical property of CNTs, their high strength and stiffness and the enormous aspect ratio make them a potential structural element for the improvement of mechanical properties of composites. Further potential advantages, which promote CNTs as ultimate fillers for polymers, are their electrical and thermal conductivities together with a low density [3–8]. Magnetic nanocomposites have potential applications in various areas such as magnetic recording, magnetic data storage devices, toners and inks for xerography, and magnetic resonance imaging. Therefore, studies on magnetic nanocomposites, especially on magnetic CNT composites, are rapidly expanding. Many researchers have attempted to fill metals or metal compounds into the CNTs. The CNTs filled with ferromagnetic metals have potential applications in anisotropic magnetic responses as high density magnetic recording media [9], microwave absorption [10–18], and in biomedicine [19]. The metallic encapsulates are effectively protected by CNTs from oxidation and consequently, showing long-term stability [20]. A great variety of metal filled CNTs have now been developed using various methods for the synthesis, including capillary action, wet-chemical methods, arc techniques, catalytic chemical vapor deposition and pyrolysis of organometallic compound [10–25], etc. The main advantages of the wet-chemical approach are its flexibility and the level of experimental control so that a wide variety of materials can be introduced into the nanotubes [13].

Microwave absorbing materials have attracted significant interest because of their applications in commercial and military industries [26–49]. The manufacture of microwave absorbing materials involves the use of compounds capable of generating dielectric and/or magnetic losses when impinged by an electromagnetic wave. Che et al. [10] investigated the microwave absorption of heat-treated in situ synthesized α-Fe-filled CNT/epoxy composites with thickness of 1.2 mm, which achieved a reflection loss below −10 dB at 2–18 GHz. Zhu et al. [11] and Lin et al. [12] calculated the microwave absorption of the in situ synthesized Fe-filled CNT/olefin composites on the basis of the measured complex permittivity and permeability at 2–18 GHz and 8–18 GHz. With matching thickness of 3.5 mm, the maximum reflection loss is about −22.73 dB for the Fe-filled CNT/olefin composites. The bandwidth corresponding to the reflection loss below −10 dB is more than 4.22 GHz [12]. But when the thickness of the composites is 2.5 mm, the bandwidth below −10 dB is less than 1 GHz [11]. Despite several studies on the microwave absorption of Fe-filled [10–13], Ni-filled [14] and Sn-filled CNTs [15], the microwave absorption studies for Co-filled CNTs prepared by the wet-chemical method are few. In this paper, we investigated the preparation of Co-filled CNTs by the wet-chemical method and the microwave absorption of

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the Co-filled CNT/epoxy composites, and the possible microwave absorbing mechanisms were discussed.

2. Experimental

The CNTs were prepared by catalytic decompose of benzene using floating transition at 1100–1200 °C in our laboratory. The CNTs were treated with boiling HNO_3 (68%) for 24 h, then washed several times with distilled water and dried in an oven at 60 °C for 24 h. The acid-treated CNTs were stirred with $CoSO_4$ solution (40 wt%) for 24 h, filtered and washed with distilled water, then dried at 60 °C for 10 h. The sample was then heated under a nitrogen atmosphere at a rate of 8 °C min^{-1} from room temperature to 100 °C and kept at this temperature for 1 h before ramping at 4 °C min^{-1} to 450 °C. The sample was then calcined at 450 °C for 6 h. The calcined sample was then heated at 450 °C with flowing 10% H_2/N_2 (100 ml/min) for 6 h to reduce the metal oxide.

The morphology and microstructure of the CNTs, Co-filled CNTs, CNT/epoxy composites, and Co-filled CNT/epoxy composites were observed by using a transmission electron microscopy (TEM, Hitachi H-800) and a field-emission scanning electron microscopy (FESEM, Hitachi S-4700). X-ray diffraction (XRD) spectra were carried out with D/Max2500VB2+PC diffraction apparatus. The magnetic properties of Co-filled CNTs were measured by a vibration sample magnetometer (VSM, Lakeshore, Model 7300).

The complex permittivity and permeability of the CNT/paraffin and Co-filled CNT/paraffin composites were measured by the coaxial line method at 2–18 GHz using HP8722ES network analyzer in agreement with the method reported in Ref. [50]. The contents of CNTs and Co-filled CNTs were 10 wt% and 20 wt% respectively. The real part (ε') and imaginary part (ε'') of the complex permittivity of paraffin are 2.22–2.26 and 0–0.02 at 2–18 GHz respectively.

Epoxy resin was dissolved in the dimethylbenzene and n-butyl alcohol solvent, the content of epoxy resin was 50 wt%. The CNTs, Co-filled filled CNTs and epoxy solution were sufficiently mixed and then sonicated for 2 h. Polyamide was used as curing agent for epoxy curing. The mixtures were painted onto an aluminum plate layer by layer until the thickness of the composites reached 1.0 mm. The composites were cured by heating under infrared radiation at 60 °C under air condition for 2 h. The contents of the CNTs and Co-filled CNTs were 5 wt% and 10 wt% respectively. The specimen dimension was 180 mm long × 180 mm wide × 1.0 mm thick. The microwave absorption characteristics of the CNT/epoxy and Co-filled CNT/epoxy composites were measured in agreement with the method reported in Ref. [51].

3. Results and discussion

Fig. 1 shows the TEM images of CNTs and Co-filled CNTs. As seen from Fig. 1, the CNTs have an inner diameter in the range of 20–40 nm and an outer diameter in the range of 40–60 nm. The CNTs have been satisfactorily filled with Co nanoparticles. Fig. 2 shows the XRD spectra of the CNTs and Co-filled CNTs. The diffraction peaks identify the Co-filled CNTs as a mixture of Co and CNTs. No obvious peaks corresponding to Co oxides were observed in the XRD pattern.

The hysteresis curve of Co-filled CNTs was obtained at room temperature with a vibrating sample magnetometer, as is shown in Fig. 3. The saturation magnetization M_s, the remanent magnetization M_r, and the coercivity H_c are the main technical parameters to characterize the magnetism of ferromagnetic materials. M_s, M_r, and H_c, are 62.81 A m^2 kg^{-1}, 3.61 A m^2 kg^{-1} and 17.12 kA m^{-1} for Co-filled CNTs, respectively.

Since the absorbing properties of microwave absorbing materials can be estimated from their magnetic and dielectric properties, the essence of researching microwave absorbers is to design the compound and structure forms of the materials, by adjusting and optimizing the dielectric and magnetic properties such as complex permittivity and permeability of the materials. In order to investigate the intrinsic reasons for microwave absorption of the CNTs and Co-filled CNTs, we measured the complex permittivity and permeability of the CNT/paraffin and Co-filled CNT/paraffin composites by the coaxial line method. As illustrated in Figs. 4 and 5, the ε', ε'' and dielectric dissipation factors ($\tan\delta_\varepsilon = \varepsilon''/\varepsilon'$) of the Co-filled CNTs are smaller than those of CNTs. While the real part (μ') and imaginary part (μ'') of the complex permeability and the magnetic dissipation factors ($\tan\delta_\mu = \mu''/\mu'$) of the Co-filled CNTs are bigger than those of CNTs. The μ'' and $\tan\delta_\mu$ of CNTs are almost zero. So the microwave enhancement absorption of Co-filled CNTs was attributed to both dielectric and magnetic losses. The microwave absorption of the CNTs resulted mainly from dielectric loss rather than magnetic loss.

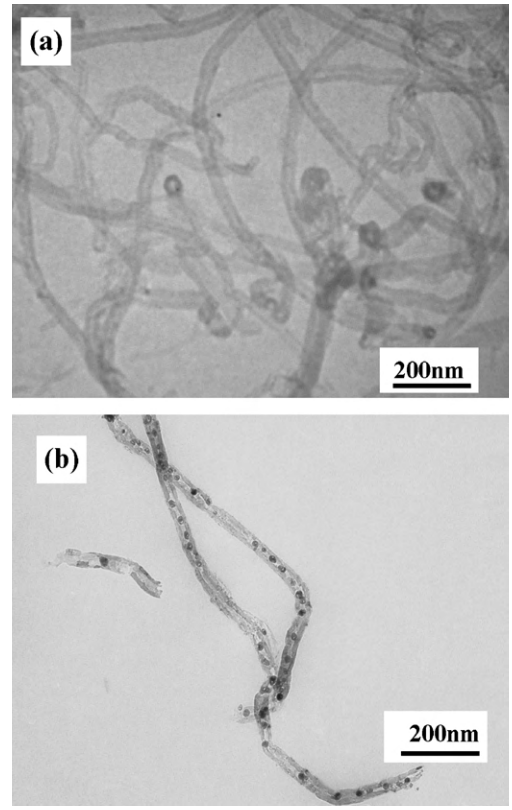

Fig. 1. TEM images of CNTs (a) and Co-filled CNTs (b).

Fig. 6 shows the SEM images of the cross sections of the CNT/epoxy and Co-filled CNT/epoxy composites. As seen from Fig. 6, the CNTs and Co-filled CNTs were pulled out from the epoxy matrix, and they were well dispersed in the epoxy matrix.

Fig. 7 shows the frequency dependence of the reflection loss of the CNT/epoxy and Co-filled CNT/epoxy composites. As can be seen from Fig. 7, the reflection loss of the CNT/epoxy composites is below −10 dB (90% absorption) at 10.1–13.1 GHz, and the minimum value is −22.89 dB at 11.4 GHz. The bandwidth corresponding to the reflection loss below −10 dB is 3.0 GHz. For the Co-filled CNTs, the

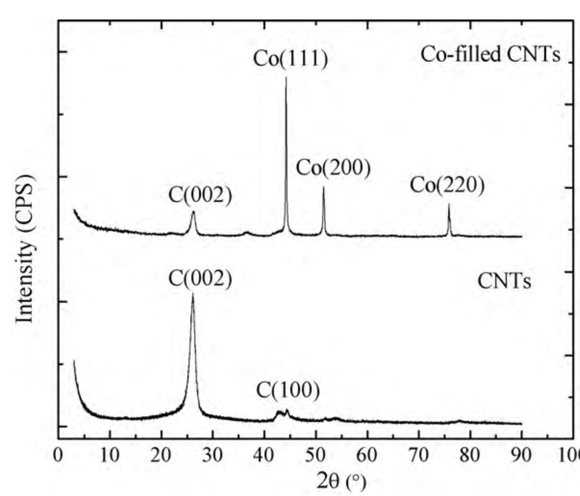

Fig. 2. XRD patterns of CNTs and Co-filled CNTs.

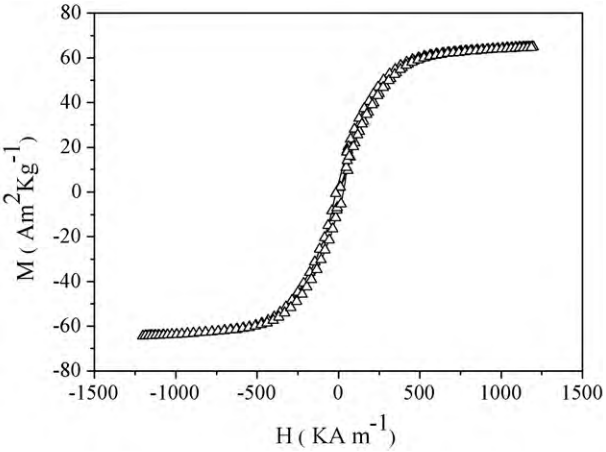

Fig. 3. *M–H* curve for Co-filled CNTs.

reflection loss of the corresponding composites is below −10 dB at 10.8–14.2 GHz, and the minimum value is −21.84 dB at 12.2 GHz. The bandwidth corresponding to the reflection loss below −10 dB is 3.4 GHz. The microwave absorbing peak of the CNT/epoxy composites moved to the higher frequency by filling the Co nanoparticles into the CNTs. Compared with the results of Refs. [10–15], the Co-filled CNT/epoxy composites in our this research work with much less thickness (matching thickness = 1.0 mm) achieved a better microwave absorbing property.

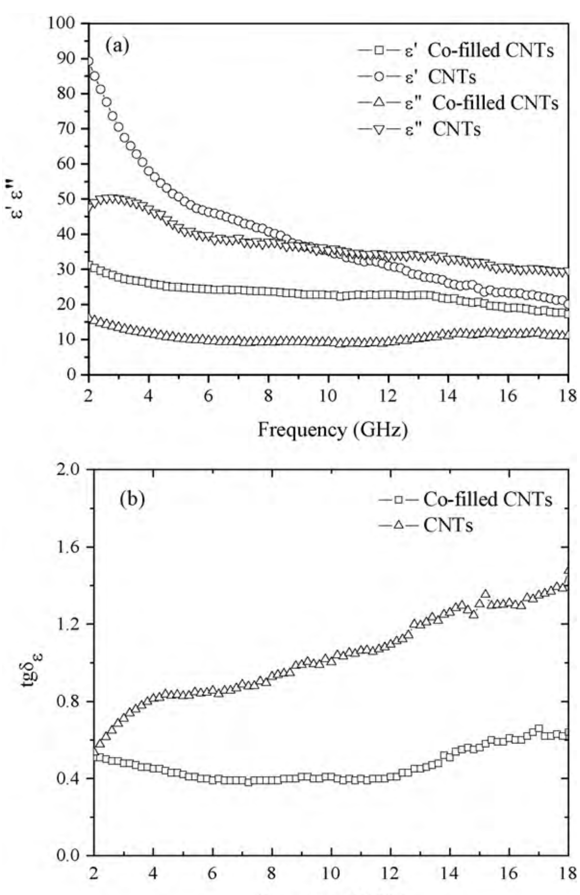

Fig. 4. Frequency dependence of permittivity (a) and tan δ_ε (b) of the CNT/paraffin and Co-filled CNT/paraffin composites.

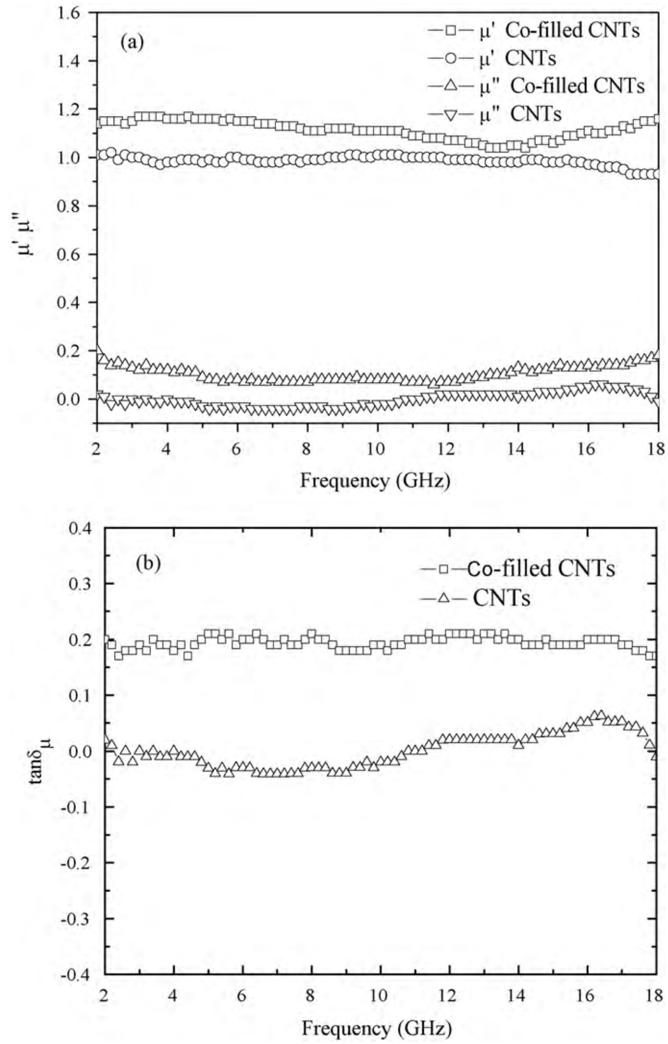

Fig. 5. Frequency dependence of permeability (a) and tan δ_μ (b) of the CNT/paraffin and Co-filled CNT/paraffin composites.

In the procedure of filling CNTs, the CNTs were almost opened and cut off after being treated with nitric acid for 24 h, so the microstructure of the CNTs changed greatly. Compared with the CNTs, there existed more defects and suspending bands in the Co-filled CNTs. And the weight of CNTs was doubled after being filled with Co nanoparticles. So the defects and suspending bands could cause multiple scattering and interfacial electric polarization, which provided an important absorbing mechanism. It occured due to the interaction of microwave radiation with charge multipoles at the interfaces between Co-filled CNTs and epoxy matrix. The quantum confine effect made the properties of Co change greatly. According to the Kubo theory, the energy levels in the Co-filled CNTs are not continuous but split because of the quantum confine effect. When an energy level is in the range of microwave energy, the electron will absorb a photon to hop from a low energy level to a higher one. There are many interfaces between the epoxy matrix and CNTs outer surfaces. Compared with the CNTs, there are more interfaces between the Co nanoparticles and CNT inner surfaces in the Co-filled CNTs. Therefore, interfacial multipoles contributed to the absorption of the epoxy composites containing Co-filled CNTs.

From our research work, the absorption peak frequency of the CNT/epoxy composites can be tuned by filling Co nanoparticles into CNTs. It is observed that the value of magnetic loss of the Co-filled CNTs is much higher than that of CNTs in the frequencies ranging

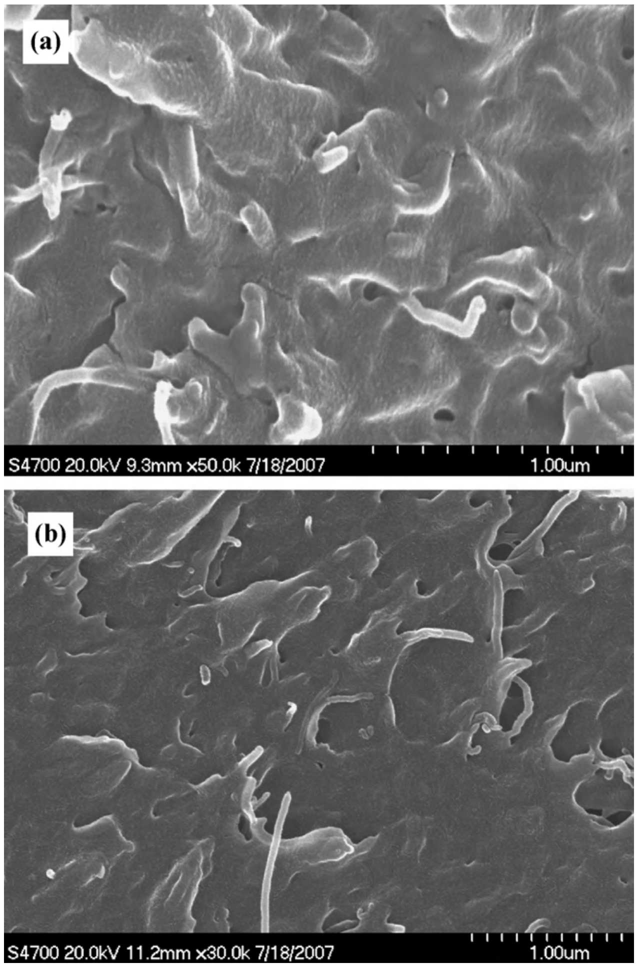

Fig. 6. SEM images of CNT/epoxy composites (a) and Co-filled CNT/epoxy composites (b).

from 2 GHz to 18 GHz in Fig. 5. So the microwave enhancement absorption of Co-filled CNTs was attributed to both dielectric and magnetic losses. The microwave absorption of the CNTs resulted mainly from dielectric loss rather than magnetic loss. The CNTs and Co-filled CNTs in epoxy matrix composites were used as dipoles to absorb the microwave. In the microwave absorbing material containing an electromagnetic loss substance and dipoles, the dipoles

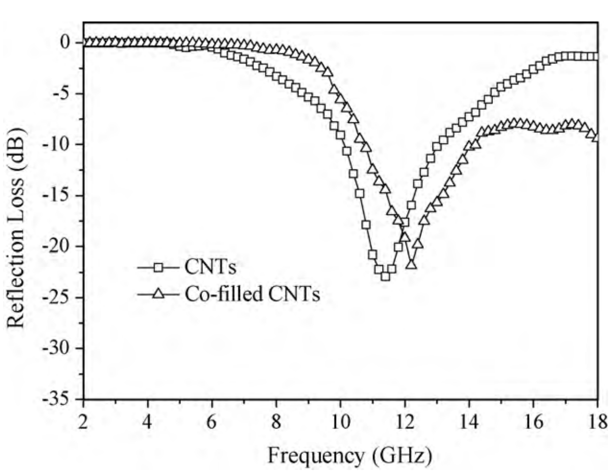

Fig. 7. Microwave absorbing properties of the CNTs/epoxy composites and Co-filled CNTs/epoxy composites.

as electron couples can generate an inductive current in the electromagnetic field. The induced current then causes a loss current and energy dissipation. This is the main mechanism in microwave attenuation. The CNTs, Co-filled CNTs will be good candidates for the microwave absorbing materials.

4. Conclusions

Compared with the CNTs, ε', ε'' and $\tan\delta_\varepsilon$ of the Co-filled CNTs were much smaller, while the μ', μ'' and $\tan\delta_\mu$ were greater. M_s, M_r, and H_c of the Co-filled CNTs were 62.81 $A\,m^2\,kg^{-1}$, 3.61 $A\,m^2\,kg^{-1}$ and 17.12 $kA\,m^{-1}$, respectively. The reflection loss of the Co-filled CNT/epoxy composites was below −10 dB at 10.8–14.2 GHz, and the minimum value was −21.84 dB at 12.2 GHz. The microwave absorbing peak of the CNT/epoxy composites moved to the higher frequency by filling the Co nanoparticles into the CNTs. The microwave enhancement absorption of Co-filled CNT/epoxy composites was attributed to both dielectric and magnetic losses. The interfacial multipoles contributed to the strong absorption of the Co-filled CNT/epoxy composites.

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