Positive Temperature Coefficient Properties of Multiwall Carbon Nanotubes/Poly(vinylidene fluoride) Nanocomposites

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ABSTRACT: Favorable positive temperature coefficient (PTC) properties of multiwall carbon nanotubes (MWCNT)/poly(vinylidene fluoride) (PVDF) nanocomposites were obtained. The results showed that such composites presented high PTC intensity, as well as eliminated negative temperature coefficient effect and high thermal stability, which indicated that the MWCNT/PVDF nanocomposites could overcome the main shortages of the current polymer-based PTC composites. By comparing with other contrastive nanocomposites through similar procedure, the mechanisms for the MWCNT/PVDF composite to overcome the shortages were studied and discussed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 838–842, 2010

Key words: carbon nanotubes; nanocomposites; poly(vinylidene fluoride); films; PTC

INTRODUCTION

In virtue of easy processing, low room temperature resistivity and high positive temperature coefficient (PTC) intensities, polymer-based PTC composites have been widely studied recently.[1–4] However, there still several critical shortages are needed to be overcome to achieve their full potential. Firstly, when heated to the temperature range above the melting point of polymer matrix, the NTC effects which could cause danger to the protected systems would appear[5–7]; secondly, if the polymer matrix was melted, the room temperature resistivity of the composites would be enhanced by 10^2–10^3 times, and the thermal stability would decrease.[8–10] Many researches were focused on the improvements of such shortages, but problems were not settled well and the current approaches were relatively complex.[11–13]

Nowadays, multiwall carbon nanotubes (MWCNT) have been widely utilized as nano-fillers of conductive nanocomposites due to its excellent electrical conductive properties,[14–18] whereas as conductive fillers in PTC composites, few researches were proposed.[19,20]

Recently, Poly(vinylidene fluoride) (PVDF) have been widely used as matrix of piezoelectric and pyroelectric composites. But PVDF have seldom been studied as polymer matrix in the PTC composite.[21]

In this research, MWCNT/PVDF nanocomposite was found to have the potential ability to overcome the two shortages as mentioned earlier. By studying a series of contrastive PTC composites through similar procedure, the mechanisms to overcome the shortages were brought forward and discussed.

EXPERIMENTAL PROCEDURES

Raw materials

The MWCNT used in this research had the outside-diameter of ∼ 50 nm, inside-diameter of 5–15 nm, and length of 10–20 μm. The average diameter of the nano-sized carbon black (Nano-CB) fillers was ∼ 50 nm. The TEM and SEM images of fillers were given in Figure 1.

Sample preparation

MWCNT/PVDF nanocomposites were prepared by solution casting. Different amount of PVDF powders were dissolved in organic solvent N,N- dimethylformamide (DMF). Then the MWCNTs with different masses were added into the PVDF solutions. Each
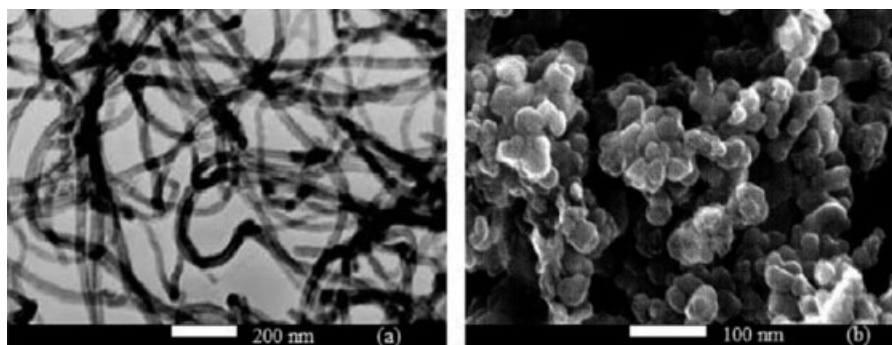
Figure 1 Carbon fillers: (a) TEM image of MWCNT, (b) SEM image of Nano-CB.

sample was acutely stirred by means of ultrasonic action for 40 min in order to drive the dispersion of MWCNT fillers. Subsequently, the samples were cast onto the glass basal plate, which was placed on a flat level made by ourselves and were heated at 90°C for 4 h to evaporate the solvent completely, and ultimately formed into films with the shape of 10 mm × 10 mm × 100 μm.

Two kinds of PTC nanocomposites were also prepared through solution casting to make contrasts. One was nano-carbon-black (Nano-CB)/PVDF nanocomposite, the other was MWCNT/low density polyethylene (LDPE) nanocomposite. The procedure to prepare the Nano-CB/PVDF nanocomposite was similar to MWCNT/PVDF nanocomposite, just replaced the MWCNT by Nano-CB. The procedure of preparing the MWCNT/LDPE nanocomposite was also similar, replaced the PVDF by LDPE and replaced the DMF solvent by *p*-xylene. The size of each sample was still 10 mm × 10 mm × 100 μm.

It was necessary to mention that, although, PVDF and LDPE powders were difficult to dissolve in organic solvents at room temperature, the ultrasonic action and the high processing temperature) (90°C) could assist the dissolving progresses.

RESULTS AND DISCUSSION

Electrical conductive percolation behaviors of MWCNT/PVDF composites

Electrical conductivities of MWCNT/PVDF composite films at room temperature as a function of MWCNT volume fractions were presented in Figure 2. The following scaling law was introduced to estimate the percolation threshold (f_c):

$$\sigma \propto \sigma_p (f - f_c)^t$$

where σ_p is the conductivity of the insulating PVDF polymer, f is the volume fraction of MWCNT fillers, and t is the critical exponent. The best fit of the conductivity data to the log–log plots of the power law was $f_c = 2.1$ and $t = 1.63$. Although the percolation threshold obtained here was in the wide range of many other studies' results,[22] it was relatively high compared with most of the previously reported results.[23–25] The pristine MWCNTs in this study were used without any special treatment was one of the reasons for the relatively high percolation threshold obtained in this study. Because this would lead to no good dispersion state of the MWCNTs in
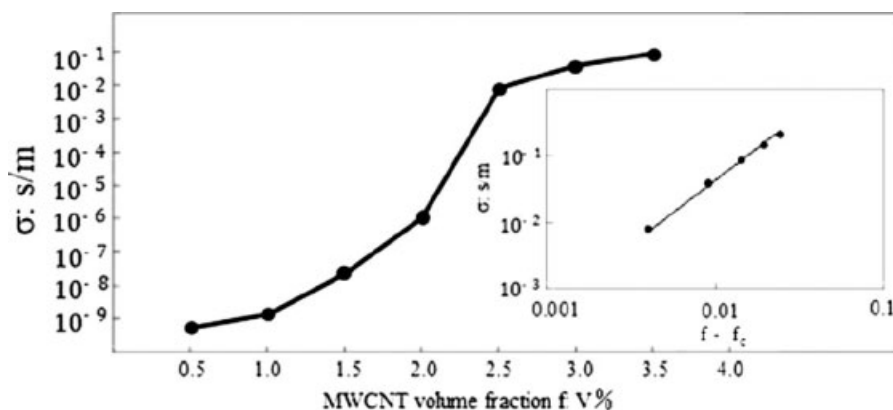

Figure 2 Dependence of electrical conductivities on the MWCNT volume fraction of MWCNT/PVDF nanocomposites and the log–log plots.
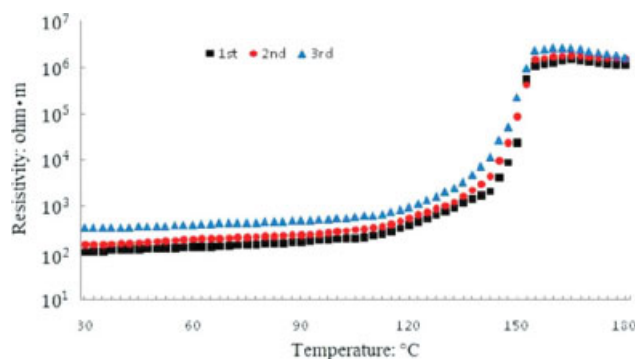
Figure 3 Temperature dependence of electrical resistivity of the MWCNT/PVDF composite film (with 2.5% MWCNT) for three heating cycles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PVDF matrix, and resulted in higher percolation threshold.[15]

PTC properties of MWCNT/PVDF composites

We further prepared samples with 2.5% MWCNT to investigate PTC properties, because for polymer based PTC composites, PTC intensity was high when the content of conductive filler was close to the percolation threshold.[26–29] The volume conductivity of the samples with 2.5% MWCNT at room temperature was 0.01 s m^{-1}.

Temperature dependence of electrical resistivity of MWCNT/PVDF composite film was shown in Figure 3. Besides significant increment of resistivity near the melting point of PVDF matrix (PTC intensity was nearly 10^{-4}), it could also be clearly seen that unlike most of the current polymer-based PTC composites, MWCNT/PVDF composite film showed eliminated NTC phenomenon after the matrix was melted (165–180°C). Moreover, the MWCNT/PVDF composite film also exhibited high thermal stability; after two heating cycles, the room temperature resistivity of the MWCNT/PVDF composite film was increased only slightly. These two important properties indicated that the MWCNT/PVDF composite film could overcome the main shortages of the current polymer-based PTC composites.

By comparing with other contrastive nanocomposites through similar procedure, the mechanisms for the MWCNT/PVDF composites to overcome the shortages were studied and discussed in Sections Role of PVDF, Role of MWCNTs, and Mechanisms of resistivity-temperature properties of MWCNT/PVDF composites.

Role of PVDF

To illustrate the contribution of PVDF, another kind of nanocomposite was prepared to make further

contrast, MWCNT/LDPE. Still, the percolation threshold of such composite was studied before PTC testing. The percolation threshold was about 1.7% (filler volume fraction) and the MWCNT/LDPE composite film containing 2.0% of MWCNT was further studied. The results in Figure 4(b) indicated that such kind of composite also had significant NTC effect and low thermal stability. This mean that PVDF played an important role for the good properties of MWCNT/PVDF nanocomposites.

For the contributions of PVDF, three main factors were proposed.

First, the PVDF molecules showed tendency to be adsorbed on the surface of carbon materials including MWCNTs (evidenced by Refs. 30 and 31). Because the MWCNT-PVDF interaction was greater than the MWCNT-LDPE interaction, it would be more difficult to redistributing MWCNTs in melted PVDF.

Second, the density of PVDF which was closer to the MWCNT than LDPE could play a role. The density of LDPE (0.91–0.94 g/cm^3) was significantly lower than MWCNT (1.5–2.1 g/cm^3), and the gravity would lead to severe redistribution of MWCNTs in the melted LDPE. On the other side, the density of PVDF (1.7–1.8 g/cm^3) was much closer to that of MWCNT. Consequently, gravity would result in much more gentle redistribution of MWCNTs in the
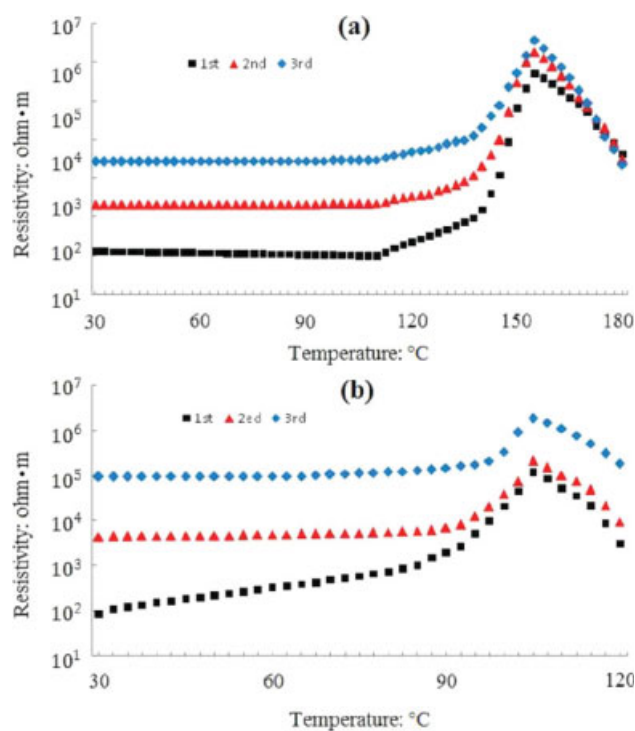

Figure 4 Temperature dependence of electrical resistivity of the contrast composite films for three heating cycles: (a) Nano-CB/PVDF composite films, (b) MWCNT/LDPE composite films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Young's Modulus of (a) Melted MWCNT/PVDF Composites and (b) MWCNT/LDPE Composites

(a) MWCNT/PVD			
Temperature	155°C	160°C	165°C
Young's modulus	184 MPa	79.3 MPa	42.7 MPa
(b) MWCNT/LDP			
Temperature	105°C	110°C	115°C
Young's modulus	30.1 MPa	13.6 MPa	8.57 MPa

melted PVDF. Thus, the distribution of MWCNTs in PVDF after melted would be maintained better than that in LDPE.

Third, the modulus of melted PVDF was much higher than that of melted LDPE (shown in Table I). In this study, Young's modulus characterized the rigidities of melted PVDF and melted LDPE. Obviously, higher rigidity of melted PVDF mean that the deformation state of melted PVDF was much lower than melted LDPE. This could be an important reason for the higher restriction state of redistribution of MWCNTs in melted PVDF matrix.

Role of MWCNTs

The special properties of MWCNT were considered to be another factor contributed to the above phenomenon. For the purpose of identifying this, the Nano-CB/PVDF composite films were prepared to make contrast. After a series of experiments, the percolation threshold of Nano-CB/PVDF nanocomposite was found to be about 2.5% (filler volume fraction), thus the Nano-CB/PVDF composite with 3.0% fillers was chosen as the contrastive materials. The results in Figure 4(a) demonstrated that the Nano-CB/PVDF nanocomposites had significant NTC effect and low thermal stability. Such results mean that the special properties of MWCNT were one of the reasons for the good properties of MWCNT/PVDF nanocomposites.

For the contributions of MWCNTs, three main factors were proposed.

The MWCNT-PVDF interaction mentioned in Section Role of MWCNTs was the first factor.

Second, in the polymer PTC composites, the redistribution of conductive particles would require polymer segments adjacent to them to move correspondingly. Because of its high aspect-ratio, the geometric size of MWCNTs is much larger than that of Nano-CB particles, so more energy is needed for their redistribution.[19] Thus, the redistribution of MWCNTs is more difficult.

Third, the high aspect-ratio and twists of MWCNTs might form strong skeletons in polymer

matrix (Fig. 5). This would also restrict the redistribution of MWCNT fillers during melting.

Mechanisms of resistivity-temperature properties of MWCNT/PVDF composites

The mechanism of this PTC effect in MWNT/PVDF composites could be attributed to the thermal expansion of the crystalline PVDF during heating, which results in the breakdown of MWCNT conductive network.[32,33] When the temperature was below 140°C, the PTC intensity was relatively low because of the low thermal expansion rate at low temperature. The sharp increase in resistivity for all materials was observed between 140°C and 155°C, which was near the melting temperature of the PVDF used here. In semicrystalline polymers, such as, polyethylene, it is well-known that the transformation of the crystalline phase to the amorphous phase causes a significant volume expansion, resulting in a sudden increase of the resistivity due to the disconnection of the conductive paths.

In the temperature range of higher than 155°C, the mechanisms of the eliminated NTC effect of MWCNT/PVDF nanocomposites could be described as follows. It is generally accepted that NTC effect is caused by the redistribution, especially agglomeration, of conductive particles. Considering the factors mentioned in Sections Role of MWCNTs and Mechanisms of resistivity-temperature properties of MWCNT/PVDF composites, it could be drawn that the redistribution of MWCNTs in PVDF matrix was restricted at a low status. Thus, the NTC effect was eliminated.

Moreover, it needed to mention that the good thermal stability after some heating cycles beyond
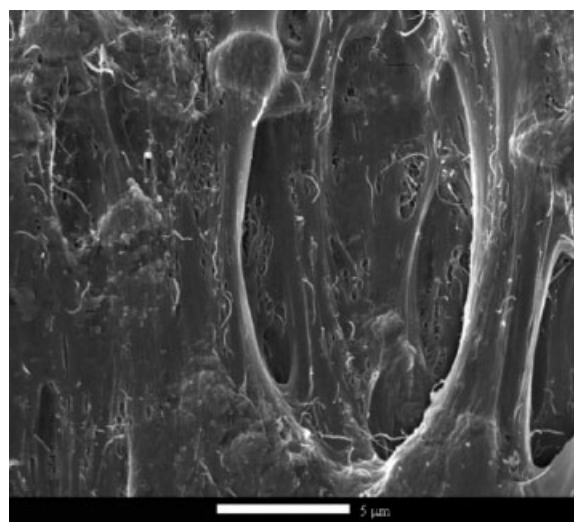

Figure 5 SEM images of MWCNT/PVDF nanocomposites.

the PVDF melting could also be attributed to the factors discussed in Sections Role of MWCNTs and Mechanisms of resistivity-temperature properties of MWCNT/PVDF composites. Because the redistribution status of MWCNTs in PVDF matrix was low after melted, the room temperature resistivity of the nanocomposites should be maintained as fine as possible.

CONCLUSIONS

In conclusion, MWCNT/PVDF nanocomposites exhibited high PTC intensity of nearly 10^{-4}, along with eliminated NTC effect and high thermal stability during several heating cycles. The results indicated that MWCNT/PVDF nanocomposites could overcome the main shortages of the current polymer-based PTC composites. The mechanisms to overcome the shortages were investigated and the results showed that both PVDF and MWCNT played important roles for the properties.

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