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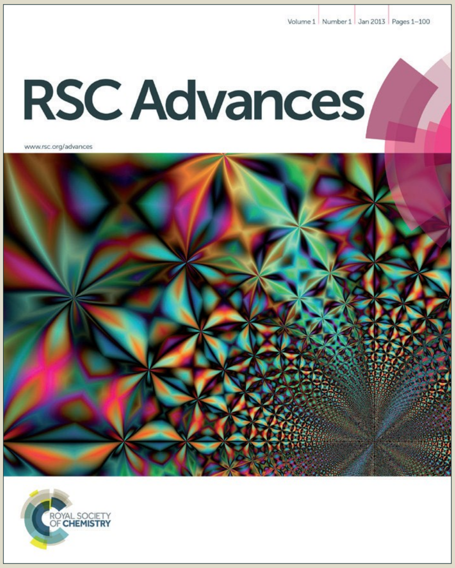

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ARTICLE

The effect of polymer polarity on the microwave absorbing properties of MWNTs

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Two different polarity polymers, polyvinylpyrrolidone (PVP) and polyethyleneimine (PEI) with same molecular weight were selected to modify the surface of MWNTs using non-covalent method. The aim was to investigate the effect of polymer polarity on the microwave absorbing properties of MWNTs. The polarization effects of PVP and PEI on MWNTs were simulated by Cole-Cole semicircle model. The structure and morphology of polymers modified MWNTs were characterized by FTIR, TGA, Raman Spectroscopy, SEM and TEM. The SEM and TEM results demonstrated that the addition of PVP and PEI could prevent MWNTs from aggregating and was helpful for the improvement of the dispersion of MWNTs. The excellent microwave absorbing properties could be obtained by adjusting the mass percentage of polymer/MWNTs hybrids in paraffin wax. The results showed that both PVP/MWNTs and PEI/MWNTs hybrids had a good microwave absorption (<-7dB) in the X-band frequency when the mass percentage of polymer/MWNTs in paraffin wax was 30%. However, the maximum reflection loss (RL) of PVP/MWNTs hybrids was larger than that of PEI/MWNTs hybrids. The maximum RL of PVP/MWNTs was -23.84dB, while the maximum RL of PEI/MWNTs was about -21.01dB. Moreover, the polymer polarity had an impact on the response frequency where the maximum RL appeared. The RL peak values of PVP/MWNTs hybrids appeared at 10.48GHz, while it was at 8.96GHz for the PEI/MWNTs hybrids. The results indicated that the polymer polarity had a significant influence on the microwave absorbing properties and microwave absorbing response frequency of MWNTs.

1. Introduction

With the rapid development of modern science and technology, serious electromagnetic interference problems have stimulated intensive study in the field of microwave absorption materials over the past few years[1, 2]. Microwave absorption materials can minimize the electromagnetic reflection from metal plate such as aircrafts, ships, tanks, and the walls of anechoic chambers and electronic equipment[3]. Microwave absorption materials are divided into dielectric loss materials and magnetic loss materials according to the microwave absorbing mechanism. MWNTs are dielectric loss absorbent. As we all known, MWNTs receive much attention because of their outstanding electronic, mechanical, thermal, chemical properties[4, 5]. These excellent properties mean that MWNTs have great potentials for applications in microwave absorbing technology field[6-9]. However, MWNTs have its own shortcomings. For example, pristine MWNTs are easily reunited with each other and hard to be dispersed uniformly because of their large specific surface energy[10]. These weaknesses impact its microwave absorbing properties. In order to overcome these shortcomings, different polymers are used to modify the surface of MWNTs. More and more researches have been conducted because polymers twining round MWNTs are useful to its dispersibility in matrix. Thomassin and coworkers[11] developed a new scalable dispersion process to prepare PMMA/CNTs nanocomposites with appropriate nanofiller dispersion. The method consists in polymerizing the monomers in presence of CNTs in a bad solvent of the polymer. A precipitation of the polymer occurs during its formation entrapping all the CNTs inside it. Rina Shvartzman-Cohen *et al.*[12] decorated the SWNTs with end-tethered polymers. Consequentially, stable dispersions of individual, well separated SWNTs can be prepared. The results suggested that polymer-induced steric stabilization provides a generic method for the separation of SWNTs from mixtures of colloidal species. Linda Vaisman *et al.*[13] reported that some progress and advances have been made on the improved dispersion of carbon nanotubes in aqueous and organic media by non-covalent adsorption of surfactants and polymers.

As a kind of dielectric loss absorbent, the polarization of MWNTs including interfacial polarization and orientation polarization play a significant role on the dielectric loss. Complex permittivity is an important parameter to characterize the dielectric properties of absorbent. It is reasonable that the complex permittivity will be changed while there are polymers covering on the surface of MWNTs due to the interfacial polarization and orientation polarization. In our previous research work[1], PVP polymers were used as surfactant to modify the surface of MWNTs. The effect of PVP on the microwave absorbing properties was studied. The results showed that the microwave absorbing properties of MWNTs modified by PVP polymers were improved obviously. In this paper, PEI polymers containing nitrogen atom were also selected to wrap MWNTs. Both PVP and PEI are polar polymers which have lone pair electrons. On the one hand, the modification of MWNTs by polymers with lone pair electrons can indeed prevent MWNTs from aggregating in the form of bundles and enhance the dispersibility, which is significant to adjust the dielectric parameter and enhance the microwave absorbing properties. On the other hand, the lone pair electrons in chain of PVP and PEI may interact with π-electrons of MWNTs, which can increase the polarization degrees of MWNTs. According to the dielectric loss mechanism, the polarization degree of MWNTs is the key factor for the enhancement of dielectric parameter and the microwave absorbing properties. PEI and PVP polymers exhibit different polarity because of the structure difference, the polarity of PVP polymer is larger than that of PEI. The focus of this work is to investigate the effects of polymers polarity on the microwave absorbing properties. The dielectric parameter of MWNTs will be measured by a vector network analyzer in the frequency range of 2-18GHz.

2. Experimental

2.1 Materials

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

2.2 Preparation of PVP/MWNTs hybrids and PEI/MWNTs hybrids

Pristine MWNTs without purification were dispersed in 60ml deionized water with PVP and PEI, respectively. Each of the mixture solutions was placed in an ultrasonic bath at 40^{o}C for 4h with constant mechanical stirring. Then the samples were filtered through a 0.2μm membrane filter, and dried under vacuum at 40^{o}C for 16h. The prepared samples label as PVP/MWNTs and PEI/MWNTs, respectively.

2.3 Characterization

FTIR was investigated with spectroscopy (WQF-310) using the KBr pellet method at room temperature. The surface structures of polymer/MWNTs hybrids were examined by Raman analysis with an excitation power of 20 mW at 514 nm. Thermal gravity analysis (TGA) measurements were performed with TGAQ50 (USA) from room temperature to 800°C at a scan rate of 10°C/min in Ar atmosphere. The transmission electron microscope (TEM) images were obtained using an accelerating voltage of 100kV with the Jeol H-600 instrument. The dispersion states of polymer/MWNTs hybrids could be observed from the TEM images. The absorbent samples were prepared by uniformly mixing the PVP/MWNTs hybrids and PEI/MWNTs hybrids in paraffin wax and the mixtures were pressed in a cylindrical shape with φ_{in} of 3.00mm, φ_{out} of 7.00mm and the thickness was 2.70mm. The mass percentage of polymer/MWNTs in absorbent samples were 16.7%, 20%, 25% and 30%, respectively[1]. These three samples were labelled as polymer/MWNTs-16.7%, polymer/MWNTs-20%, polymer/ MWNTs-25% and polymer/MWNTs-30%, respectively. The dispersion state of modified MWNTs in paraffin wax was observed by scanning electron microscope (SEM, QUANTA200, Japan). The relative complex permittivity of PEI/MWNTs hybrids and PVP/MWNTs hybrids were measured by the coaxial line method in the frequency range of 2-18 GHz using a vector network analyzer (HP8501B, USA).

The wave reflection loss (RL) was calculated by the following equations[14]:

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

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

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

In these equations, R is reflection loss. Z_0 represents the impedance of free space; μ_0 and ε_0 are the permeability and permittivity of free space; Z_{in} represents the input impedance of the absorber; d is the thickness of the absorber; f is microwave frequency; c(3×10^{8} m/s) is the light velocity in vacuum. $\varepsilon_r=\varepsilon'-j\varepsilon''$ is the complex permittivity and in this expression, ε' and ε'' represent the real part and the imaginary part of permittivity, respectively. $\mu=\mu'-j\mu''$ is the complex permeability, but in this study, μ' would be taken as 1 and μ'' is taken as 0.

3. Results and discussions

3.1 FITR and Raman analysis of the polymers modified MWNTs hybrids

The FITR spectra of the PEI/MWNTs hybrids, PVP/MWNTs hybrids and pristine MWNTs are shown in Fig.1a, Fig.1b, and Fig.1c, respectively.

As shown in the curve (a) of Fig.1, there is no obvious vibration absorption peak for the pristine MWNTs. In the curve (b), the peaks at 3443cm^{-1} and 1636cm^{-1} can be associated with the stretching and flexural vibration of N-H bond in the PEI polymer. The peaks at around 1045cm^{-1} correspond to the stretching vibration of C-C bond of PEI polymers. In the curve (c), the peak at 1636cm^{-1} is due to C=O stretching vibrations in amide group in PVP. The peak at around 1154cm^{-1} is due to the stretching vibration of C-C bond of PVP polymers. Meanwhile, the peaks at 3440cm^{-1} in curve (b) and curve (c) are from the O-H stretching vibration in H_2O absorbed by polymers. And the peaks at 2920cm^{-1} in the curve (b) and curve (c) are due to the antisymmetric and symmetric vibration of methylene groups in polymers.

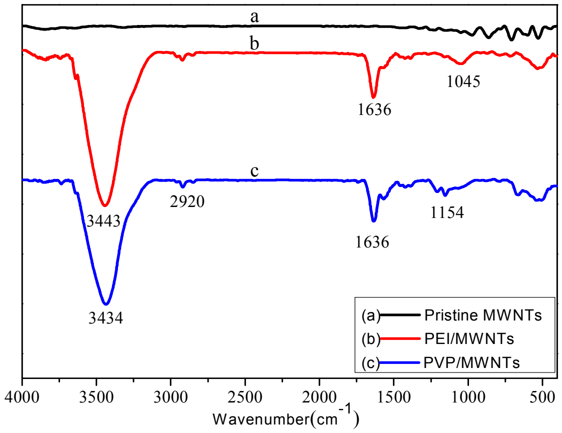

Fig.1 FTIR spectra of pristine MWNTs (a), PEI/MWNTs (b) and PVP/MWNTs (c) hybrids.

The FTIR curves indicate that PEI polymers and PVP polymers are coated onto MWNTs.

Figure 2 demonstrates the Raman spectra of the pristine MWNTs (a), PEI/MWNTs hybrids (b) and PVP/MWNTs hybrids (c). Obviously, the major differences lie in the values of ratio I_D/I_G, which are related to the graphitic structures of polymer modified MWNTs.

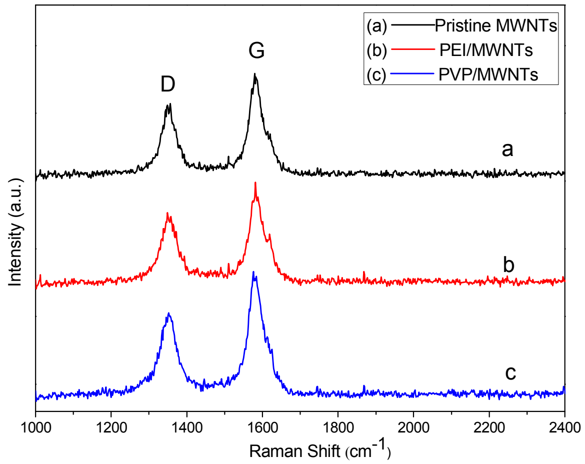

Fig.2 Raman spectra of pristine MWNTs (a), PEI/MWNTs (b) hybrids and PVP/MWNTs (c)

The peak at about 1580cm^{-1} is the graphite band (G-band) which is related to the vibration of sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice[15], and generally used to identify well-ordered CNTs. The peak at about 1350cm^{-1} is the disorder-induced phonon mode (D-band), which is related to the mode of boundaries in Brillouin zone. It is caused by the disordered components, and mainly originated from phonon mode of M-point and K-point of the hexagonal Brillouin zone. It has a high sensitivity to the disordered structures in carbon materials. The presence of D-band for two samples infers that a defective structure of MWNTs modified by polymers. The ratio of D band and G band intensity (I_D/I_G) represents the defects of the MWNTs modified by polymers[16]. As shown in Fig.2, the I_D/I_G values of PEI/MWNTs hybrids and PVP/MWNTs hybrids are similar, which are about 0.697 and 0.695, respectively, while the I_D/I_G value of pristine MWNTs is 0.70. The results indicate that wrapping of PVP and PEI doesn't increase the defect numbers of MWNTs and maintains the structural integrity of MWNTs.

For the pristine MWNTs, the G-band was observed at 1579.3 cm^{-1}, but for PVP/MWNTs and PEI/MWNTs, the G-band showed blue shifted to 1583.8cm^{-1}and 1580.8cm^{-1}, respectively. The possible reason for this phenomenon was that the lone pair electrons of N atoms in PVP and PEI chains may interact with π-electrons of MWNTs. Due to the p-π conjugation, the electron density of MWNTs was strengthened and the polarization degree of MWNTs surface was increased.

3.2 TGA analysis of polymer modified MWNTs hybrids

The loading contents of PVP and PEI wrapped on the surface of MWNTs are analyzed by TGA method. The results are shown in Fig.3.

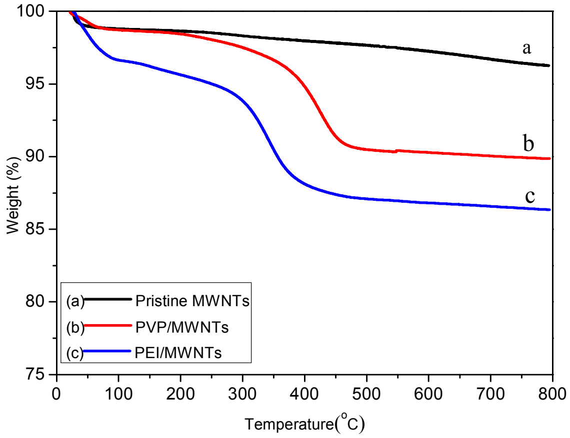

Fig.3 TGA curves of pristine MWNTs (a), PVP/MWNTs (b) and PEI/MWNTs (c) hybrids.

Below 100°C, as shown in Fig.3 (a), Fig.3 (b) and Fig.3 (c), there is a very small weight loss, which is due to the loss of moisture and the decomposition of micro-molecular organics. Curve (a) shows the decomposition of MWNTs in the temperature range of 26-800°C. On the curve (b), the weight loss which occurs in the temperature range of 300-500°C is the decomposition of PVP. The decomposition temperature range of PEI is 250-450°C according to the curve (c). In the temperature range of 550°C to 800°C, the weight loss of the hybrids is attribution to the decomposition of the carbon structure of MWNTs[17].

The PVP content of PVP/MWNTs and PEI content of PEI/MWNTs are measured to be about 7.5wt% and 7.4wt%, respectively.

3.3 TEM and SEM observation of the PVP/MWNTs hybrids and PEI/MWNTs hybrids

The effects of PVP and PEI on the dispersion of MWNTs were investigated by TEM. As shown in Fig.4a, pristine MWNTs are prone to aggregation because of their large specific surface energy and length-diameter ratio. For the PVP modified MWNTs and PEI modified MWNTs, the agglomeration states can be reduced, shown as Fig.4b and Fig.4c. The dispersion of polymer modified MWNTs remained fairly uniform; the wrapped polymer acted as a "protective layer" to prevent dispersed MWNTs from attracting one another. The presence of PVP polymers and PEI polymers play an important role in the uniformity and distribution of MWNTs. In order to observe the dispersion state of polymers/MWNTs in paraffin wax, SEM is used to investigate the absorber morphology. Figure 4d, e and f are the SEM micrographs of pristine MWNTs, PEI/MWNTs and PVP/MWNTs hybrids in paraffin wax, respectively; the mass ratio of MWNTs and paraffin is 3:7. Obviously, the volume fraction of MWNTs in the absorbent mixture is so large that it is difficult to make a clear distinction of the dispersion between the samples of PVP/MWNTS and PEI/MWNTs.

However, because of difference of electronic structure and steric hindrance between PVP and PEI, the effect of the electron density and the electron distribution of polymers on MWNTs are different. On the other hand, the lone pair electrons of PVP and PEI can interact with the π-electrons to increase the polarization degrees of MWNTs, which is more important to enhance the dielectric parameter and the microwave absorbing properties. Therefore, the polymers covered on the MWNTs not only improve the dispersion of carbon nanotubes, but also effect the electron cloud distribution of MWNTs, which will lead to the different dielectric properties.

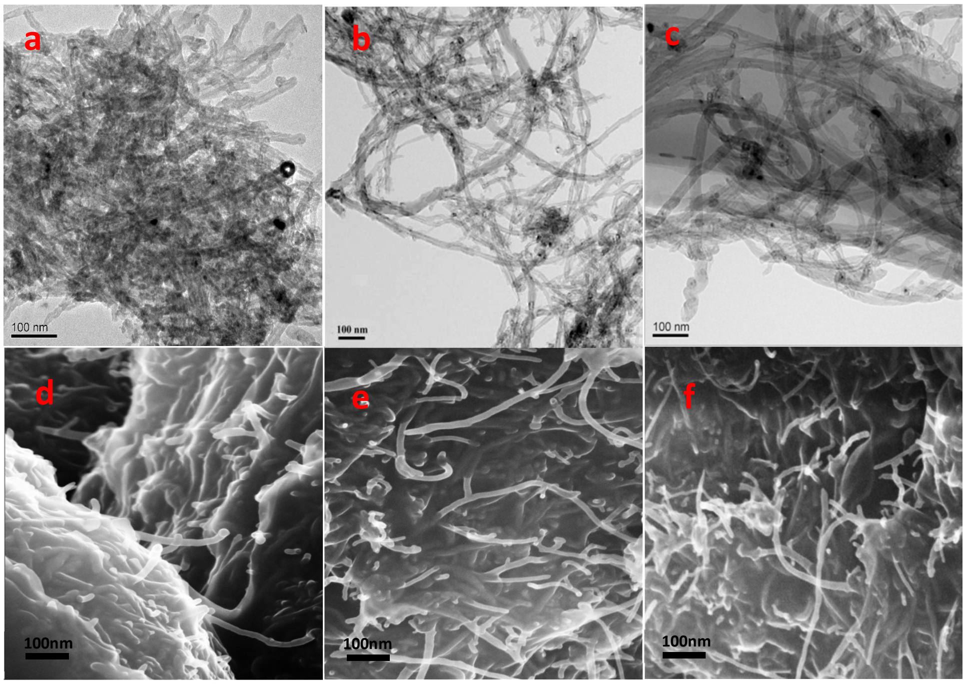

Fig.4. TEM micrographs of pure MWNTs (a), MWNTs modified by PEI (b) and MWNTs modified by PVP (c), and SEM micrographs of pure MWNTs (d), MWNTs modified by PEI (e) and MWNTs modified by PVP (f) in paraffin(30wt.%).

3.4 The microwave absorbing properties of PEI/MWNTs and PVP/MWNTs hybrids

Figure 5 is the comparison of microwave absorption properties of pristine MWNTs and polymer modified MWNTs. The mass percentage of pristine MWNTs and polymer/MWNTs in paraffin matrix is same (25wt.%). It's clear that the polymer/MWNTs hybrids have higher RL values than that of pristine MWNTs. The results indicated the addition of PVP and PEI polymer is helpful for the improvement of microwave absorption properties. The coating of polymer on the surface of MWNTs can not only enhance the dispersion of MWNTs to form effective conductive network, but also increase the interfacial polarization effect of the materials which result in strong dielectric loss.

Figure 6 demonstrates the microwave absorption characteristics of PEI/MWNTs hybrids and PVP/MWNTs hybrids with different mass contents in paraffin wax in the frequency range of 2-18GHz. Comparison with curve (a), (b), and (c), the RL values vary with the mass content of the PVP/MWNTs hybrids in paraffin matrix. The absorber shows greater microwave absorbing properties while the content of polymer/MWNTs in paraffin wax is 30%. For the sample of

PVP/MWNTs-30%, the maximum RL reaches -23.84dB at 10.48GHz, and the responding bandwidth below -5dB is approximately 7.84GHz (7.44-15.28GHz); the RL below -10dB is about 3.92GHz (8.96-12.88GHz), and the bandwidth of RL less than -20dB is 0.56 GHz (10.24-10.80GHz). For the sample of PEI/MWNTs-30%, the maximum RL reaches -21.01dB at 8.96GHz; the bandwidth of RL less than -5dB is 8.40GHz (6.32-14.72GHz), and the values below -10dB is 3.04GHz (7.28-10.32GHz). For the sample of PVP/MWNTs-16.7%, the maximum RL is about -9.6dB at 10.64GHz and for the sample of PEI/MWNTs-16.7%, the maximum RL is about -7.9dB at 10.50GHz.

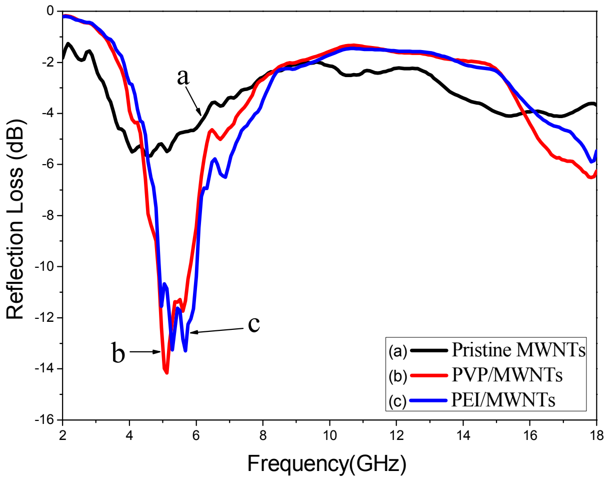

Fig.5. The reflection loss of pristine MWNTs (a), PVP/MWNTs hybrids (b) and PEI/MWNTs (c); the mass fractions of MWNTs or modified MWNTs in paraffin matrix is 25%.

In the comparison of these eight curves in figure 6, the maximum reflection loss of PVP/ MWNTs hybrids is larger than that of PEI/MWNTs hybrids. But more importantly, both PEI/MWNTs and PVP/MWNTs hybrids could have a wide absorbing bandwidth by adjusting the mass ratio of polymer/MWNTs and paraffin matrix. For example, in the X-band frequency region, the reflection loss values of PVP/MWNTs-30% and PEI/MWNTs-30% are all below -7dB (more than 80.0% absorption).

The dispersion and the interfacial electric polarization of MWNTs are important factors to improve and regulate the microwave absorbing properties. However, it is not easy for PVP/MWNTS and PEI/MWNTs to make clear that which one has a better dispersion state from Fig.4b and Fig.4c. Therefore, we think that the reason resulted in the different absorbing peak between PEI/MWNTs and PVP/MWNTs may come from the polarity differences of PEI and PVP. For the polymer/MWNTs composites, dielectric loss caused by polarization plays an important role in the microwave absorption. The lone pair electrons in polymers can interact with π-electrons to increase the polarization degrees of MWNTs, which is significant for the enhancement of the dielectric parameter and the microwave absorbing properties. However, PEI and PVP polymers exhibit different polarities. PVP polymers have lots of branched chains containing amide bonds and pyrrolidone rings, while PEI polymers are linear polymers. The polarity of PVP is higher than that of PEI. So the p-π interaction between PVP and MWNTs may be stronger than that of PEI, which may induce different polarization degree, and the difference of polarization degree will cause the differences of maximum RL values and the response frequency of microwave absorbents.

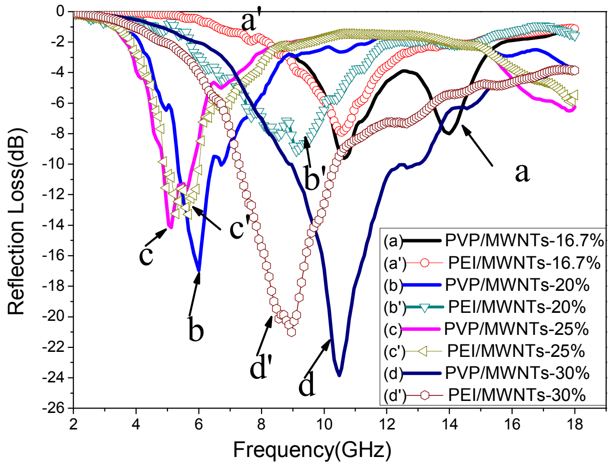

Fig.6. The reflection loss of PVP/MWNTs and PEI/MWNTs hybrids in paraffin; the mass fractions of hybrids in the absorbents are 16.7% (a, a'), 20% (b, b'), 25% (c, c') and 30% (d, d').

3.5 The analysis of dielectric properties of Polymer MWNTs hybrids

Complex permittivity, ε_r ($\varepsilon_r=\varepsilon'-j\varepsilon''$), is an important parameter to characterize the dielectric properties of absorbents. The real part (ε') of complex permittivity represents the ability of storing electromagnetic wave energy[18], while the imaginary part (ε'') represents the degree of dielectric loss of electric energy transforming into joule heat absorbed by materials. PVP/MWNTs-30% and PEI/MWNTs-30% samples are selected for the investigation of dielectric properties.

The results show that the permittivity value decreases with increasing frequency for these two samples, as shown in Fig.7, in the frequency range of 2-18GHz. The value of the real part and imaginary part of permittivity of PEI/MWNTs-30% hybrids is 18.9-7.6 and 13.6-3.7, respectively, while the value for PVP/MWNTs-30% hybrids is 12.4-6.7 and 9.2-2.4, respectively. It is noticed that the value of permittivity of PEI/MWNTs-30% hybrids is larger than that of PVP/MWNTs-30% hybrids. Taking into account the frequency characteristics, the modulus of complex permittivity decreasing with increasing frequency can indeed help to broaden the absorbing bandwidth. According to the microwave absorbing mechanism, MWNTs is one of the dielectric loss absorbents. For the dielectric absorbents, the tanδ plays an important role in the improvement of microwave absorbing properties. It can be seen from curve (e) and curve (f) that the tanδ of PEI/MWNTs-30% is from 0.79 to

0.41, and it is from 0.74 to 0.48 for PVP/MWNTs-30%. The results indicate that these two samples have very strong and efficient dielectric loss over the frequency range of 2-18GHz[19].

The mechanism of the microwave absorption properties difference is not very clear; whereas, for dielectric loss materials, Debye dipolar relaxation is an important mechanism. The relative complex permittivity can be expressed by the following equation[20]:

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j2\pi f\tau} \qquad (4)$$

Where f, ε_s, ε_∞ and τ are the frequency, static permittivity, relative dielectric permittivity at the high-frequency limit, and polarization relaxation time. The ε' and ε'' can be described by:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (2\pi f)^2\tau^2} \qquad (5)$$

$$\varepsilon'' = \frac{2\pi f\tau(\varepsilon_s - \varepsilon_\infty)}{1 + (2\pi f)^2\tau^2} \qquad (6)$$

According to Eqs.(5) and (6), the relationship between ε' and ε'' can be expressed as follow:

$$(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_s - \varepsilon_\infty}{2})^2 \qquad (7)$$

The plot of ε′ versus ε″ would be a single semicircle, usually expressed as the Cole-Cole semicircle. Each semicircle corresponds to one Debye relaxation[21].

Figure 8 shows the ε′-ε″ curves of these two samples. A distinct Cole-Cole semicircle is found in the curve (a), which can be ascribed to relaxation phenomena due to the contribution of interface polarization. However, in the curve (b), there is only a small inconspicuous Cole-Cole semicircle in the ε′ range of 9.7-10. From the comparison Fig.6 with Fig.8, it can be found that the permittivity range where the Cole–Cole semicircle appears is in the same position as the reflection loss peaks appear for these two samples. The ε′-ε″ curves results indicated that polarizations exist in the composites and play an important role in microwave absorption. It is the wrapping of PVP and PEI polymers on MWNTs that improve the polarization of absorbent. Because of the different polarities of these two kinds of polymers, the absorbent hybrids exhibit different wave absorption characteristics. The maximum absorbing peaks of PVP/MWNTs shift towards a higher frequency compared with PEI/MWNTs, and there is a

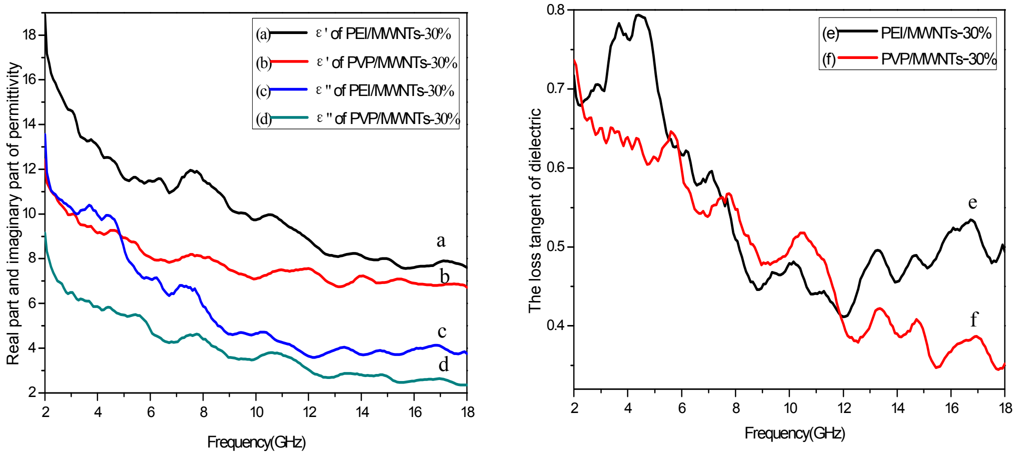

Fig.7. Real part of permittivity of PEI/MWNTs-30% (a), PVP/MWNTs-30% (b) and imaginary part of permittivity of PEI/MWNTs-30% (c), PEI/MWNTs-30% (d), tanδ values of PEI/MWNTs-30% (e) and PVP/MWNTs-30% (f) hybrids.

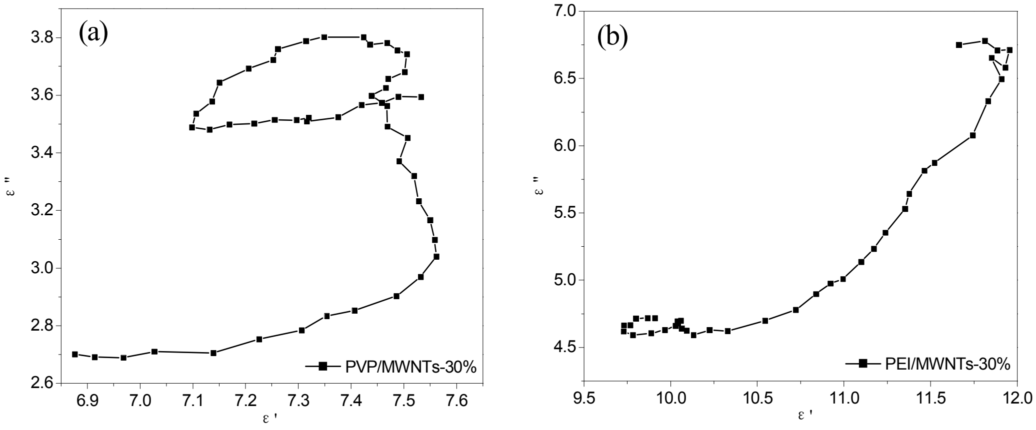

Fig.8. ε′-ε″ curves of PVP/MWNTs-30% (a) and PEI/MWNTs-30% (b) hybrids.

difference of about 2.8dB between their maximum absorption values. In conclusion, it is imperative that the polarity of polymers used to modify the surface of MWNTs has significant influence on the maximum reflection loss value and the frequencies where the absorption peaks appear may be affected meanwhile. However, a lot more work need to be done to investigate the deeper mechanism.

4. Conclusions

In this paper, PVP and PEI polymers are used to modify MWNTs as non-covalent modifiers. TEM results demonstrate that the addition of PVP and PEI can prevent MWNTs from aggregating and are useful to the improvement of the MWNTs dispersibility. The optimal microwave absorbing results obtained from calculation demonstrate that the maximum reflection loss of PEI/MWNTs hybrids could reach about -21.01dB at 8.96GHz by adjusting the mass percentage of polymer/MWNTs in matrix, and the bandwidth corresponding to the reflection loss below -10 dB is more than 3.04GHz (7.28-10.32GHz). However, to the PVP/MWNTs hybrids, the maximum reflection loss turns into -23.84dB at 10.48GHz, and the bandwidth corresponding to the reflection loss below -10 dB is more than 3.92 GHz (8.96-12.88GHz). A distinct Cole-Cole semicircle is found for PVP/MWNTs hybrids, and there is only a small inconspicuous Cole-Cole semicircle in the ε' range of 9.7-10 for the PEI/MWNTs hybrids. The permittivity range where the Cole-Cole semicircle appears is in the same position as the reflection loss peaks appear for these two samples. It can be deduced that polymer polarity has significant influence on the maximum reflection loss value.

Acknowledgements

This work is supported by the National Natural Science Foundation (No.51373136, No.51373137), and Shaanxi Natural Science Foundation (No.2014JM6241).

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