Composites Science and Technology 68 (2008) 2290–2296

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Large dielectric constant of the chemically functionalized carbon nanotube/polymer composites

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ARTICLE INFO

Article history:
Received 22 October 2007
Received in revised form 17 April 2008
Accepted 21 April 2008
Available online 26 April 2008

Keywords:
A. Carbon nanotubes
A. Polymers
A. Functional composites
B. Electrical properties

ABSTRACT

Pristine, carboxylic and ester functionalized multi-walled carbon nanotube (MWCNT)/poly(vinylidene fluoride) (PVDF) composites were fabricated by evaporating suspensions of the nanotubes in PVDF. Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that carboxylic groups and ester groups had been introduced on the surface of MWCNTs. The Raman spectroscopy showed that the amorphous carbon materials and impurities had decreased by chemical functionalizations. The electrical conductivity and dielectric properties of the composites were investigated. The percolation thresholds of the pristine, carboxylic and ester functionalized MWCNT/PVDF composites are approximately equal, about 3.8 vol%, but the dielectric constants are enhanced significantly. The largest dielectric constant of 3600 is obtained in the carboxylic functionalized MWCNT/PVDF composite with 8 vol% MWCNT at 1 kHz, which can be attributed to the preparation procedure and the interface effect between the MWCNTs and the polymer.

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1. Introduction

Owing to the extraordinary electrical, thermal and mechanical properties, carbon nanotubes (CNTs) have been widely studied in the past few years. They have been pursued extensively to enhance the electrical, thermal, and mechanical properties of the composites by using CNTs as the nanofibers [1–8]. Recently, attention was focused on the remarkable enhancement in electrical, thermal, and mechanical properties of CNT-based composites which have very small percolation threshold. Barrau et al. [2] reported the percolation threshold of the CNT/epoxy composites was only 0.3 wt%, and found that the electrical conductivity of the CNT/epoxy composites increased about 12 orders of magnitude around the percolation threshold. Yu et al. [5] investigated the effect of the purity of the single-walled carbon nanotubes (SWCNTs) on the thermal conductivity of SWCNT/epoxy composites, and found that the thermal conductivity of the purified SWCNT/epoxy composites was approximately five times larger than that of pristine SWCNT/epoxy composites.

In order to enhance the physical properties of CNTs, the chemical functionalization has been introduced in recent years. The chemical functionalization consists of the covalent functionalization and noncovalent functionalization [7–14]. The noncovalent functionalization has been investigated intensively, for instance, the surfactant has been adopted to improve the dispersion of CNTs in the polymer composites [7,8]. Besides, the polymer wrapped CNTs by in situ polymerization and the covalent functionalizations, for instance, the carboxylic, amine, ester functionalizations, were also investigated widely before [9–14]. Many theories, Maxwell–Garnett theory, Jonscher theory, and the percolation threshold theory, were all discussed to study the relationship between the dielectric constant, conductivity and the filler concentration in composites. Recently, the Improved Interparticle Distance (IPD) model was reported by Li et al. to study the influence factors of the percolation threshold. The aspect ratio of CNTs, disentanglement of CNTs agglomerates on the nanoscale, and the uniform distribution of individual CNTs or CNT agglomerates on the microscopic scale will all influence the percolation threshold of the composites [15].

In this paper, the pristine and chemically functionalized multi-walled carbon nanotube/poly(vinylidene fluoride) (MWCNT/PVDF) composites were fabricated. The percolation thresholds of the composites are relatively large, but the dielectric constants are enhanced significantly. The largest dielectric constant of 3600 is obtained in the carboxylic functionalized MWCNT/PVDF composite with 8 vol% MWCNT at 1 kHz, which can be attributed to the preparation procedure and the interface effect between the MWCNTs and the polymer.

2. Experimental

2.1. Materials and instruments

The MWCNTs (purity > 95 wt%, diameter 10–20 nm, length about 30 μm, density 2.1 g/cm^3) synthesized by chemical vapor

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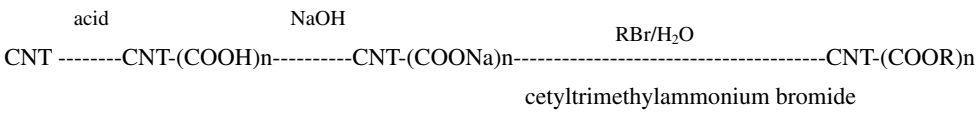
doi:10.1016/j.compscitech.2008.04.019

deposition were purchased from Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Science. The PVDF powder (particle size about 50 μm, density 1.7 g/cm^3) was purchased from 3F Co. Ltd., Shanghai, China. 1-Bromohexadecane (CP) was purchased from Shanghai Chemical Co. Ltd., China. Cetyltrimethylammonium bromide (AR), concentrated sulfuric acid (AR), concentrated nitric acid (AR), ethanol (AR), sodium hydroxide (AR), and chloroform (AR) were all purchased from Tianjin Chemical Co. Ltd., China. Ultrasonicator (HK2200, 100 W) was purchased from High Kugod Science Instrument Co. Ltd., Shanghai, China. LCR digital meter (TH2828) was purchased from Tonghui Electronic Co. Ltd., Changzhou, China.

2.2. Preparation and measurement

The MWCNTs were functionalized following the route reported by Qin et al. [12–14]. Briefly, 1 g of the pristine MWCNTs was suspended in 100 mL mixture of concentrated sulfuric acid and concentrated nitric acid (3:1 (v/v)) for 6 h with the ultrasonicator. The MWCNTs were filtrated and washed with deionized water until pH 5–7, and dried at 55 °C in a vacuum for 8 h. The carboxylic functionalized MWCNTs were obtained. In order to convert it into the sodium salt form, the carboxylic functionalized MWCNTs were sonicated in sodium hydroxide aqueous solution (0.01 M, 100 mL) for 15 min. Then 2 g of cetyltrimethylammonium bromide which were used as the phase transfer catalyzer and 2 mL of 1-bromohexadecane were poured into the solution. The suspension was kept at 80 °C for 8 h under vigorous stirring. The precipitation (the mixture of the carboxylic functionalized MWCNTs and ester functionalized MWCNTs) was poured into chloroform. Because the carboxylic functionalized MWCNTs cannot be dissolved in chloroform, the mixture can be filtrated to get rid of carboxylic functionalized MWCNTs. The solution was poured into an excess amount of ethanol. The ester functionalized MWCNTs, as the black solid, were precipitated, and the products were washed with ethanol for several times. The ester functionalized MWCNTs were prepared via the esterification reaction of the carboxylate salt of MWCNTs and 1-bromohexadecane. The 1-bromohexadecane was the pristine materials, and the long alkyl chain can be introduced on the surface of MWCNTs. The cetyltrimethylammonium bromide was used as the phase transfer catalyzer [12]. The action can be explained simply as follows:



In order to form a stable suspension, the pristine and chemically functionalized MWCNTs were respectively ultrasonically dispersed in ethanol for 3 h. Then the different volume fraction PVDF powder was dissolved in this suspension, and the mixture was ultrasonically dispersed for another 2 h. The mixture was dried for 3 h at 70 °C to remove any excess ethanol [16]. The low evaporation temperature would not bring to MWCNT agglomeration again. The composites were broken into powder with millimeter scale by simple milling method. The composite powder was cold pressed to disk-shape sample with 15 mm in diameter and 2 mm in thickness at 20 MPa. Then the samples were kept at 200 °C for 3 h. All samples were polished to control their flatness, and the silver paste was painted on both sides of the samples to provide a good contact with the filler network within the samples. The structures of the pristine and chemically functionalized MWCNTs were characterized by using XPS, FT-IR, Raman spectroscopy and transmission electron microscopy (TEM) micrographs. The sections of the composite samples were examined by scanning electron microscope (SEM). The alternating current (ac) electrical properties of the samples were measured by using four-probe method with LCR digital meter in the frequency range of 20–10^6 Hz at room temperature.

3. Results and discussion

3.1. Chemical functionalization

X-ray photoelectron spectroscopy was used to character the surface elements and their concentration. Fig. 1a and b is, respectively, the full X-ray photoelectron spectroscopy and narrow scan spectra of O 1s of three kinds of MWCNTs. As shown in Fig. 1a, the C 1s (285 eV) and O 1s (555 eV) peak are all shown in these MWCNTs. The oxygen element of the pristine MWCNTs can be attributed to the production of MWCNTs. As shown in Fig. 1b, the area of the peak of carboxylic and ester functionalized MWCNTs are larger than that of pristine MWCNTs, which means that the concentration of oxygen element of chemically functionalized MWCNTs is larger than that of pristine MWCNTs. The oxygen element concentration of MWCNTs is, respectively: 1.23 at% (pristine MWCNTs), 8.99 at% (carboxylic functionalized MWCNTs), and 6.69 at% (ester functionalized MWCNTs). The oxygen element concentration of chemically functionalized MWCNTs increases obviously [17].

The FT-IR spectroscopy of the pristine and chemically functionalized MWCNTs was shown in Fig. 1c. The peak around 1735 cm^{-1} and 1575 cm^{-1} shows the C=O vibration peak, which means the carboxylic group has been introduced onto the surface of pristine MWCNTs. The peak around 1196 cm^{-1} and 2906 cm^{-1} are respectively represented for the C–O–C vibration peak and C–H vibration peak in ester functionalized MWCNTs. All these proofs demonstrate that the carboxylic and ester groups had been introduced on the surface of MWCNTs [18].

The Raman spectroscopy which was fitted by mixing a Gaussian shape is shown in Fig. 1d. We have known that the peak near 1350 cm^{-1}, called D band, indicated the multicrystal or amorphous carbon materials, and the peak near 1580 cm^{-1}, called G band, indicated the graphite crystal structure in carbon materials. As shown in the Raman spectroscopy, we found that the D band at 1350 cm^{-1} was more intense than the G band at 1580 cm^{-1} in pristine MWCNTs because of a great number of amorphous carbon and impurities. However, the intensity of D band and G band are approximately equal in the carboxylic functionalized MWCNTs, and even the D band was weaker than the G band in the ester functionalized MWCNTs, which means the amorphous carbon materials and impurities have decreased by chemical functionalizations. During strong chemical processing, it is possible to produce additional defects where carbon atoms are eliminated. The ultrasonication processing is not a vigorous processing course relatively in our experiment. The amorphous carbon and impurities have been removed, and the MWCNT skeleton has not been destroyed in this experiment [10]. From the spectroscopy, we can also get a conclusion that the peak position of carboxylic functionalized MWCNTs shifts to higher wave numbers, while that of the ester functionalized MWCNTs shifts to lower wave numbers. The electron-withdrawing group (carboxylic

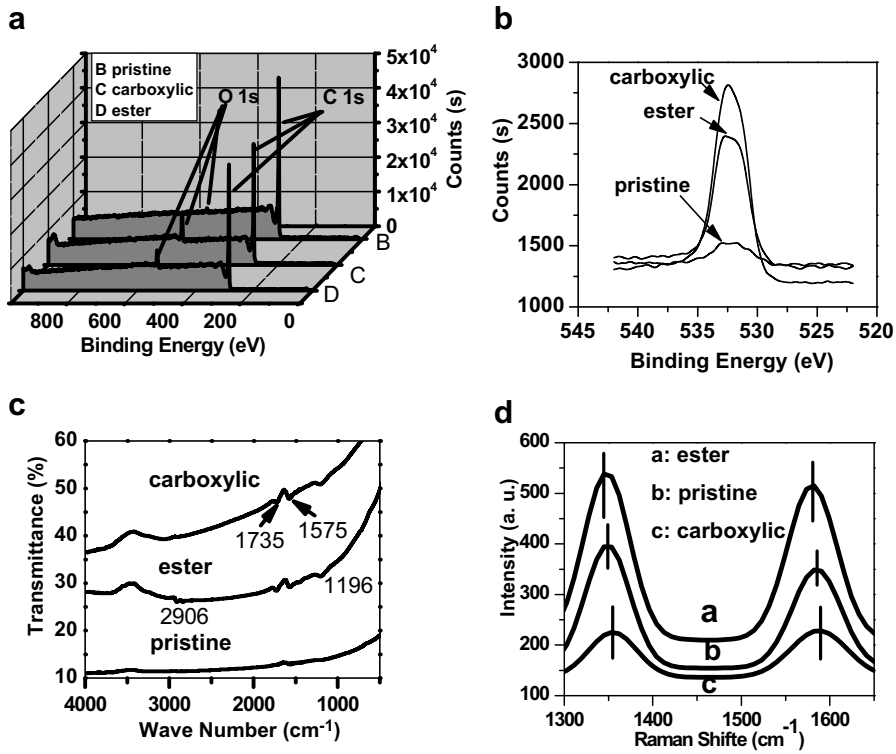


Fig. 1. XPS full spectroscopy (a) and narrow scan spectroscopy of O 1s (b); FT-IR spectroscopy (c); and Raman spectroscopy (d) of the pristine and chemically functionalized MWCNTs.

group) makes the peak position of carboxylic functionalized MWCNTs shift to higher wave numbers, and the electron-donating group (alkyl) makes the ester functionalized MWCNTs shift to lower wave numbers.

Fig. 2 shows the TEM images of the pristine and carboxylic functionalized MWCNTs in our experiment. As shown in Fig. 2a and d, the length of the carboxylic functionalized MWCNTs is obviously shorter than that of pristine MWCNTs. The Fig. 2b and e shows that the amorphous carbon materials in carboxylic functionalized MWCNTs are less than that in pristine MWCNTs, and as shown in Fig. 2c and f, the catalysts embedded in the tip of MWCNTs have been removed. The closed tube tip was opened and the wall structure of the tubes was not damaged by acid treatment [12–14,17]. Fig. 3 shows the SEM images of the composite sections, which indi-

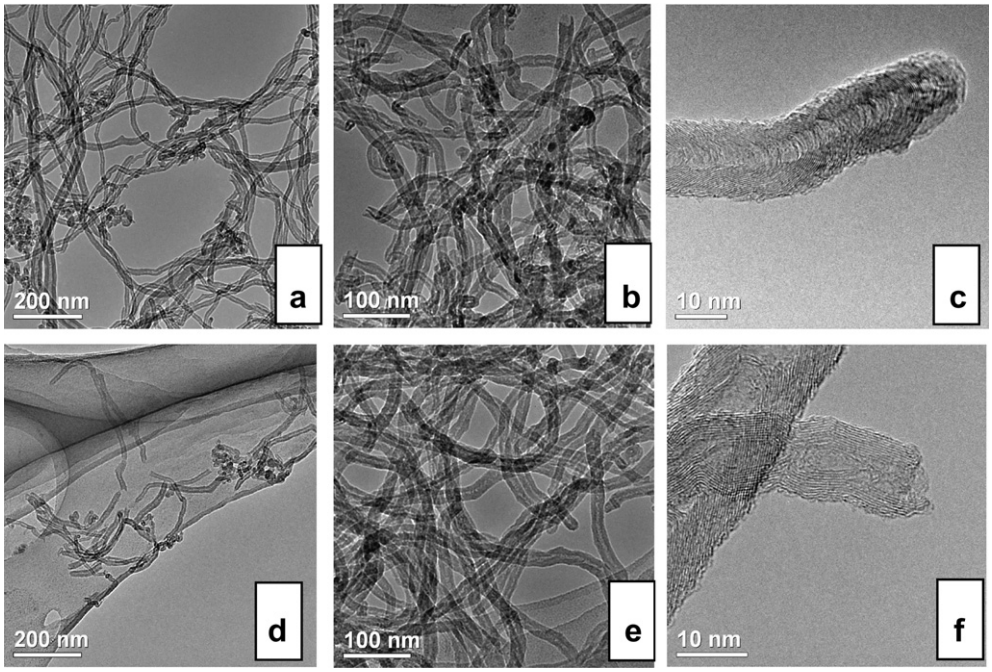


Fig. 2. TEM images of pristine (a–c); and carboxylic functionalized (d–f) MWCNTs.

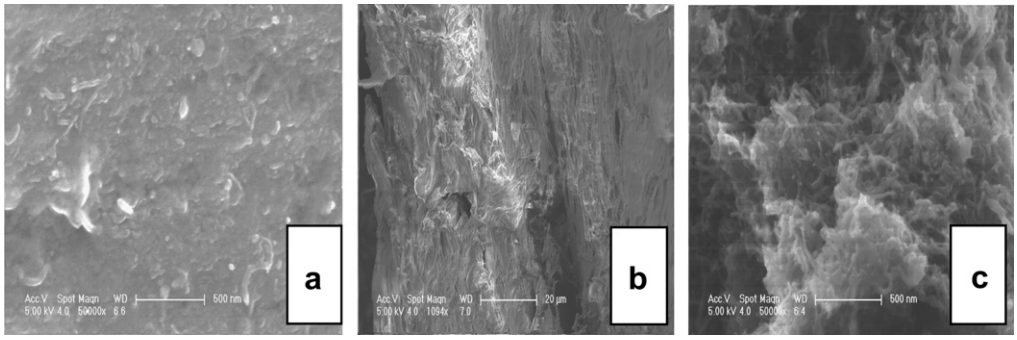


Fig. 3. SEM images of pristine (a), carboxylic functionalized (b) and ester functionalized (c) MWCNT/PVDF composite sections.

cated that the chemically functionalized MWCNTs were dispersed in the PVDF matrix homogeneously.

3.2. Electrical conductivity

Fig. 4 shows the frequency dependence of ac conductivity of the pristine MWCNT/PVDF composites and chemically functionalized MWCNT/PVDF composites. With small MWCNT concentration, the conductivity of the composites increases with increasing frequency. And with further increasing MWCNT concentration, the conductivity indicates the direct current (dc) conductivity and non-dielectric behavior at low frequency. The electrode polarization can be negligible [1,2]. However, the conductivity of these three composites with the same MWCNT concentration is different. For instance, the conductivity of the pristine MWCNT/PVDF composite is nearly two orders of magnitude larger than that of the functionalized MWCNT/PVDF composite with 6 vol% MWCNT concentration. Yu et al. [5] also reported the electrical conductivity of pristine SWCNT/epoxy composites was several orders higher than that of carboxylic functionalized SWCNT/epoxy composites with the same SWCNT concentration. The length of MWCNTs has been shortened by the acid treatment, and the conductive network is more difficult to form in the chemically functionalized MWCNT/PVDF composites. Therefore, when the MWCNT concentration is larger than the composite percolation threshold, the conductivity of chemically functionalized MWCNT/PVDF composites is much smaller than that of pristine MWCNT/PVDF composites with the same MWCNT concentration.

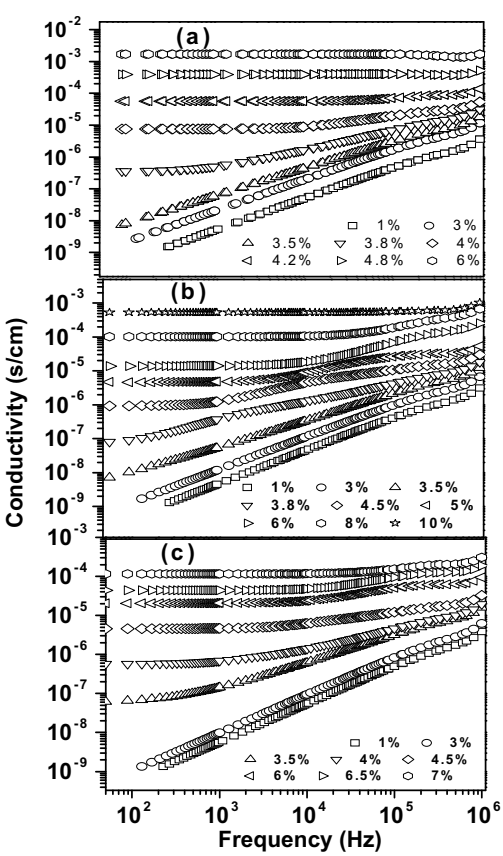


Fig. 4. Frequency dependence of the ac conductivity of pristine (a), carboxylic functionalized (b), and ester functionalized (c) MWCNT/PVDF composites with different MWCNT volume contents.

Fig. 5 shows the ac conductivity of the pristine and chemically functionalized MWCNT/PVDF composites as a function of MWCNT volume fraction, measured at room temperature and 1 kHz. The conductivity can be further analyzed with the critical MWCNT concentration p_c by the following scaling law [2–4,19]:

$$\sigma_{\text{eff}} \propto \sigma_i (p_c - p_{\text{MWCNT}})^{-s'}, \text{for } p_c > p_{\text{MWCNT}} \quad (1)$$

$$\sigma_{\text{eff}} \propto \sigma_c (p_{\text{MWCNT}} - p_c)^{t}, \text{for } p_c < p_{\text{MWCNT}} \quad (2)$$

where, σ_{eff} is the effective conductivity of the composites, σ_i is the conductivity of the insulating PVDF polymer, σ_c is the conductivity of the conducting component, p_{MWCNT} is the MWCNT volume fraction, p_c is the percolation threshold, s' is the critical exponent in the insulating PVDF polymer in the composites, and t is the conductivity exponent. From the insets of Fig. 5, we can get the percolation thresholds are approximately equal, about 3.8 vol%, and the values t of the pristine, carboxylic and ester functionalized MWCNT/PVDF composites are, respectively, 1.83, 3.16 and 1.72.

Wang and Dang [20] reported that the percolation threshold of the pristine MWCNT/PVDF was about 1.6 vol%. Compared with these results, our result is larger. The result is larger than that reported before, which can be attributed to the different preparation procedure. The PVDF material can dissolve in the (*N*, *N*-dimethylformamide (DMF)) solution. However, the PVDF material can only disperse in the ethanol solution. The different preparation procedure is the major reason for the different percolation threshold. According to the classical percolation threshold theory, the threshold of the composites has tight relations with the length of the MWCNTs. Yu et al. [5] also reported the threshold of the carboxylic functionalized SWCNT/epoxy composites was larger than that in pristine SWCNT/epoxy composites. However, the results in our experiment are approximately equal. As shown in Fig. 5, the percolation transition scope is wide, and little difference may be difficult to observe. The conductivity of the pristine MWCNT/PVDF composites increases remarkably near the percolation threshold, and exhibits a typical insulator–conductor transition. However, the

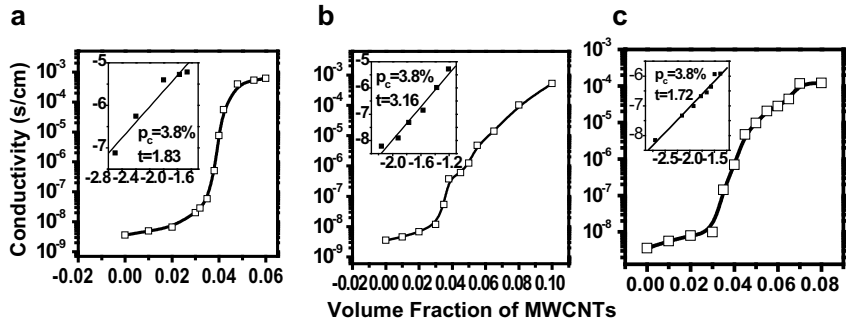


Fig. 5. Dependence of the ac conductivity of pristine (a), carboxylic functionalized (b) and ester functionalized (c) MWCNT/PVDF composites on the MWCNT volume fraction at 1 kHz; each inset shows a log–log plot of the conductivity as a function of $p_{MWCNT} - p_c$ to Eq. (2).

conductivity of the chemically functionalized MWCNT/PVDF composites increases slowly with increasing the MWCNT volume fraction, which is different from the previous studies [3,5]. Several workers demonstrated that if the electrons could tunnel through the insulating layer of polymer separating two neighboring fillers, the conductivity should follow the rule [2,3,21,22]:

$$\ln \sigma \propto -p^{-1/3} \tag{3}$$

where, σ is the conductivity, and p is the volume fraction. Fig. 6 shows the relationship between the nature logarithmic of conductivity and volume fraction. The linear relationship indicates that the tunneling conduction mechanism is the primary transport mode in these composites. The carboxylic groups on the surface of MWCNTs can make the tunneling current get smaller. In another word, it becomes difficult for the tunneling current to occur, if there are carboxylic groups between MWCNTs. Therefore, the tunneling current will decrease relatively, and the conductivity will increase slightly with increasing MWCNT concentration. The longer alkyl chains of the ester functionalized MWCNTs can be imbedded in the matrix, so the percolation transition of the ester functionalized MWCNT/PVDF composite is more obvious than that of carboxylic functionalized MWCNT/PVDF composite.

The theoretical value of the t related to the composite system dimension showed values ranging from 1.6 to 2.0 [3]. However, various values of exponent t have been reported. For instance, 1.61–1.71 [2], 1.71–2.01 [3], and 1.80 [4] were reported. The t can be affected by lots of factors. The preparation temperature, filler component surface, even the simulation methods will all affect the values of the t. The different t of MWCNT/PVDF composites may be attributed to the chemically functionalization. The large critical exponent of the carboxylic functionalized MWCNT/PVDF composites can be explained by Swiss-Cheese model. In this model, the conducting fillers embedded in an insulting matrix. The real critical exponent $\bar{t}$ can be evaluated as follows [23]:

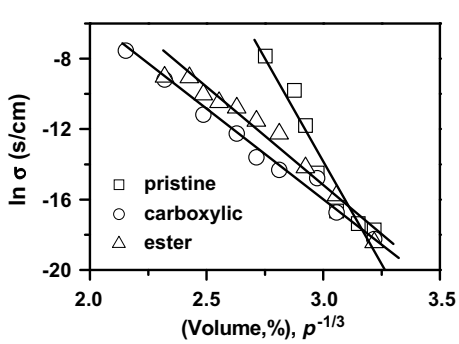


Fig. 6. Linear relationship of lnσ and $p^{-1/3}$ in three kinds of composites.

$$\bar{t} = t + (a/l)(1 - l/a) \tag{4}$$

where, l is the tunneling-distance coefficient and a is the average distance between two tubes. Because of the chemically functionalization, the carboxylic groups were introduced onto the surface of MWCNTs, which prevents the direct contact between MWCNTs. The average distance will become larger relatively. The large critical exponent of the carboxylic functionalized MWCNT/PVDF composites can be attributed to these reasons. However, the longer alkyl chains on the surface of MWCNTs can make the eater functionalized MWCNTs more compatible with polymer matrix and the longer alkyl chains can be imbedded in the matrix, which bring the little critical exponent of the ester functionalized MWCNT/PVDF composite [14].

3.3. Dielectric properties

The polymer matrix composites with large dielectric constant have been paid more attentions in recent years. There are two kinds of usual methods to increase the dielectric constants of the composites: doping high dielectric constant component [24–26], or doping conductive component [20,23,27–29]. PVDF and its copolymer have attracted more attentions for their broad applications in electromechanical systems [30,31]. However, the large dielectric constant will be demanded if these materials are employed as the functional materials, such as high charge-storage capacitors, electrostriction for artificial muscles, and "smart shins" for drag reduction and so on. By doping ceramic, semiconductor, metal, and CNTs, the dielectric constants of the PVDF composites were enhanced [20,24,25,27]. Until now, however, the dielectric constants of all the polymer composites above were only several hundreds.

Fig. 7 shows the frequency dependence of the dielectric constants of pristine MWCNT/PVDF composites and chemically functionalized MWCNT/PVDF composites. The dielectric constants demonstrate a slight correlation to the frequency before the MWCNT concentration is smaller than 3.8 vol%. The dielectric constant increases remarkably, when the MWCNT concentration near the percolation threshold. And the dielectric constant decreases dramatically from low frequency to high frequency.

Fig. 8 shows the dielectric constant as a function of MWCNT concentration at room temperature and 1 kHz. When the MWCNT concentration approaches to the percolation threshold (3.8 vol%), the dielectric constant increases remarkably. But the largest dielectric constants of the composites are different. The largest dielectric constant of the pristine MWCNT/PVDF composites is about 1700 with 6 vol% MWCNT at 1 kHz. However, the largest dielectric constant reaches 3600 for the carboxylic functionalized MWCNT/PVDF composite with 8 vol% MWCNT, and the largest dielectric constant of the ester functionalized MWCNT/PVDF composites is 2400, with about 6.5 vol% MWCNT, which can be attributed to the different

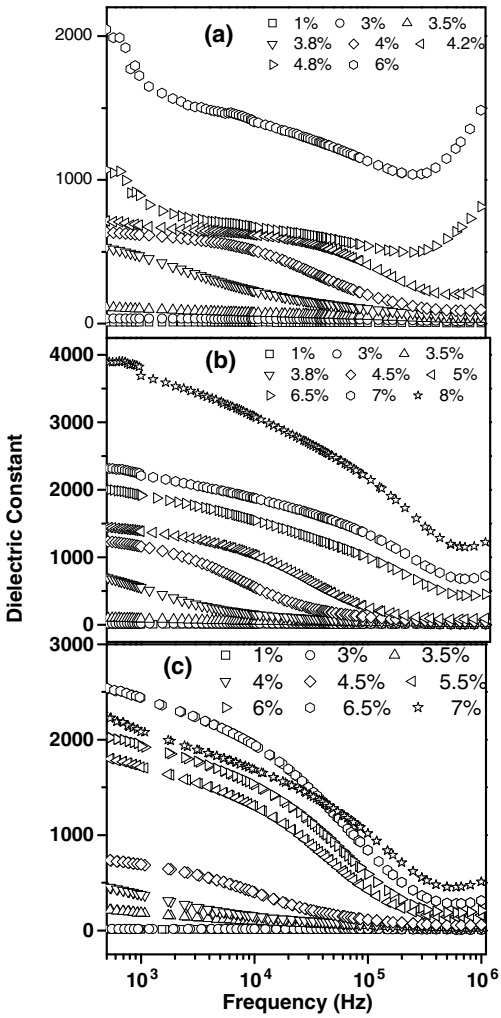


Fig. 7. Frequency dependence of the dielectric constants of pristine (a), carboxylic functionalized (b), and ester functionalized (c) MWCNT/PVDF composites with different MWCNT volume contents.

functionalizations. The experimental data is fitted to a power law as follows [4,19,20,27]:

$$\varepsilon_{\mathrm{eff}} \propto \varepsilon_{\mathrm{PVDF}}(p_c - p_{\mathrm{MWCNT}})^{-s}, \text{for } p_c > p_{\mathrm{MWCNT}} \quad (5)$$

where, $\varepsilon_{\mathrm{eff}}$ is the effective dielectric constant of the composites and s is the critical exponent. From the best fits of the law, the values s of the pristine, carboxylic and ester functionalized MWCNT/PVDF composites are, respectively, 1.13, 1.05 and 1.23 (the insets of the Fig. 8). From Eq. (1), the critical exponent values s' of these three kinds of MWCNT/PVDF composites are respectively 1.15, 1.08 and 1.18. According to the theoretical value, the values s should be in the range of 0.8–1.0, and $s' = s$. Our results are larger than the theoretical values. However, the values s' are all very close to s. Fig. 9 shows the dependence of the dielectric loss of the pristine and chemically functionalized MWCNT/PVDF composites on the MWCNT volume fraction at 1 kHz. As shown in this figure, the dielectric loss increases rapidly after 3.8 vol%, which is the same as the previous studies [4,20,27]. This phenomenon is attributed to the special structure of CNTs. The CNT materials can produce electrical current under electrical filed, which cause part of electrical energy transfer into the thermal energy. The higher the CNTs concentration is, the larger the dielectric loss is.

The large dielectric constant can be understood by a minicapacitor principle [4,20]. In the composites, the MWCNTs were distributed in the insulated matrix, which can form a lot of minicapacitors. The number of the minicapacitors increases with increasing MWCNT concentration. Compared with the pristine MWCNTs, even some carboxylic functionalized MWCNTs contact with each other, the minicapacitor may be also formed because of the carboxylic groups on the surface of MWCNTs. Due to the large MWCNT concentration and the carboxylic groups on the surface of the MWCNTs, there are more minicapacitors in the composites. And, the isolation distance between the MWCNTs decreases with increasing the MWCNT concentration so that the capacitance of the single minicapacitor increases. The carboxylic functionalized MWCNT/PVDF composites are made up of much more minicapacitors, whose capacitance is relatively large. Therefore, the different largest dielectric constants of MWCNT/PVDF composites can be attributed to the different MWCNT concentration and the different chemical functionalizations. In ester functionalized MWCNT/PVDF composites, the longer alkyl chains on the surface of MWCNTs can make the eater

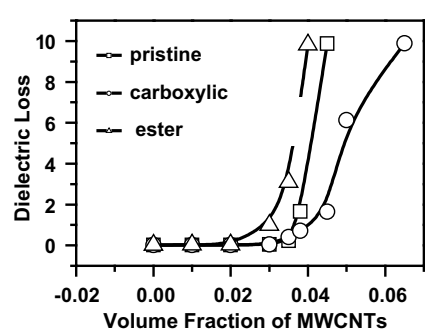


Fig. 9. Dependence of the dielectric loss of the pristine and chemically functionalized MWCNT/PVDF composites on the MWCNT volume fraction at 1 kHz.

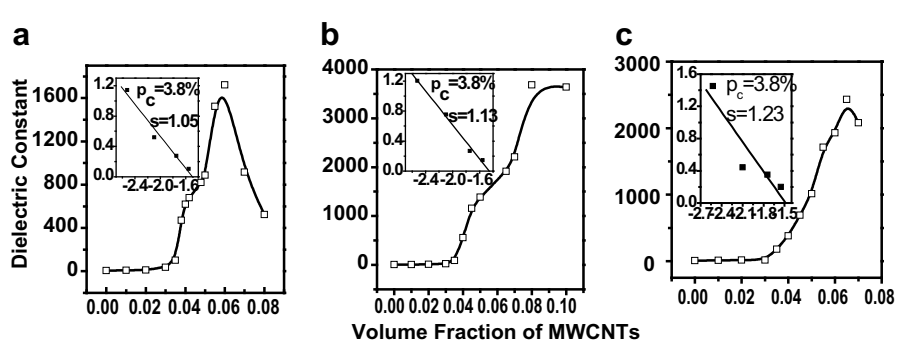


Fig. 8. Dependence of the dielectric constants of pristine (a), carboxylic functionalized (b) and ester functionalized (c) MWCNT/PVDF composites on the MWCNT volume fraction at 1 kHz; each inset shows a log–log plot of the dielectric constant as a function of $p_c - p_{\mathrm{MWCNT}}$ to Eq. (5).

functionalized MWCNT more compatible with polymer matrix [14]. Therefore, the ester functionalized MWCNT/PVDF composites can make the conductive net with smaller MWCNT concentration. The smaller dielectric constant of the ester functionalized MWCNT/PVDF composites is attributed to the smaller MWCNT concentration.

Bai et al. [24] reported the largest dielectric constant of the ceramic/PVDF composites was about 250. Wang and Dang [20] reported that the largest dielectric constant of the pristine MWCNT/PVDF was about 300 with 2 vol% MWCNT. The dielectric constant of our specimen is nearly ten times larger than that of the PVDF composites reported before. Of course, the MWCNT concentration in our composites is larger than that reported before. As discussed before, the percolation threshold is about 3.8 vol%. The different preparation procedure makes the larger MWCNT concentration in our experiment. This means that there will be a lot of minicapacitors. So the dielectric constants of the composites with more MWCNTs become larger. The performance of our composites is superior to the composites with larger concentration ceramic material. The dielectric constant of the chemically functionalized MWCNT/PVDF composites is larger than that of the pristine MWCNT/PVDF composites with the same volume fraction MWCNTs. However, the difference is not obvious. For instance, the dielectric constant of 5 vol% pristine MWCNT/PVDF composite is about 900. However, it reaches 1300 for the 5 vol% carboxylic functionalized MWCNT/PVDF composite. The length of the chemically functionalized MWCNTs will be shortened. So there will be more MWCNTs in the same volume fraction. In other words, the minicapacitor amount will increase in the chemically MWCNT/PVDF composites.

4. Conclusions

We investigated the electrical properties of the pristine and chemically functionalized MWCNT/PVDF composites. The XPS and FT-IR spectroscopy showed that carboxylic and ester groups had been introduced on the surface of the pristine MWCNTs. Raman spectroscopy and TEM micrographs indicated that the catalysts metal particles and amorphous carbon had been removed from the functionalized MWCNTs. The percolation thresholds of the composites are relatively large, about 3.8 vol%. The pristine MWCNT/PVDF composites and the chemically functionalized MWCNT/PVDF composites have different dependence of conductivity on MWCNT concentration, which can be attributed to the different chemical functionalizations. The conductivity of the pristine MWCNT/PVDF composites exhibits a typical insulator–conductor transition. However, the conductivity of the chemically functionalized MWCNT/PVDF composites increases slowly with increasing MWCNT concentration. The most important result is that the dielectric constants of the composites are enhanced significantly. The largest dielectric constant of 3600 is obtained in the carboxylic functionalized MWCNT/PVDF composite with 8 vol% MWCNT at 1 kHz. The large dielectric constant can be attributed to the preparation procedure and the interface effect between the MWCNTs and the polymer.

Acknowledgments

This work was supported by the CNPC Innovation Fund under Contract No. 06E1024 and Shandong Natural Science Foundation under Contract No.Y2005A10.

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