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A study of the electromagnetic properties of Cobalt-multiwalled carbon nanotubes (Co-MWCNTs) composites

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ABSTRACT

Electroless plating was utilized to deposit Cobalt (Co) on the surface of multi-walled carbon nanotubes (MWCNTs), and the technological parameters of electroless plating were optimized. To obtain optimized processing parameters, field-emission scanning electron microscope (FESEM) as well as energy dispersive spectroscopy (EDS) results were presented to show the morphology, components of as-prepared Co-MWCNTs. Based on the optimized processing parameters, Co-MWCNTs were prepared and filled into the epoxy resin to fabricate Co-MWCNTs composites. The electromagnetic properties of pure MWCNTs composites and Co-MWCNTs composites were studied. To sum up, the pure MWCNTs composites with a filler concentration of 2 wt% had an intense absorbing peak at 15.20 GHz, where the highest reflection loss (R) reached −21.41 dB. Compared to the pure MWCNTs composite at the same concentration, the Co-MWCNTs composites showed a higher impedance which implies a better potential absorbing property and makes Co-MWCNTs probable to be utilized in electromagnetic absorbing field.

1. Introduction

The discovery of carbon nanotubes (CNTs) has stimulated intense interest in many scientific fields [1–3] due to their fascinating electronic, mechanic and chemical properties. The magnetic modification of CNTs makes them possess unique electromagnetic properties [4], and modified CNTs have potential applications [5–8] as magnetic data storage, nano-ferromagnetic, microwave absorbing materials, magnetic composites for drug delivery, etc. Several approaches [9,10] have been explored for the preparation of metal-nanotubes compounds, such as filling metals into nanotubes, electron-beam deposition and electroless plating. Electroless plating has been widely used as a simple way to combine the magnetic metals and CNTs, in which Fe, Co, Ni usually play as magnetic roles [11–13] to modify CNTs and enhance their electromagnetic properties. Several publications had shown that, the uniformity of the coating varies drastically depending on the coating conditions. Therefore, controlling the coating conditions becomes a crucial issue to obtain uniform coating of the metal. As reported in former research [8], uniform coating without surplus metallic particles was hard to synthesize because the nanoparticles, driven by the minimization of surface energy, tend to aggregate into large coalescences during their formation process [6].

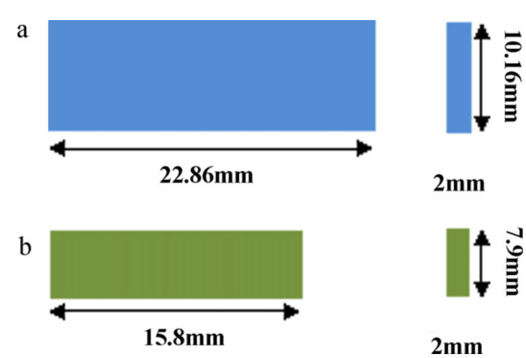

Fig. 1. The schematic of specimen for electromagnetic testing (a: specimen for testing in the frequency range of 8.2–12.4 GHz, and b: specimen for testing in the frequency range of 12.4–17.8GHz).

The former study [8] manifested the trend that the metallic particles aggregate will be enlarged especially when the content of the metallic salt is increasing. As a result, it is better to lower the amount of metallic salt during the electroless plating process. Meanwhile, it is undesirable that the Fe, Co or Ni are coating together in one plating process as reported in the former work [8] because the coating was not uniform and the aggregation of metallic particles could not be avoided. Since the research of plating Co alone was rare [14,15], it is worth to plate Co alone on the MWC-

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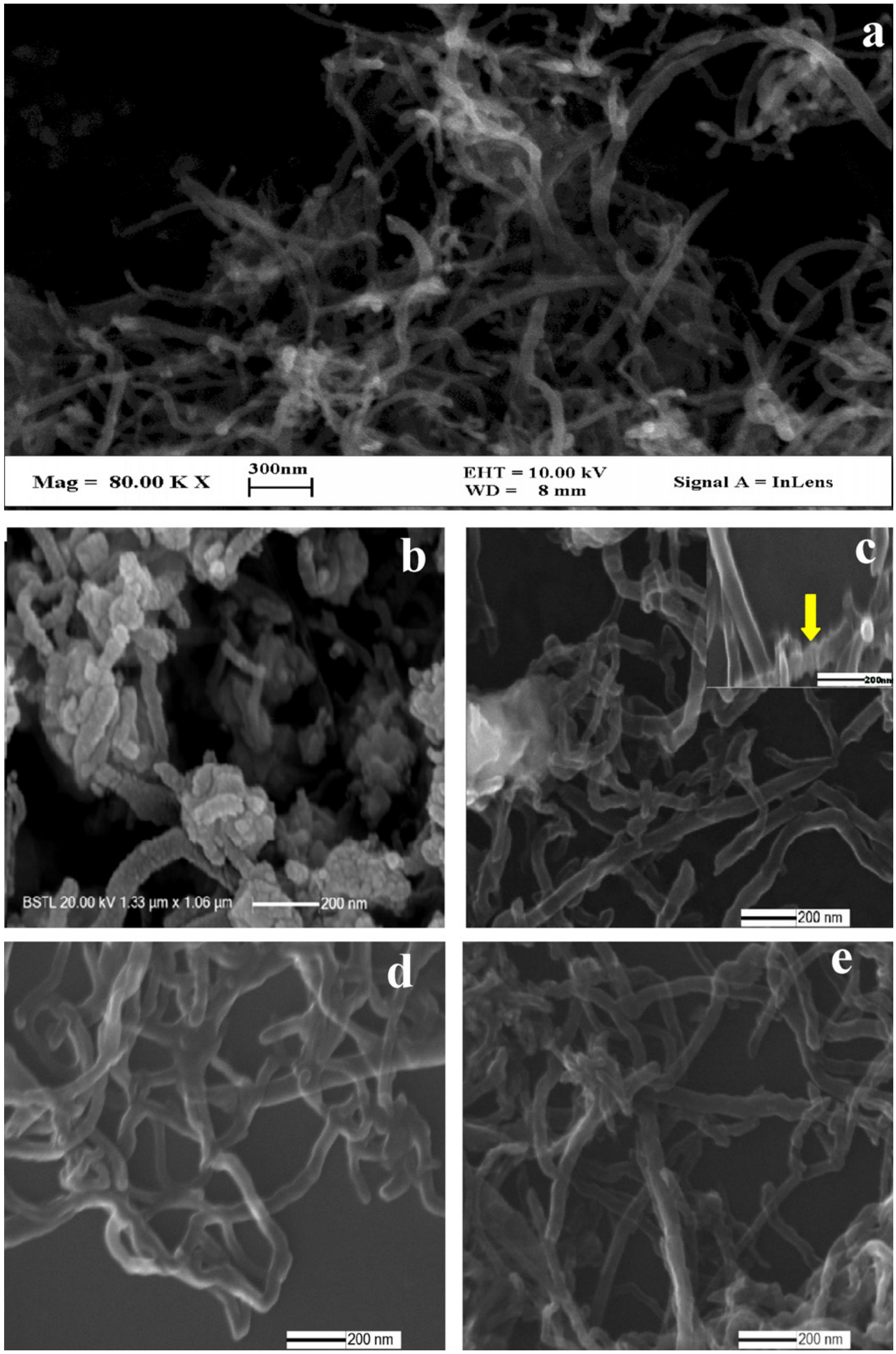

Fig. 2. FESEM of MWCNTs and Co-MWNTs (a: raw MWCNTs; b: Co-MWCNTs prepared with 0.06 mol metallic salt and pH 11; c, d: CO-MWCNTs prepared with 0.006 mol metallic salt and pH 11; e: Co-MWCNTs prepared with 0.006 mol metallic salt and pH 9).

NTs and lower the metallic salt to get uniform coating as well as excellent electromagnetic properties.

In our work, electroless plating was utilized to deposit Cobalt (Co) on the surface of multiwalled carbon nanotubes (MWCNTs). To optimize the processing parameters, the morphology, components of Co-MWCNTs were characterized by field-emission scanning electron microscope (FESEM) equipped with energy dispersive spectroscopy (EDS). The coating was effectively controlled and the aggregation of magnetic nanoparticles was avoided successfully. Pure MWCNTs and as-prepared Co-MWCNTs were filled into Epoxy resin (E-51) to fabricate MWCNTs composites and Co-MWCNTs composites, separately. The electromagnetic parameters of MWCNTs composites, Co-MWCNTs composites were measured to calculate absorbing properties. It was found that the microwave absorption properties of MWCNTs composites could be improved by coating Co onto MWCNTs.

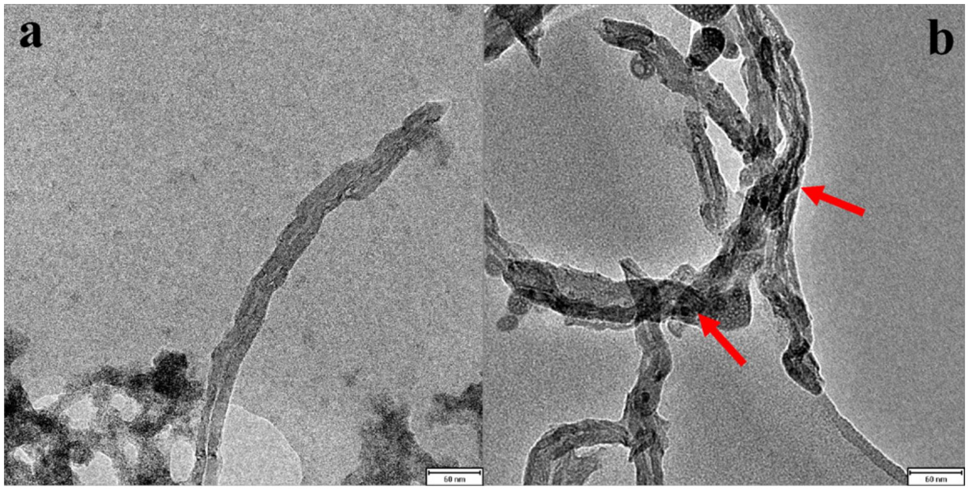

Fig. 3. TEM images of MWCNTs (a) and Co-MWNTs(b).

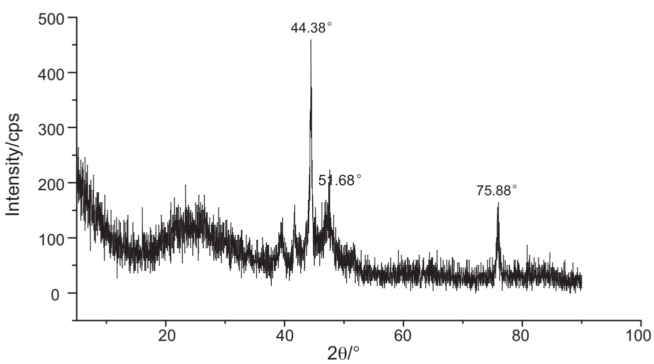

Fig. 4. XRD pattern of Co-MWCNTs.

2. Experiment

2.1. Electroless plating Co onto MWCNTs

MWCNTs prepared by chemical vapor deposition (CVD) on Fe templates were purchased from Shenzhen Nanoport Company, and the purity was claimed to be 95% by the manufacturer. The MWCNTs are purified by ultrasonication in a concentrated sulfuric acid/nitric acid (3:1, v/v) for 4 h. The purified MWCNTs are filled in the aqueous solution of $SnCl_2$ and concentrated muriatic acid to reacting for 60 min followed by filtrating and drying. Then the MWCNTs particles are filled into the aqueous solution of $PdCl_2$ and concentrated muriatic acid to reacting for another 60 min. The as-prepared MWCNTs are finally filled in the aqueous solution of $Na_3C_6H_5O_7$, $CoSO_4 \cdot 7H_2O$ and NaH_2PO_2. The pH of the solution is adjusted by ammonia. The reaction continues until no bubbles arising. The solution is filtrated under vacuum and the as-prepared Co-MWCNTs are dried in a vacuum drier.

2.2. Composites preparation

Appropriate amount of fillers (MWCNTs/Co-MWCNTs) are weighed out and dispersed in solution of epoxy (E-51) and diluter. The epoxy-CNTs suspension is ultrasonicated for 1 h at 60 °C. Then the curing agent is added in the suspension. Well stirred mixture is poured into moulds as shown in Fig. 1 and the liquid were cured at room temperature for 24 h to fabricate specimens for electromagnetic parameters testing. Both of the composites were prepared to have concentrations of 0.5 wt%, 1 wt% and 2 wt%.

2.3. Material characterization

The morphology of MWCNTs was observed by FESEM (Apollo-300 OXFORD Corporation) and Transmission Electron Microscope (JEM-2100F) as well as the elemental components was presented by the energy-dispersive X-ray detector (EDX, HORIBAEX-250). X-ray diffraction pattern was tested by D/max diffraction instrument. An 8722ES vector network analyzer was applied to determine the complex relative permeability $\mu = \mu' - j\mu''$ (μ': the real part of permeability, μ'': the imaginary part of permeability) and relative permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ (ε': the real part of permittivity, ε'': the imaginary part of permittivity) in the frequency range of 8.2–12.4 GHz and 12.4–17.8 GHz for the calculation of reflection loss and impedance.

3. Result and discussion

To optimize the parameters of the processing, the morphologies of Co-MWCNTs under different conditions are shown in Fig. 2. The raw MWCNTs are shown in Fig. 2a. In Fig. 2b and c, the treated MWCNTs are prepared with 0.06 mol and 0.006 mol metallic salt at the same pH value respectively, while in Fig. 2d and e, the treated MWCNT were prepared under different pH (pH 9 for Fig. 2d, pH 11 for Fig. 2e) with the same amount of metallic salt. As it is shown in Fig. 2, the MWCNTs were wrapped with a metal layer, which is conspicuous in Fig. 2b. The top right corner of Fig. 2b was partial enlarged detail of the Co-MWCNTs prepared with the metallic salt of 0.006 mol, in which the highlight of arrow shows the surface roughness of a single carbon nanotube meaning that the MWCNTs have been coated well by Cobalt. This result is also confirmed by the TEM image of raw materials and Co-MWCNTs. Black dots are found on the walls of the nanotubes, as shown in Fig. 3b (the red arrow), which indicated that the metal has been deposited on the surface of the nanotubes, since in the TEM image of raw materials, no such black dots exist according to Fig. 3a. (For interpretation of the references to color in text, the reader is referred to the web version of the article.) However, in Fig. 2b there are plenty of dissociative metal aggregations and the metallic layer is not uniform, indicated that the plating state is inferior. With the decreasing of the metallic salt, the amount of dissociative metals was significantly reduced. When the content of the metallic salt was decreased to 0.006 mol as shown in Fig. 2c and d, there are scarcely any dissociative metals in the images and the coating is smooth. In Fig. 2d and e, as the amounts of the metallic salt were both 0.006 mol, the metallic aggregations cannot be seen in both of the two images, which

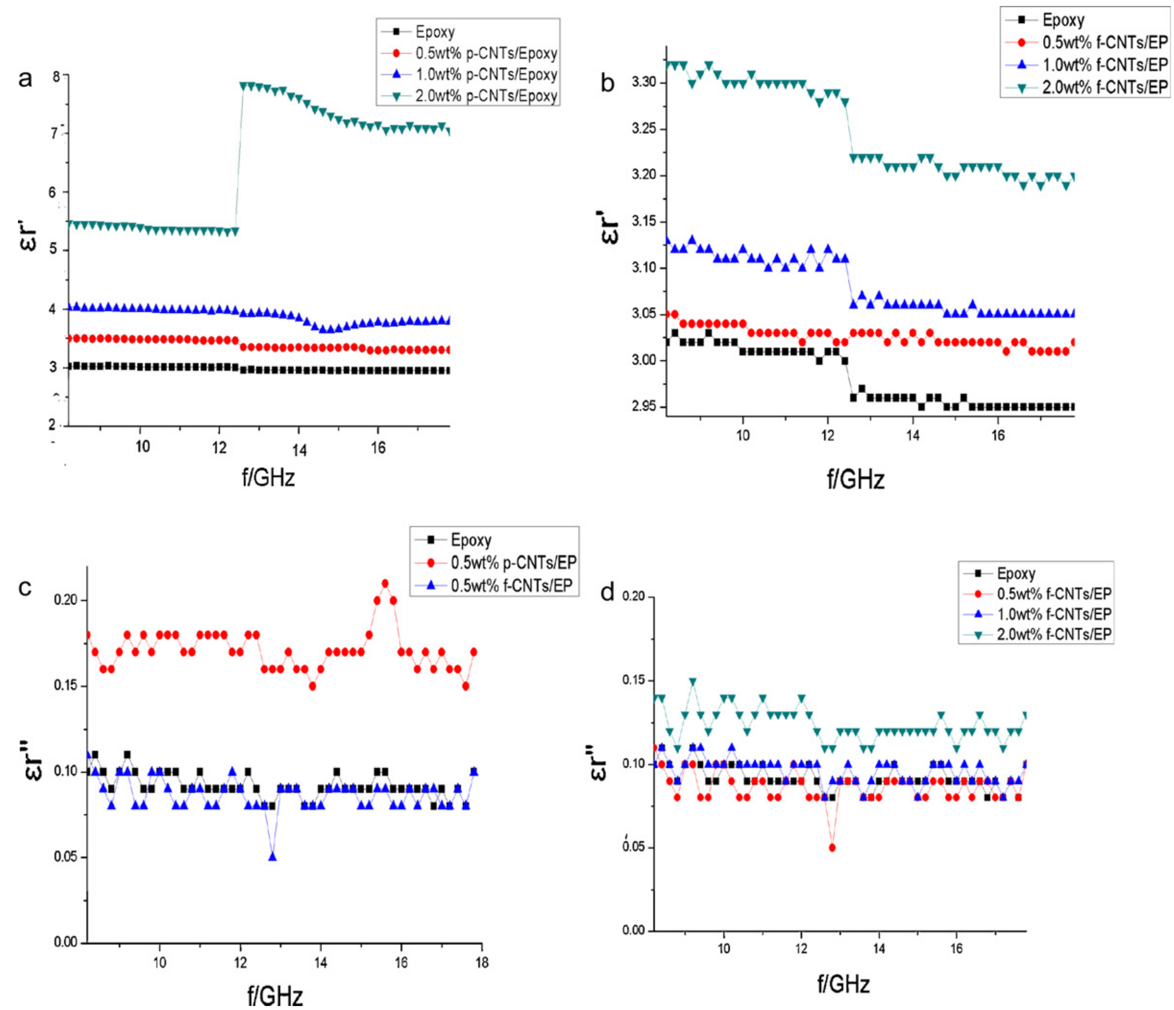

Fig. 5. The complex permittivity of composites (a: ε' of MWNTs composites, b: ε' of Co-MWNTs composites, c: ε'' of MWNTs composites, and d: ε'' of Co-MWNTs composites).

means that the changing of pH has no influence on the forming of the metallic agglomerates.

The elemental components of Co-MWCNTs with different amounts of metallic salt were shown in the third and fourth rows of Table 1. The element of Oxygen (O), Carbon (C), Cobalt (Co) and Ferrum (Fe) are found in the treated MWCNTs. Of these elements, Carbon is the main component of MWCNTs. Purifying the CNTs with mixed acid can not only eliminate the amorphous carbon, but it also brings many functional groups such as –OH, –COOH on the CNTs [16] which brings in the element O. The Co and Fe are obtained from plating and syntheses of MWCNTs respectively. The result of EDS (Table 1) shows that the content of O is decreased as the increasing of the Co which can be explained by the reaction [8] during electroless plating. The reaction equation is shown in Eqs. (1) and (2). Since the reaction linking Co onto the surface of MWCNTs expends oxygenic functional groups on the surface of MWCNTs, the increasing Co will result in the reducing of oxygenic element. The content of Co was demonstrated in Table 1 to decrease with the reducing of metallic salt. With a relative low metallic salt content of 0.006 mol, the EDS result shows the mass content of Co is still as high as 35.19%. Combining with the result of SEM, the dissociative metal aggregations were disappeared at this condition, so the Co must be wrapped on the MWCNTs. As a result, the 0.006 mol was chosen as the optimized parameter of the content of metallic salt. The elemental contents of Co-MWCNT with different pH values were also shown in Table 1. The result illustrates that with a higher pH, the amount of Co on the MWCNTs is enlarged. The fact that the increasing of pH could promote the plating reaction degree has been reported before [8]. So pH of 11 was chosen as optimized plating parameter.

$$H_2PO^- + OH^- \xrightarrow{pd} HPO_3{}^{2-} + 2H \quad (1)$$

$$Co^{2+} + 2H \rightarrow Co + 2H^+ \quad (2)$$

XRD patterns of the Co-MWCNTs are also tested to further ensure the existing of Co, as shown in Fig. 4. For Co-MWCNTs, the diffraction peaks at 2XRD patterns of the Co-MWCNTs are shown in Fig. 4. For Co-MWCNTs, the diffraction peaks at $2\theta = 44.4^\circ$, 51.6°, and 75.8° can be well indexed to the cubic fcc-type Co crystals.

Fig. 5 manifests the complex permittivity of pure MWCNTs composites and Co-MWCNTs composites of different concentrations, which represents the typical dielectric and magnetic properties of the samples investigated in this work. Both of the real part of permittivity ε' and the imaginary part of permittivity ε'' were apparently rising with the concentration for both of the composites, as is shown in Fig. 5a and b respectively. But the increasing pace of ε' was much lower for Co-MWCNTs composites than MWCNTs composites. CNT has high conductivity which tends to form conducting network in the composite based on its special morphology which leads to the increase of the ε' in composites [20]. However, the purification of MWCNT with concentrated acid destroyed the structure of the MWCNTs and the coating of Co would affect the forming of the conduct network which finally leads to the decrease of the ε' com-

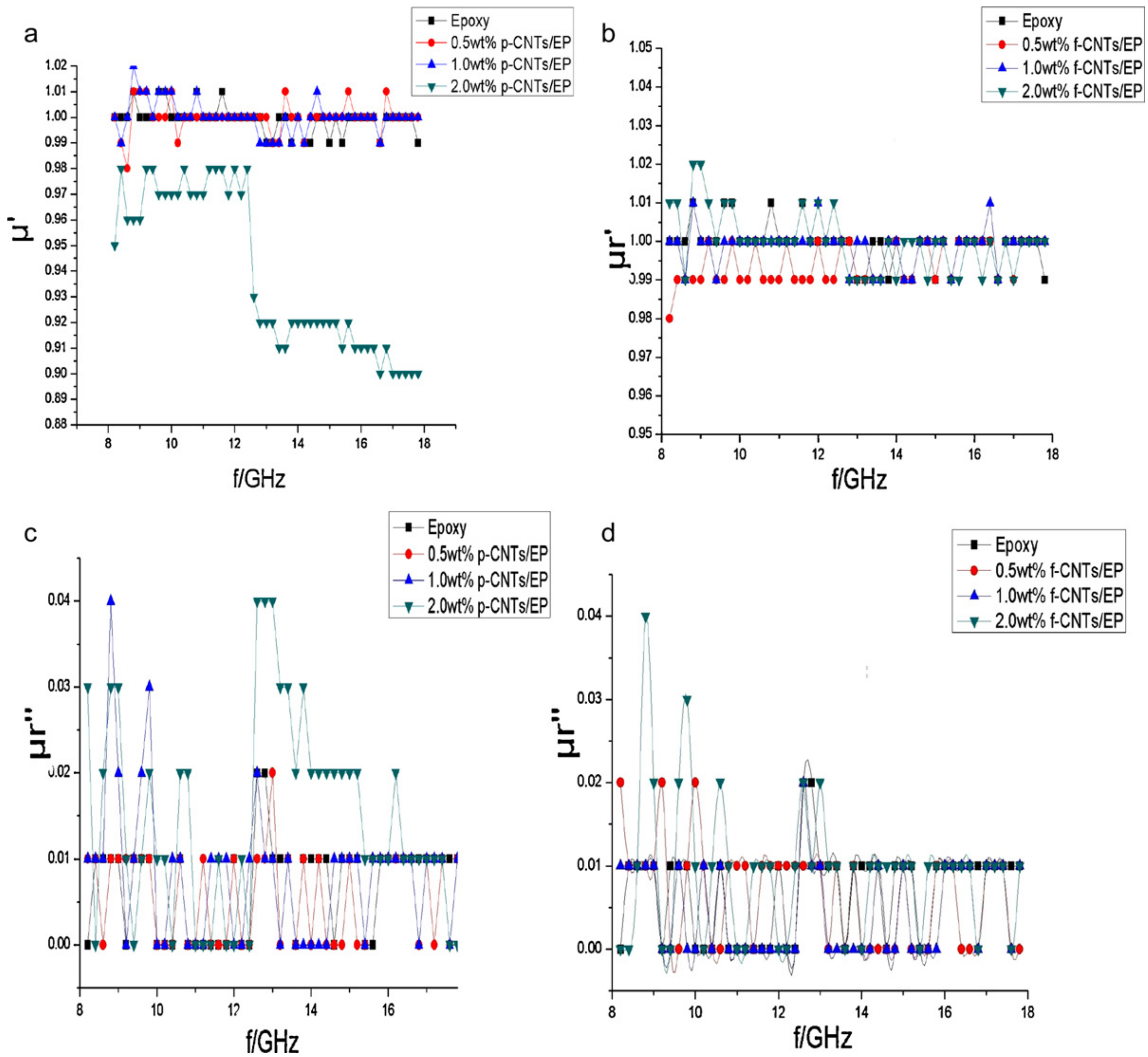

Fig. 6. The complex permeability of composites (a: μ' of MWNTs composites; b: μ' of Co-MWNTs composites; c: μ'' of MWNT composites; and d: μ'' of Co-MWNTs composites).

Table 1
The EDS result of Co-MWNTs with different processing.

Processing	Mass percent				Atomy percent				
	C	O	Co	Fe	C	O	Co	Fe	
Metallic salt (mol)	0.06	11.11	2.35	81.82	1.07	37.03	5.88	55.58	0.77
	0.006	41.78	22.31	35.19	0.72	63.45	25.43	10.89	0.24
pH	11	21.61	4.25	72.56	1.58	54.13	7.99	37.03	0.85
	9	44.46	19.85	34.97	0.72	66.72	22.36	10.70	0.23

pared with the pure MWCNT composites. The rise of ε' implies that the filler could increase the electrical loss in the composite. The MWCNT composite shows a higher ε'' at frequency of 12.4–17.8 GHz which illustrated better electrical loss at high frequency.

The magnetic metal Co could enhance the magnetic properties of CNT, but in this work the increase was not obvious as the content of metallic salt was limited. Fig. 6 shows the complex permeability of MWCNTs and Co-MWCNTs composites with different filler content. As it is shown in Fig. 6, both the real part of permeability μ' and the imaginary part of permeability μ'' in all composites were almost the same as the pure resin, except that Co-MWCNT composite with 2.0 wt% fillers had a little peak at 8.4 GHz showing the trend of elevated magnetic properties.

For further investigation of the microwave absorption, the reflection loss of MWCNTs composite (2 wt%; p-CNTs) and Co-MWCNTs composite (2 wt%; f-CNTs) are calculated. The reflection loss curves of MWCNTs, Co-MWCNTs are shown in Fig. 7. The reflection loss of a microwave absorbing layer is given by [17–19]

$$R(dB) = 20\log\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \quad (3)$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[j\left(\frac{2\pi}{c}\right)\sqrt{\mu_r\varepsilon_r}fd\right] \quad (4)$$

where Z_{in} is the normalized input impedance, c is the velocity of electromagnetic waves in free space, f is the microwave frequency, and d is the thickness of the absorbing layer. Therefore, microwave

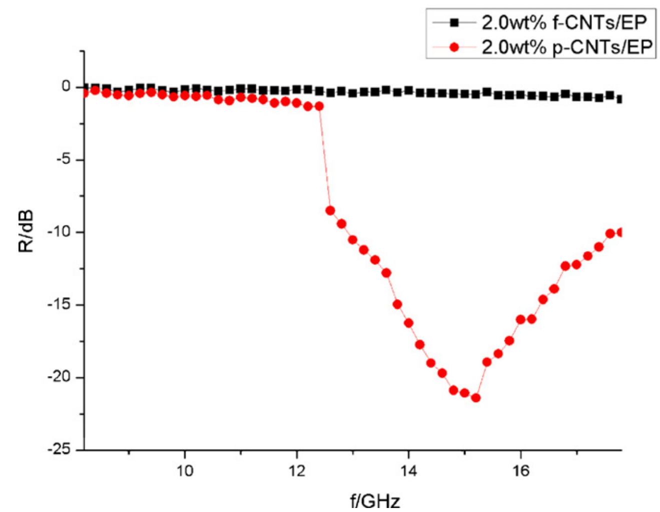

Fig. 7. The reflect reflection loss curves (f-CNTs:Co-MWNTs, p-CNTs: MWCNTs).

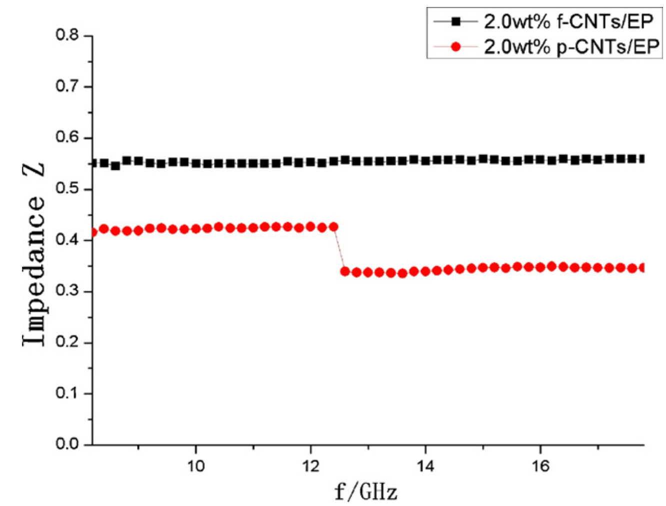

Fig. 8. The impedance of composites at different frequency (f-CNTs:Co-MWNTs, p-CNTs:MWCNTs).

propagation in electromagnetic media is largely determined by the complex relative permeability and permittivity of the absorbing materials. All the calculated values were predicted based on a constant thickness $d = 2.0$ mm.

In the reflection loss curve, the MWCNTs composite shows a wide absorbing peak at about 15.20 GHz, and the highest reflectivity(R) has reached −21.41 dB. The frequency width of the $R < -10$ dB was 4.80 GHz. However, the reflection loss curve of Co-MWCNTs is flat without any peak and has a high R of 0 dB.

The results of reflection loss curves can be explained in terms of the resonant absorb theory [22], in which to obtain resonant absorption of a single-layer absorber, the thickness and wavelength should obey the following relationship [22,23]:

$$d = \frac{\lambda_0}{4\sqrt{\varepsilon\mu}} \tag{5}$$

where d is the thickness of the layer; λ_0 is the wavelength of electromagnetic wave under vacuum; ε is the relative permittivity; and μ is the relative permeability.

To investigate the possible mechanisms and effects giving rise to the enhancement of microwave absorptions, the impedance curve and resonant thickness curve are calculated based on the resonant absorb theory and Eqs. (3)–(5) and the result presents in Figs. 8 and 9. When a bunch of electromagnetic waves enter a medium, part of the waves are enter into the medium, and the other are reflected by the surface of the medium. According to matching condition theory [21], when the impedance reaches Z_0 (Z_0 is impedance under vacuum; its value is 1), the reflection of the surface is vanished and all of the wave will enter into the interior of the composites. The impedance of pure MWCNTs composite ranging from 0.30 to 0.45 is far away from the Z_0. However, the calculated resonant thickness is 1.86 based on resonant theory which is almost equal to the real thickness of 2.0 mm in the experiment. Therefore, it shows a wide absorbing peak at 15.20 GHz. On the other hand, the impedance of Co-MWCNTs composite in a range of 0.5–0.6 is much close to the Z_0. This result can be explained by the data of electromagnetic parameters. The implement is proportional to the ratio of permittivity to permeability. Compared to the MWCNTs composite, the treated material has a lower permittivity and a higher permeability which leads the two parameters to be nearly equal and the implement is closer to 1. As a result, the reflection from the surface can be better restrained for the Co-MWCNTs composites and more waves could enter into the medium. But a high absorbing property is not prominently shown in the reflection loss curves, which can be explained by resonant thickness curve. The calculated thicknesses

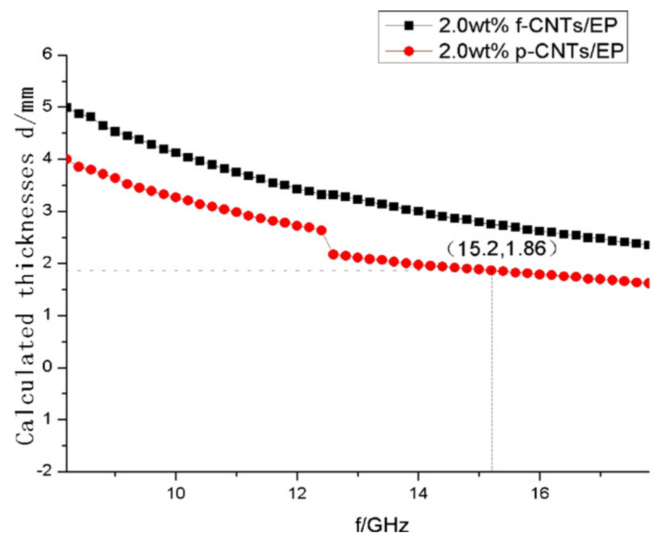

Fig. 9. The resonant thickness of composites at different frequency (f-CNTs:Co-MWNTs, p-CNTs:MWCNTs).

of Co-MWCNT composites are much larger than its real thickness of 2 mm, which means that the reflecting waves from the surface and the inner of the composites are not counteracting adequately. However, the implement of the Co-MWCNTs is closer to Z_0. As a result, as for the Co-MWCNTs composites, the microwave could enter into its body easily, which makes Co-MWCNTs composites probable to be utilized as the first layer of two-layer absorbing material.

4. Conclusion

Co-MWNTs are prepared successfully with optimized condition, in which the metallic salt is down to 0.006 mol and pH value is 11. As-prepared Co-MWCNTs are filled into epoxy resin to fabricate composites. With the electromagnetic analysis, the Co-MWNT composites were demonstrated to have lower surface reflection, which have the potential to be applied as the matching part in two-layer absorbing material.

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] Y.C. Qing, W.C. Zhou, et al., J. Inorg. Mater. 25 (2010) 181.

[3] Y. Zhao, L. Yuan, Y.X. Duan, J. Nanosci. Nanotechnol. 10 (2010) 5339.
[4] Y. Lu Yuan, Zhao, YXDuan, Acta Mater. Compos. Sinica 25 (2008) 78.
[5] Z.J. Fan, G.H. Luo, Z.F. Zhang, L. Zhou, F. Wei, Mater. Sci. Eng. B 132 (2007) 85.
[6] H. Zhu, H.Y. Lin, H.F. Guo, L.F. Yu, Mater. Sci. Eng. B 138 (2007) 101.
[7] D.L. Zhao, X. Li, et al., Mater. Sci. Eng. B 150 (2008) 105.
[8] H. Zheng, Y. Zhao, et al., Chin. J. Aeronaut. 23 (2010) 377.
[9] W.W. Wang, Mater. Chem. Phys. 108 (2008) 227.
[10] Y.J. YZhao, H. Xue, Y.X. Zheng, Duan, New Carbon Mater. 25 (2010) 65.
[11] R.S. Turtelli, G.V. Duong, W. Nunesc, R. Grossinger, M. Knobel, J. Magn. Mater. 320 (2008) 339.
[12] D.L. Zhao, X. Li, J. Alloy Compd. 71 (2009) 457.
[13] Ruitao Lv, Feiyu Kang, et al., Appl. Phys. Lett. 93 (2008) 223.
[14] H. Bi, XLWu, M.Q. Li, Aeros. Mater. Technol. 35 (2005) 34.
[15] B. Du, H. Yuan, J.F. Liu, J.Y. Cao, D.H. Huang, Ord. Mater. Sci. Eng. 31 (2008) 30.
[16] S.Y. Yang, C.C.M. Ma, et al., Carbon 48 (2010) 592.
[17] Jan Sumfleth, Kirsten Prehn, et al., Compos. Sci. Technol. 70 (2010) 173.
[18] P Xu, X.J. Han, X.R. Liu, B. Zhang, C. Wang, X.H. Wang, Mater. Chem. Phys. 14 (2009) 556.
[19] R. Che, L. Peng, X. Duan, Q. Chen, X. Liang, Adv. Mater. 16 (2004) 401.
[20] P. Xu, X. Han, C. Wang, H. Zhao, J. Wang, X. Wang, B. Zhang, J. Phys. Chem. B 112 (2008) 2755.
[21] H. Lin, H. Zhu, H. Guo, L. Yu, Mater. Lett. 61 (2007) 3547.
[22] P. Xu, X. Han, J. Jiang, X. Wang, X. Li, A. Wen, J. Phys. Chem. C 111 (2007) 12603.
[23] P. Xu, X. Han, C. Wang, D. Zhou, Z. Lv, A. Wen, X. Wang, B. Zhang, J. Phys. Chem. B 112 (2008) 10443.