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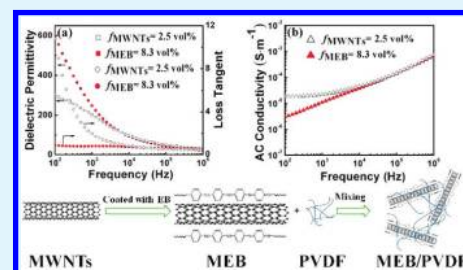
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ABSTRACT: A comparative study of the dielectric properties of poly(vinylidene fluoride) (PVDF) based nanocomposites with pristine multiwalled carbon nanotubes (MWNTs) and surface-modified MWNTs with core/shell structure (denoted as MEB) as fillers, was reported. Compared with MWNTs/PVDF composites, the MEB/PVDF composites exhibited lower loss tangent and higher dielectric permittivity. It is suggested that the conductive/nonconducting core/shell structure of the MEB filler is the main cause of the improved dielectric properties. Percolation based MWNTs networks is in charge of the improvement of dielectric permittivity, and the nonconducting emeraldine base layer of the MEB filler supports the low loss tangent and low conductivity in the MEB/PVDF composites.

KEYWORDS: dielectric permittivity, carbon nanotubes, emeraldine base, core/shell structure, loss tangent, ferroelectric



1. INTRODUCTION

Polymer materials with high dielectric permittivity have received increasing interest for their potential application as embedded capacitor to meet the requirement of further miniaturization of electronics.^{1–8} Ferroelectric polymers, such as poly(vinylidene fluoride) (PVDF), are usually employed as the matrix due to their high dielectric constants.^{8–10} To further improve the dielectric constants of the polymers, one simple method is introducing ceramic particles with high dielectric constant into the polymer matrix.^{4,8,11–14} However, it is difficult to obtain composites with the dielectric constant over 100 even with high filler content. Another strategy focuses on dispersing conductive fillers including carbon black, carbon nanotubes (CNTs), nickel particles, etc., into the polymer matrix to achieve percolative composites.^{15–19} Among these fillers, CNTs have received great attention because their large aspect ratio can lead to lower percolation threshold in nanocomposites.^{20,21} High dielectric constants of composites can be expected when the filler concentration approaches percolation threshold according to percolation theory. However, the significant increase in dielectric constant of the CNTs/polymer composites is usually in company with a large increase of dielectric loss and conductivity, which makes the percolative composites hardly considered as effective materials for the embedded capacitors.^{16,18,22}

Much work has focused on how to improve the dielectric properties of the materials by changing the interface properties of the composites.^{4,14,23,24} For example, Shen et al. used Ag particles coated by organic shells as fillers to realize composites with high dielectric and low loss tangent.²³ Kohlmeyer et al. pointed out that insulating polymer should be used for surface

modification of CNTs to improve the dielectric properties of CNTs/polymer.²² In this letter, in situ polymerization was used for preparing surface modified MWNTs according to the reported study.²⁵ Polyaniline (PANI) base, namely, the emeraldine base (EB), was employed as the nonconducting layer coating the surface of the MWNTs. Nanotubes, with conductive core and nonconducting outer layer, were fabricated and denoted as MEB. Dielectric properties of the MWNTs/PVDF and MEB/PVDF composites were measured in a wide frequency range (1×10^2 to 1×10^6 Hz). Compared with MWNTs/PVDF nanocomposites, MEB/PVDF nanocomposites could reach higher dielectric constant and lower loss tangent.

2. EXPERIMENTAL SECTION

MWNTs (20–40 nm in diameter, 5–15 μ m in length) were purchased from Shenzhen Nanotech Port Company. The core/shell fillers, MWNTs core with EB coating as the outer layer, were prepared through in situ oxidative polymerization of aniline. A suspension of MWNTs (0.30 g) in ethanol (150 mL) was first obtained by sonication and then mixed with aniline (0.18 g, 1.9 mmol) and hydrochloric acid (1 M, 1.9 mL). Then aqueous solution of ammonium peroxydisulfate (0.43 g, 1.9 mmol) was added into the mixture. The whole reacting system contains 150 mL ethanol and 150 mL water. The polymerization was performed at 0 $^{\circ}$ C for 6 h and then at room temperature for 12 h. The crude product was obtained by

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filtration through a 0.45 μm nylon membrane and then washed by deionized water. Afterward, it was immersed in excess amount of 1 M ammonia to convert protonated PANI into the nonconducting EB form. At last, the MEB was filtered through a 0.45 μm nylon membrane, washed with deionized water, and then dried at 80 $^{\circ}\text{C}$ for 12 h in vacuum oven.

MEB/PVDF and MWNTs/PVDF nanocomposites, with various filler loadings, were prepared by simple blending and subsequent hot-molding. Predetermined amount of the fillers was first dispersed in *N,N*-dimethylformamide through sonication. Then PVDF powders were added into the suspension to form uniform slurry by vigorous mechanical stirring at 80 $^{\circ}\text{C}$ for 2 h. The slurry was casted on glass plate at room temperature and then dried at 80 $^{\circ}\text{C}$ for 4 h in oven. The obtained composite films were further compression molded into plates at 190 $^{\circ}\text{C}$ for 10 min under a pressure of 20 MPa. Disk samples with diameter of about 11 mm and thickness of about 1 mm were cut from the plates and used for the dielectric and conductivity measurements. Morphologies of the pristine MWNTs and the MEB were characterized by transmission electron microscopy (TEM) (Hitachi H7650). Alternating current electrical properties of the samples were measured using impedance analyzer (Agilent 4294A).

3. RESULTS AND DISCUSSION

Figure 1 shows the morphologies of the pristine MWNTs and the MEB. From Figure 1b it can be clearly seen that MWNTs are coated by EB layers. The coating is fairly uniform, and no

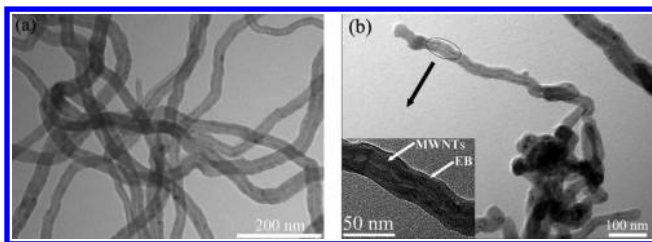


Figure 1. TEM pictures of (a) MWNTs and (b) MEB. The areas related to MWNTs and EB shell are indicated by arrows in the inset picture.

EB in the internal cavity of the MWNTs was observed. The average thickness of the EB layer is about 5 nm. Such a thin nonconducting shell should prevent the direct contact of MWNTs with each other when blended with PVDF, as shown in Figure 2. The introducing of nonconducting EB shell on the surface of the MWNTs will change the dielectric properties of the composites, and the results will be discussed in the following section.

Figure 3 shows the frequency dependence of the dielectric constant of the MWNTs/PVDF and MEB/PVDF nano-

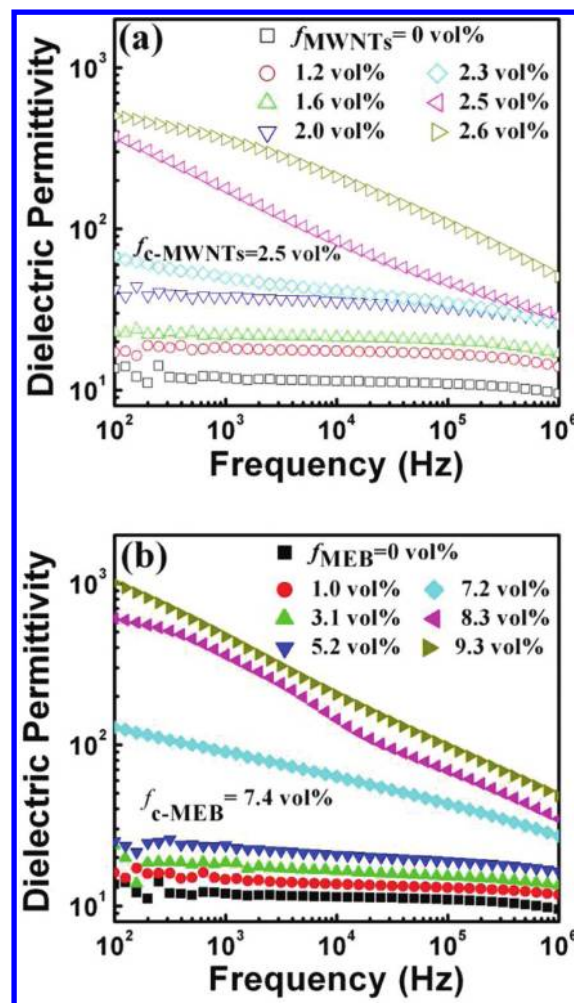


Figure 3. Frequency dependence of the dielectric constant of (a) MWNTs/PVDF nanocomposites and (b) MEB/PVDF nanocomposites with various filler contents at room temperature. The percolation threshold volume fraction, f_c is given for both systems.

composites at room temperature. The volume fraction of the fillers at the percolation threshold, f_c is the critical parameter for the electrical properties of the conductive filler loaded composites. Significant changes in the electrical properties will happen when the filler concentration approaches the percolation threshold. The power law showing the enhancement of the dielectric constant near the percolation threshold can be expressed by the following equation

$$\epsilon_{\text{eff}} \propto \epsilon_{\text{PVDF}}(f_c - f)^{-s} \text{ for } f < f_c \quad (1)$$

where ϵ_{eff} and ϵ_{PVDF} are the dielectric constants of the composites and pure PVDF, respectively, f is the volume

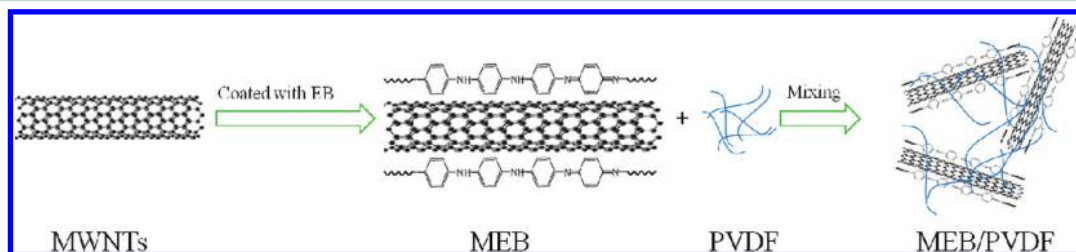


Figure 2. Schematic diagrams of the preparation of MEB/PVDF composites.

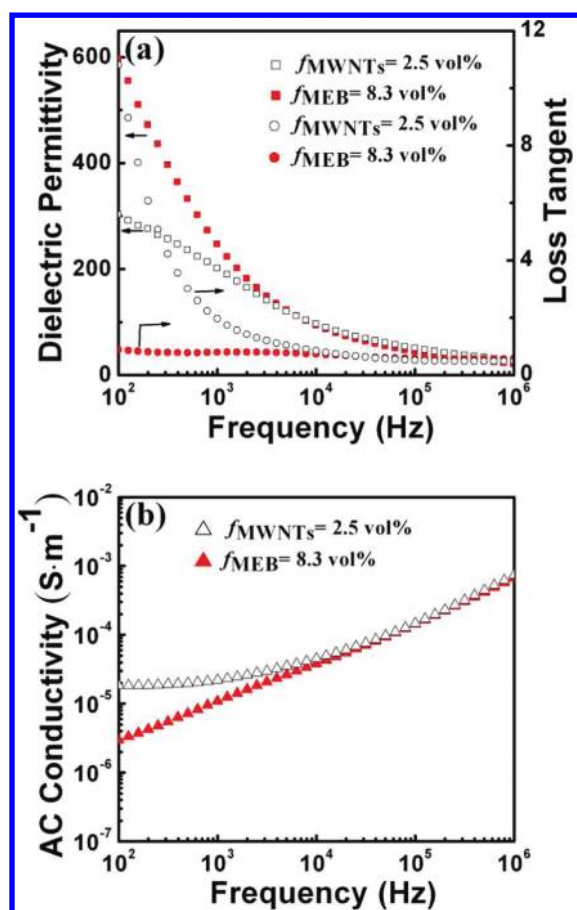


Figure 4. Frequency dependence of (a) dielectric permittivity and loss tangent, and (b) conductivity of the MWNTs/PVDF and MEB/PVDF nanocomposites.

fraction of fillers of the composites, f_c is the percolation threshold, and s is the critical exponent. The fitting of the experimental data according to the power law gives $f_{c-\text{MWNTs}} = 2.5 \text{ vol\%}$ and $f_{c-\text{MEB}} = 7.4 \text{ vol\%}$. The percolation threshold of the MEB/PVDF composites is much higher than that of the MWNTs/PVDF composites mainly because the nonconducting EB outer layer prevents the direct contact of the MWNTs. Namely, it is more difficult to form conductive network in the MEB/PVDF composites than in the MWNTs-PVDF composites.

Composites with the $f_{\text{MWNTs/PVDF}}$ of 2.5 vol % and the $f_{\text{MEB/PVDF}}$ of 8.3 vol %, both of which are equal to or slightly above the f_c , were compared to further clarify the effect of EB shell. As shown in Figure 4a, the MEB/PVDF composites exhibit higher dielectric constants and lower loss tangent at lower frequencies ($<1 \times 10^4 \text{ Hz}$). However, for the higher frequencies, the dielectric properties of both composites are very close to each other. According to the microcapacitor model, the dispersed MWNTs could form a great number of microcapacitors in the polymer matrix, which results in improvement in the dielectric constant of the composites. Because there are more MWNTs in the MEB/PVDF composites than in the MWNTs/PVDF composites, it endows the MEB/PVDF with a higher dielectric constant. Moreover, the MWNTs may connect with each other directly near the percolation threshold in the MWNTs/PVDF composites. That will minimize the number of microcapacitor and bring leakage loss in composites. However, this cannot happen in the MEB/

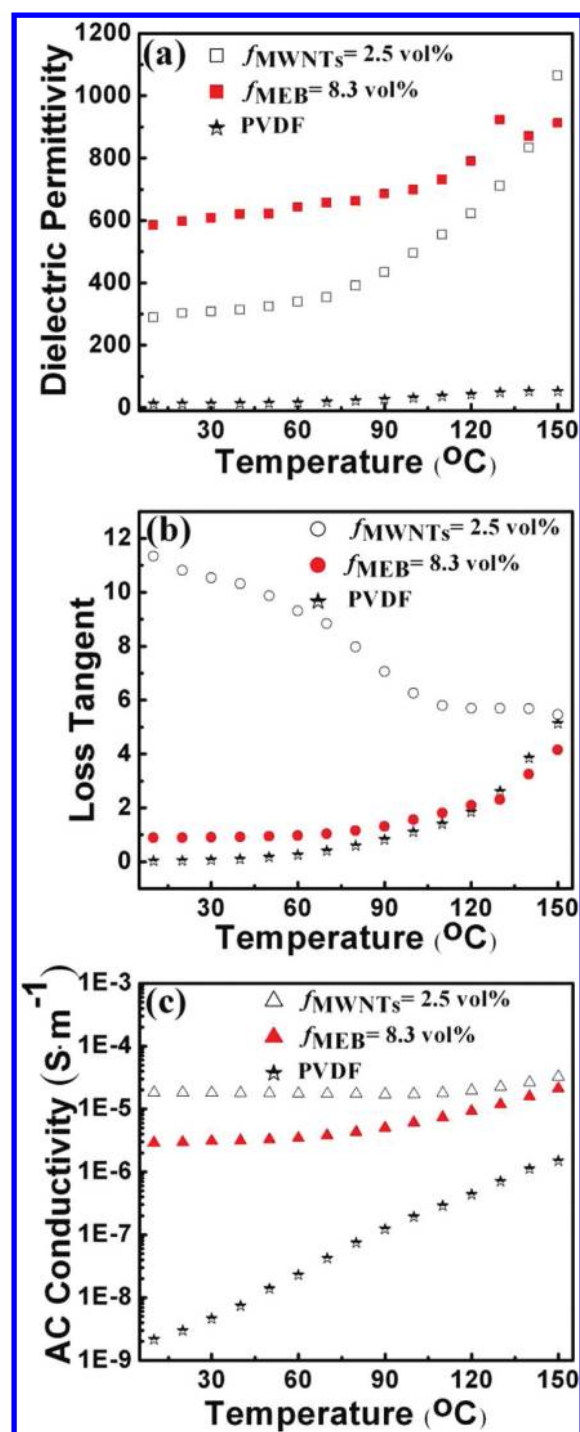


Figure 5. Temperature dependence of (a) dielectric permittivity, (b) loss tangent, and (c) conductivity of the MWNTs/PVDF nanocomposites, MEB/PVDF nanocomposites and PVDF.

PVDF composites because of the nonconducting EB shell coating on the surface of the MWNTs, which makes the direct contact of MWNTs impossible. As a result, higher dielectric constant and lower loss tangent is obtained in the MEB/PVDF composites. Figure 4b shows the frequency dependence of the conductivity of the two composites. As expected, the MEB/PVDF nanocomposites show much lower conductivity than the WMNTs-PANI/PVDF nanocomposites at lower frequency.

Panels a and b in Figure 5 present the dielectric constant and loss tangent of the two nanocomposites and PVDF over a wide

range of temperatures at 1×10^2 Hz. It can be seen that the dielectric constants of all the samples increase with increasing temperature. Because the mobility of the PVDF chain segments increased at higher temperature, larger polarization of the PVDF can be realized under the same electric field. Consequently, larger dielectric constant is achieved at higher temperature. For the dielectric loss, the loss tangent of the MEB/PVDF increases with increasing temperature, and it can be attributed to the loss tangent elevating of the PVDF polymers. However, the temperature dependence of loss tangent is significantly different in the two composites. To explain this phenomenon, temperature dependence of conductivity of the samples is given in Figure 5c. The conductivity of the pure PVDF samples increases with increasing temperature. Similar behavior is also exhibited by the MEB/PVDF nanocomposite. However, with increasing temperature, the conductivity of the MWNTs/PVDF first decreases, but then increases above 100 °C. The decrease in the conductivity is attributed to the destruction of the conductive network in the composites. As the coefficient of thermal expansion of the MWNTs is lower than that of the PVDF polymers, the increasing temperature could separate the MWNTs. As the filler contents are near the percolation threshold, it is easy to destroy the conductive network in the composites. MWNTs could directly contact each other in the MWNTs/PVDF composites. Separating MWNTs will significantly influence the conductivity of the composites. However, because of the existence of nonconducting emeraldine base shell between the neighboring MWNTs, the separating increases the distance between MWNTs and plays less influence on the conductivity of MEB/PVDF than that of the MWNTs/PVDF composites. The breakage of the conductive network will decrease the conductivity and minimize the leakage loss of the MWNTs/PVDF composites, so the loss tangent decreases with increasing temperature in the MWNTs/PVDF composites.

4. CONCLUSIONS

In conclusion, MEB fillers with conductive/nonconducting core/shell structure were synthesized. MWNTs/PVDF and MEB/PVDF composites were prepared by simple blending and hot-molding procedure. Compared with the MWNTs/PVDF composites, improved dielectric properties are achieved in the MEB/PVDF nanocomposites. Higher dielectric permittivity together with lower loss tangent and conductivity makes the MEB/PVDF nanocomposites more attractive in application. These results could be due to the adoption of the MEB materials with conductive/nonconducting core/shell structure as the filler.

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