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The Effect of Modifier Contents of Polyvinyl Pyrrolidone on the Enhanced Dielectric and Microwave Absorbing Properties of Multiwalled Carbon Nanotubes

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ABSTRACT:: Polyvinyl pyrrolidone (PVP) polymers were used as non-covalent modifiers to modify the surface of multi-walled carbon nanotubes (MWNTs) by ultrasonic dispersion method. The transmission electron microscope results suggest that a layer of polymers is wrapped on the surface of MWNTs, and the thickness is about 2.5 nm. The addition of PVP helps to facilitate uniform distribution of MWNTs and increases the interfacial multipoles formed between PVP and MWNTs, which plays an important role in the regulation of the dielectric parameter and the enhancement of the microwave absorbing properties. The effects of PVP loadings and thickness of PVP/MWNTs hybrids on the dielectric parameter of MWNTs are investigated. The microwave absorbing properties are calculated from the dielectric constants. The results show that the maximum reflection loss is −26.27 dB at 7.8 GHz while the loading of PVP on MWNTs is 8.0 wt % with a thickness of 3.0 mm. These results suggest that the PVP contents and absorber thickness are important factors for the improvement of dielectric loss and microwave absorption properties of MWNTs. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41007.

KEYWORDS: composites; dielectric properties; surfaces and interfaces

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INTRODUCTION

With the rapid development of modern science and technology, serious electromagnetic (EM) interference problems have stimulated intensive research in the EM wave absorption materials in recent years.[1] The microwave absorbing materials can be used to minimize the EM reflection from the metal plate such as aircrafts, ships, tanks, and the walls of echoic chambers and electronic equipment. Multiwalled carbon nanotubes (MWNTs) have been drawing increasing attention due to their special nanostructure, unique mechanical strength, excellent flexibility, low density, and promising EM properties. These interesting properties mean that MWNTs have great potentials for applications in microwave absorbing technologies.[2–5] According to the microwave absorbing mechanism, MWNTs are one of the dielectric loss absorbers. For the dielectric absorbers, loss is primarily generated via the finite conductivity of the material. Incident EM waves impinging upon a conductive surface induce currents as the electric field interacts with mobile electrons within the material; therefore, the design of microwave absorbing materials requires control over material properties such as complex permittivity. However, the effectiveness of the absorber depends on the content of the filler and the degree of its dispersion in the composite.[1–6] In order to optimize the performances of carbon nanotubes (CNTs) as microwave absorbers, it is necessary to modify CNTs by coating and filling with other nanomaterials because the coated or encapsulated second phase nanostructures on the CNTs surface may exhibit ideal EM absorption properties.[7,8] Surfactants encapsulation and polymer wrapping are typical strategies which have been extensively investigated.[9] Ting et al. investigated the microwave absorbing properties of polyaniline/MWNTs composites with various polyaniline (PANI) contents. The results showed that the addition of PANI was useful for achieving a large absorption over a wide frequency range, especially for higher frequency values.[10]

Anju et al. fabricated poly(trimethylene terephthalate)/MWNT composites with an aim to investigate the potential of such composites as an effective light weight EM interference shielding material in the frequency range of 12.4–18 GHz.[11] Jean-Michel et al. modified the surface of CNTs using PP-g-MA, PP-g-Py, and PP-g-AMP as compatibilizers to promote the dispersion of CNTs in PP. The good EMI shielding effectiveness of the PP matrix were attained at a low CNTs concentration (2 wt %).[12]

Additional Supporting Information may be found in the online version of this article.

Despite these advances, much work is still needed for the development of CNT-incorporated composites as EMI shielding materials.

In our previous work polyvinyl pyrrolidone (PVP) polymers were used as dispersants to modify the surface of MWNTs while preparing the Fe_3O_4/PVP/MWNTs hybrids. The results showed that the adding of PVP can not only greatly prevent MWNTs aggregation in the form of bundles and improve the degree of its dispersion, but also significantly enhance the microwave absorption properties.[13] The use of PVP would produce interfacial polarization between PVP and MWNTs. This interfacial polarization affects the microwave absorption properties and the interfacial polarization intensity is affected by the content of PVP wrapped on the surface of MWNTs.[6,13,14] The aim of this study is to investigate the effect of adding PVP contents on the dielectric parameters and microwave absorbing properties of PVP/MWNTs hybrids.

EXPERIMENTAL

Materials

MWNTs (30–50 nm diameter, 10–20 µm long), with a purity of 95%, were provided by Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences. Other chemical reagents were all of analytical grade and used without further purification.

Preparation of PVP/MWNTs Hybrids

Pristine MWNTs without purification was dispersed in 60 mL deionized water with PVP concentration of 0.25, 0.33, 0.5, and 1.0 wt %. Each of the mixture solutions was placed in an ultrasonic bath at 50°C for 4 h with constant mechanical stirring. Then the samples were filtered through a 0.2-µm membrane filter, and dried under vacuum at 50°C for 16 h. The prepared dense samples of PVP/MWNTs hybrids were labeled as PVP/MWNTs-1, PVP/MWNTs-2, PVP/MWNTs-3, and PVP/MWNTs-4, respectively.

Characterization

The molecular structure of the hybrids was observed using a Fourier transform infrared spectrometer (FTIR, WQF-310). Thermogravimetric analysis (TGA) measurements were performed with TGAQ50 (The United States) from room temperature to 800°C at a scan rate of 10°C/min in an air atmosphere. The transmission electron microscope (TEM) images were obtained using an accelerating voltage of 100 kV with the Jeol H-600 instrument. The dispersion states of the hybrids were examined by using a scanning electron microscopy (SEM, Stereoscan 250MK3, Cambridge). The relative complex permittivity of pristine MWNTs and PVP/MWNTs were measured by the coaxial line method in the frequency range of 2–18 GHz using a vector network analyzer (HP8501B) on October 15, 2013. The samples were prepared by uniformly mixing the PVP/MWNTs hybrids in a paraffin matrix with a mass ratio of 1 : 7, and then by pressing the mixtures in a cylindrical (toroidal) shapes with φ_{out} of 7.00 mm, φ_{in} of 3.00 mm, and thickness of 3.00 mm.[15] The reflection loss (RL) was calculated by the following equations:[16]

$$\mathrm{R(dB)} = -20\log\left|\frac{Z_{\text{in}}-Z_0}{Z_{\text{in}}+Z_0}\right| \tag{1}$$

$$Z_0=\sqrt{\frac{\mu_0}{\varepsilon_0}} \tag{2}$$

$$Z_{\text{in}}=Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}\cdot\tanh\left[j\left(\frac{2\pi fd}{c}\right)\sqrt{\mu_r\varepsilon_r}\right] \tag{3}$$

where R (dB) represents reflection loss, Z_0 is the impedance of free space, μ_0 and ε_0 are the permeability and permittivity of free space, Z_{in} is the input impedance of the absorber, d is the thickness of the absorber, c is the light velocity, and f is microwave frequency. $\varepsilon_r=\varepsilon'+j\varepsilon''$ is the complex permittivity, where ε' is the real part of permittivity, and ε'' is the imaginary part of permittivity. $\mu_r=\mu'+j\mu''$ is the complex permeability. In the present case, the magnetic loss of pristine MWNTs is so small that μ' can be taken as 1 and μ'' can be taken as 0.

RESULTS AND DISCUSSION

FITR and TG Analysis of the PVP/MWNTs Hybrids

The FITR spectra of the PVP polymer, pristine MWNTs, and PVP/MWNTs hybrids are shown in Figure 1(a–c).

As shown in the curve (b) of Figure 1, pristine MWNTs have no obvious vibration absorption peak. In the curve (a) and curve (c) of Figure 1, the stretching vibration absorption peak at 1640 cm^{-1} is attributed to the characteristic carbonyl in PVP. The absorption peak at 2910 cm^{-1} results from C—H stretching in PVP. The peak at 1422 cm^{-1} is attributed to methylene scissors bending vibration, and the absorption peak at 1282 cm^{-1} is assigned to the absorption of C—N bond in PVP.[17] Stretching vibration peaks at 3450 cm^{-1} correspond to water absorbed by PVP. The existence of these peaks indicates that the PVP polymers were coated onto MWNTs.

In order to investigate the loading contents of PVP wrapped on the surface of MWNTs, samples of pristine MWNTs, PVP polymers, and PVP/MWNTs hybrids (PVP/MWNTs-1, PVP/MWNTs-2, PVP/MWNTs-3, and PVP/MWNTs-4), were analyzed by TG method. The result is shown in Figure 2. Below 100°C, there was less weight loss due to the loss of moisture.

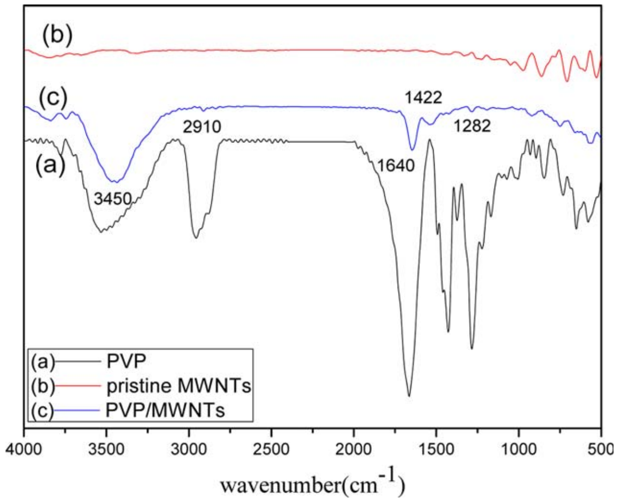

Figure 1. FTIR spectra curves of (**a**) PVP; (**b**) pristine MWNTs; and (**c**) PVP/MWNTs hybrids. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

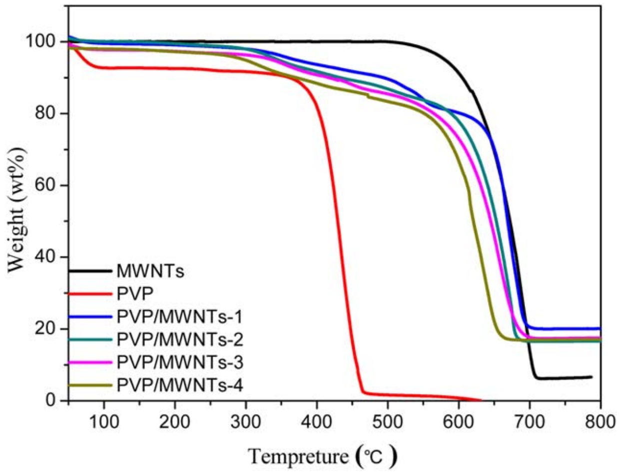

Figure 2. TG curves of pristine MWNTs, PVP polymer, and PVP/MWNTs hybrid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The weight loss which occurred over the temperature range of 360°C–470°C was the decomposition of PVP wrapped on the surface of MWNTs. The weight loss from 550°C to 800°C was attributed to decomposition of the carbon structure.[18] The PVP contents of PVP/MWNTs-1, PVP/MWNTs-2, PVP/MWNTs-3, and PVP/MWNTs-4 were measured to be about 6.5, 8.0, 9.5, and 11.0 wt %, respectively, excluding the amount of water.

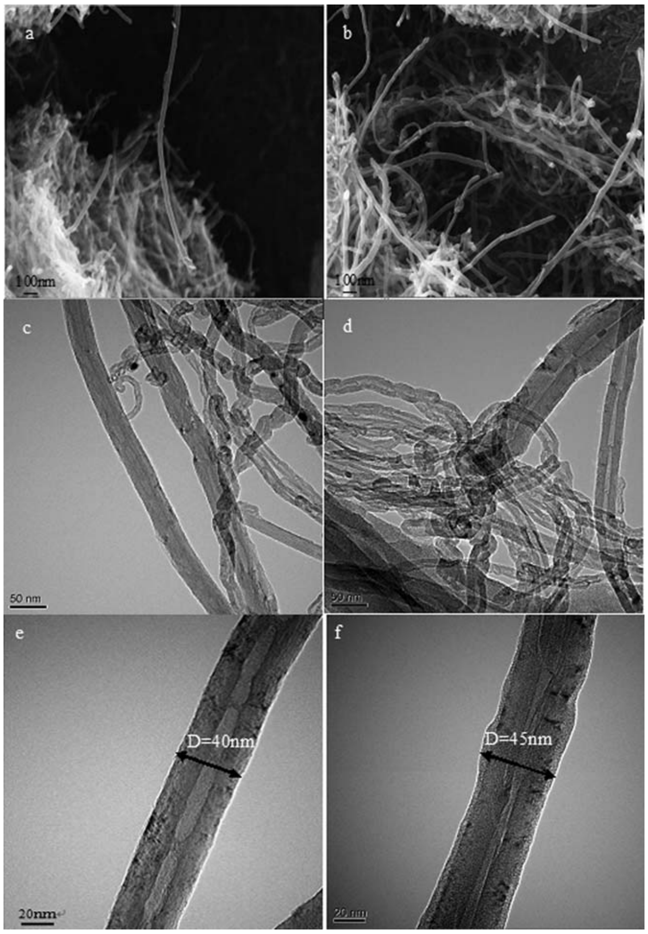

Figure 3. TEM images of (**a**) pristine MWNTs; (**b**) PVP modified MWNTs.

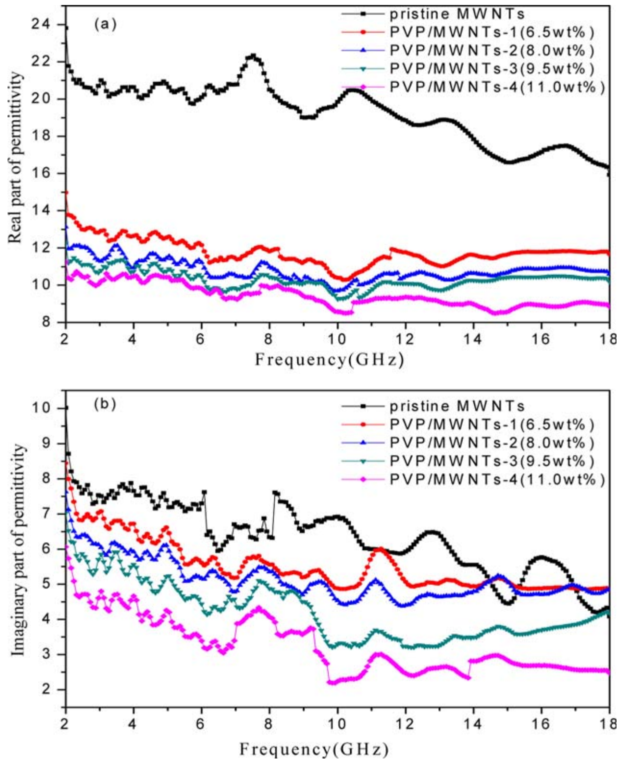

Figure 4. Complex permittivity of pristine MWNTs and PVP/MWNTs hybrids with 6.5, 8.0, 9.5, and 11.0 wt % PVP loadings: (**a**) real part ε'; (**b**) imaginary part ε''. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SEM and TEM Observation of the PVP/MWNTs Hybrids

The morphology and size distribution of pristine MWNTs and PVP wrapping MWNTs were investigated by SEM and TEM. There are several distinctive characteristics in the SEM [Figure 3(a,b)] and TEM images [Figure 3(c–f)].

As shown in Figure 3, SEM images of the CNTs in PVP/MWNT hybrids appear thicker and have rough surface features [Figure 3(b)] relative to the non-wrapped MWNTs [Figure 3(a)]. It was found that PVP wrapped on the surface of MWNTs could improve the dispersion of MWNTs and prevent MWNTs from aggregating. Figure 3(c–f) shows the TEM images of MWNTs before and after wrapped with PVP. As shown in Figure 3(e), the pristine MWNTs have smooth and clear surface with 45-nm diameters, while the PVP wrapped MWNTs [Figure 3(f)] have fuzzy and translucent edges with 50-nm diameters. Compared with Figure 3(e), MWNTs in Figure 3(f) became slightly thicker after the PVP wrapping. A polymer layer was wrapped on the surface of MWNTs with a thickness of about 2.5 nm.

Dielectric Properties of the PVP/MWNTs Hybrids

Complex permittivity, $\varepsilon_r = \varepsilon' + j\varepsilon''$, is an important parameter to characterize the dielectric properties of absorbers. It is well known that the real part (ε') of complex permittivity represents the ability of storing EM wave energy, which is mainly

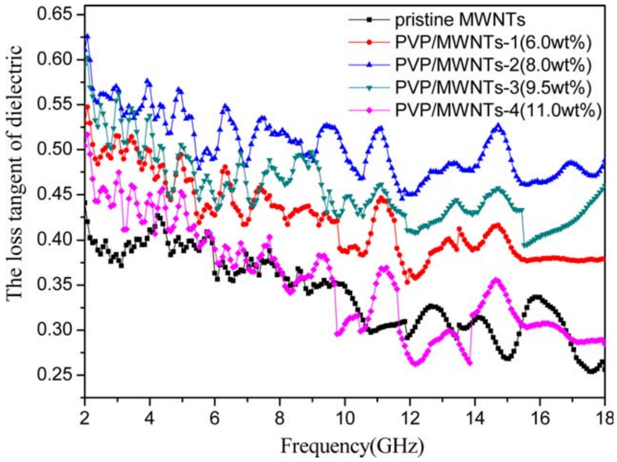

Figure 5. The dielectric loss tanδ of pristine MWNTs and PVP/MWNTs hybrids with 6.5, 8.0, 9.5, and 11.0 wt % PVP loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

associated with the amount of polarization occurring in the material, while the imaginary part (ε'') represents the ability of dissipating EM wave energy, which is mainly related to the electronic conductivity of the materials.[19]

There are many factors making contributions to the dielectric properties, such as dielectric relaxation, resonance, the motion of conduction electrons, defects in the nanotubes, length, diameters, chirality, etc.[20] To investigate the intrinsic mechanism of microwave absorption of PVP/MWNTs hybrids, the complex relative permittivity of pristine MWNTs and PVP/MWNTs samples were measured in the frequency of 2–18 GHz, as shown in Figure 4. A few multi-resonance peaks and leaping data points which appeared in the curves of complex permittivity, as shown in the imaginary part of permittivity in the range of 6–18 GHz, are a consequence of polarization relaxation effect.[21] It can also be found that the ε' and ε'' values of permittivity of pristine MWNTs decrease with increasing frequency, which is in the range of 23.9–18.1 and 10–4.2 over a frequency of 2–18 GHz.

Of vital importance, the ε' values of PVP/MWNTs hybrids are much lower than that of pristine MWNTs, which is due to that MWNTs have lots of defects on their surfaces. These unpaired lattice defects on the surface of MWNTs act as active centers of dipoles leading to higher value of ε’ for MWNTs. For the PVP/MWNTs hybrids, PVP molecular chains interact with these unpaired lattice defects on the surface of MWNTs and thus restricting the motion of dipoles.[22,23] It leads to smaller ε’ value of PVP/MWNTs as compared with that of pristine MWNTs. However, the ε'' values of PVP/MWNTs hybrids slightly decreased comparison with that of pristine MWNTs, which is due to the decrease of electronic conductivity. According to the expression of dielectric loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$), the low ε' or the high ε'' is beneficial to the enhancement of dielectric loss. In this work the dielectric loss tanδ of PVP/MWNTs hybrids was improved significantly compared with that of pristine MWNTs, as shown in Figure 5.

It can be seen that the tanδ values of PVP/MWNTs hybrids are larger than that of pristine MWNTs in the frequency range of 2–18 GHz, which indicates that the PVP coated on MWNTs can improve the dielectric loss. The tanδ values reach the largest when the loading of PVP coated on MWNTs is 8.0 wt %. However the dielectric loss continuously decreased while more than 8.0 wt % PVP incorporation into the MWNTs. On the one hand, PVP coated on the surface of MWNTs would generate the interfacial polarization effect and the associated relaxation, which is helpful for the enhancement of dielectric loss. On the other hand, the insulating PVP polymers wrapped on the MWNTs surface would increase the contact electrical resistance of MWNTs electronic network, which will effectively inhibit the form of electronic conducting pathway and lead to a decrease in the electrical conductivity. Therefore the loading contents of PVP coated on MWNTs play an important role for the improvement of dielectric loss. Both dielectric relaxation and electric resistance effect may be responsible for the dielectric properties.

The Microwave Absorbing Properties of the PVP/MWNTs Hybrids

Figure 6 shows the absorption characteristics of pristine MWNTs and PVP/MWNTs in the frequency range of 2–18 GHz, the corresponding experimental data are given in the Supporting Information Figure S6. The curve (a) in Figure 6 is the variation of R for the pristine MWNTs. The maximum reflection loss peak is -11.59 dB at 7.2 GHz for which the corresponding value of matching thickness (d_m) is 3 mm, the bandwidth of the R below -10 dB is 0.86 GHz.

Curves of b, c, d, and e are the variation of R for PVP/MWNTs hybrids. It is clear that PVP/MWNTs hybrids have higher R values and broader bandwidth than that of pristine MWNTs. The results indicate that the coating of PVP on MWNTs is helpful for the enhancement of microwave absorption properties. This is due to that the coating of PVP on MWNTs, which on the one hand, can enhance the dispersion of MWNTs to form effective conductive network, which probably offers much higher microwave absorbing performance.[13] On the other hand, the

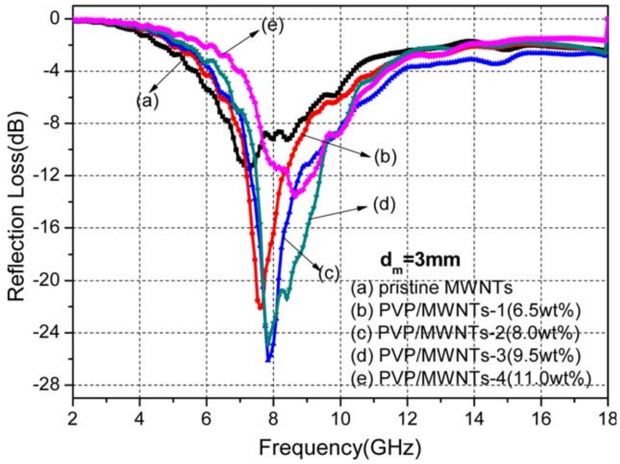

Figure 6. The reflection loss of pristine MWNTs and PVP/MWNTs hybrids with 6.5, 8.0, 9.5, and 11.0 wt % PVP loadings. The thickness of all samples is 3.0 mm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coating of PVP on MWNTs might increase the interfacial multipoles formed between PVP and MWNTs, which is beneficial for the enhancement of dielectric loss. The interfacial polarization plays a crucial role for the enhancement of microwave absorption. Therefore, the multi-interfaces between PVP and MWNTs are beneficial to the microwave absorption due to the interactions of microwave radiation with charge multipoles at the interfaces.

Curves of b, c, d, and e are the variation of R of PVP/MWNTs at loading contents of 6.5, 8.0, 9.5, and 11.0 wt %, respectively. The comparison of the curves b, c, d, and e show that the microwave absorbing properties vary from the loading contents of PVP on MWNTs. When the loading contents of PVP on MWNTs is 8.0 wt %, the absorption peak value reaches the maximum value of −26.27 dB at 7.8 GHz of curve (c), and the bandwidths of R below −10 dB is 2.45 GHz. When the loading contents of PVP on MWNTs are 6.5, 9.5, and 11.0 wt %, respectively, the maximum reflection loss peak is −22.1 dB at 7.5 GHz of curve (b), −24.72 dB at 7.9 GHz of curve (d), and −13.7 dB at 8.6 GHz of curve (e), respectively. The bandwidth below −10 dB is 1.64 GHz [curve(b)], 2.12 GHz [curve(d)], 1.71 GHz [curve(e)], respectively. The results clearly demonstrate that the contents of PVP on MWNTs have an important effect on the microwave absorbing properties of PVP/MWNTs hybrids. It is believed that the interfacial polarization level of the conductor/insulator composites and the width of the dielectric relaxation frequency band are affected by the conductor's electrical conductivity: the higher the conductivity, the higher the interfacial polarization and the wider the dielectric relaxation frequency band. In general, the improved electrical conductivity and proper dielectric relaxation effect are favorable for improving microwave absorption properties.[24–26] For the PVP/MWNTs, the wrapping of PVP on the surface of MWNTs is obviously efficient at dispersing MWNTs as individual nanotubes, which is helpful to form an electronic conducting network and to enhance the interfacial polarization degree. However, it is not good for MWNTs to add too much PVP, because PVP is an insulator, so PVP layer wrapped on the MWNTs surface would increase the contact electrical resistance of MWNTs electronic network, which will effectively inhibit the form of electronic conducting pathway and lead to a decrease in the electrical conductivity.[27] Therefore, the proper PVP contents coated on the surface of MWNTs are important for the enhanced reflection loss value of PVP/MWNTs hybrids.

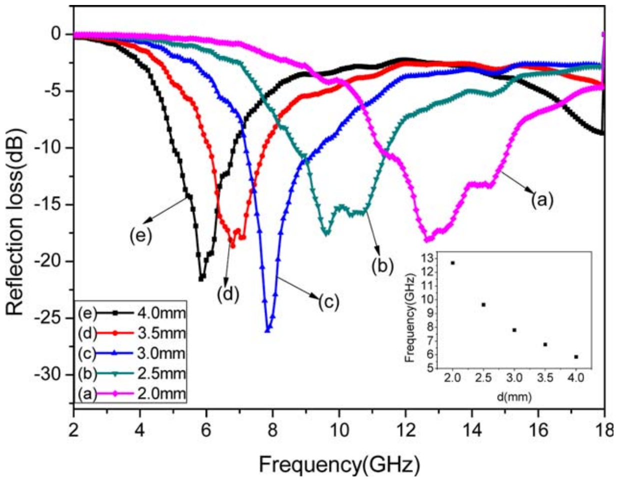

Figure 7. The reflection loss of PVP/MWNTs-2 hybrids at different thickness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Maximum R and Bandwith Over −10 dB of PVP/MWNTs-2 Hybrids

Thickness (mm)	Maximum R and frequency	Bandwith over −10 dB (GHz)
2.0	−18.08 dB at 12.68 GHz	11.2–15.1 (3.9 GHz)
2.5	−17.37 dB at 9.64 GHz	8.6–11.47 (2.87 GHz)
3.0	−26.27 dB at 7.80 GHz	7.2–9.65 (2.45 GHz)
3.5	−18.69 dB at 6.75 GHz	6.07–7.7 (1.63 GHz)
4.0	−21.58 dB at 5.85 GHz	5.1–6.85 (1.75 GHz)

According to the microwave absorption theory,[28] the absorbing property is related to the absorbent, the thickness of the material and the required absorption wave band. Attention should be paid to optimize the absorbent's content and the thickness of the microwave absorbing materials in the required frequency range. Figure 7 shows the frequency dependence of the reflection loss of PVP/MWNTs-2 hybrids (8.0 wt %) which was calculated from the dielectric constants, while the sample thickness is 2.0, 2.5, 3.0, 3.5, and 4.0 mm in the frequency range of 2–18 GHz. The corresponding experimental data of reflection loss of PVP/MWNTs hybrids at different thickness are given in the Supporting Information Figure S7. Table I shows the maximum reflection loss R and bandwidth below −10 dB in frequency of 2–18 GHz. This result clearly demonstrates that the intensity and frequency of the maximum reflection loss for the sample depend on the material's thickness. With the increasing of sample thickness, the maximum absorbing peaks shift toward a lower frequency.

For the PVP/MWNTs hybrids, the maximum reflection loss is −26.27 dB at 7.8 GHz with an absorber thickness of 3.0 mm. The bandwidth below −10 dB becomes narrower with the sample thickness increasing, which is 3.9 GHz ($d_m = 2.0$ mm), 2.87 GHz ($d_m = 2.5$ mm), 2.45 GHz ($d_m = 3.0$ mm), 1.63 GHz ($d_m = 3.5$ mm), and 1.75 GHz ($d_m = 4.0$ mm), respectively. The results indicate that the sample thickness is also an important parameter affecting the intensity and position of the frequency at the point of maximum reflection loss.

CONCLUSION

PVP polymers were used as non-covalent modifiers to modify the surface of MWNTs by ultrasonic dispersion method. The effect of loading contents of PVP wrapped on the surface of MWNTs on the dielectric parameters and microwave absorbing properties of MWNTs were investigated. The results show that:

1. The TEM results suggest that the addition of PVP would help to facilitate uniform distribution of nanotubes and to increase the interfacial multipoles formed between PVP and

MWNTs, which would improve and regulate the microwave absorbing property.

2. The ε' values of PVP/MWNTs hybrids are much lower than that of pristine MWNTs. However, the ε'' values of PVP/MWNTs hybrids slightly decreased comparison with that of pristine MWNTs. As a result, the dielectric loss tanδ of PVP/MWNTs hybrids was improved significantly compared with that of pristine MWNTs, which indicates that the coating of PVP on MWNTs can improve the dielectric loss.
3. The microwave absorbing properties results show that the maximum reflection loss is −26.27 dB at 7.8 GHz while the loadings of PVP on MWNTs is 8.0 wt % with an absorber thickness of 3.0 mm. These results suggest that the proper PVP content and absorber thickness are important factors for the improvement of dielectric loss and microwave absorption properties of MWNTs.

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