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Effect of carbon nanotubes shape on the properties of multiwall carbon nanotubes/polyethylene flexible transparent conductive films

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Abstract Transparent conductive material is used in a wide range of applications and is particularly interesting. In the present work, a series of multiwall carbon nanotubes/low density polyethylene nanocomposites with different carbon nanotubes were prepared via solution casting method. The optical transparency, morphology, and resistivity of transparent conductive films have been characterized by using UV–Vis Spectrophotometer, Field emission scanning electron microscope and Multimeter, respectively. Their electrically conductive and optically transparent properties were studied and compared. The result showed that thinner and longer multiwall carbon nanotubes were more suitable for the fabrication of flexible transparent conductive nanocomposites. The sample filled with 1 wt% of T.1 (outside diameter <8 nm, length 10–30 μm) had good transparent conductive properties (volume conductivity of 3.12×10^{-3} S m^{-1} and optical transmittance of 62.8 % at the light wavelength of 600 nm). The high volume conductivity and optical transparency demonstrated that such kind of nanocomposite films had favorable potential in the applications from electromagnetic interference shielding to transparent electrodes.

1 Introduction

Optically transparent and electrically conductive materials are required for a wide range of applications: electrostatic charge mitigation, electromagnetic interference shielding, transparent electrodes, large area displays and so on. The most commonly transparent conductive material was indium tin oxide (ITO). However, there are still several disadvantages of ITO, such as relatively high processing temperature, high fabrication costs, and its intrinsic brittleness [1, 2]. Other kinds of transparent conductive materials such as films made of carbon nanotube or conductive polymers were also suffered from high cost and complex processing [3, 4].

Carbon nanotubes (CNTs)/polymer nanocomposites have become a focal point of nanocomposites research since the discovery of CNTs [5–7]. Because of CNTs' high electrical conductivity and high aspect-ratio, the electrical conductivities of CNTs/polymer nanocomposites could be increased much even with only a small amount of CNTs fillers [8–10]. This advantage has the potential to enhance the optical transparency of such nanocomposites [11–13]. Therefore, CNTs/polymer nanocomposites offer a conceivable class of transparent conductive films which could have another important virtue-flexible. Indeed, in recent years, some studies on this issue have been carried out [14–18]. Most of them have chosen single-walled carbon nanotubes (SWCNTs) which are very expensive. From the point of industry view, multiwall carbon nanotubes (MWCNTs) which cost much less also have the potential to become the suitable fillers [19–21]. However, how will the

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shape of MWCNTs affect the properties of such nanocomposites and what is the suitable shape of MWCNTs for such nanocomposites are still unclear.

In this study, a series of MWCNTs with different diameters and lengths have been used as fillers to investigate this question. In order to find out the influence of MWCNTs' diameters on the properties of transparent conductive films, nanocomposites filled with MWCNTs of similar lengths but different diameters were studied and compared.

2 Experiment

Four kinds of MWCNTs were used in this study (marked as T.1–T.4), and their shapes were as follows: T.1 outside diameter <8 nm, length 10–30 μm; T.2 outside diameter 20–30 nm, length 10–30 μm; T.3 outside diameter >50 nm, length 10–20 μm; T.4 outside diameter <8 nm, length 0.5–2 μm. Low density polyethylene has been chosen as polymer matrix for its high optical transparency, good flexibility and easy processing.

All of the nanocomposite films with the thicknesses of ~30 μm were prepared as follows. (1) LDPE powders were dissolved in the organic solvent: *p*-xylene. (2) Sodium dodecyl benzenesulfonate (SDBS) was dissolved in the above solutions (SDBS was a very efficient surfactant to disperse CNTs in organic solvents [22, 23]). (3) MWCNTs with different mass were added into the LDPE solutions and stirred. (4) All the samples were ultrasonic cleansed for 2 h to drive the dispersion of MWCNTs. (5) The samples were cast onto the glass basal plate which was placed on a level flat made by ourselves and were heated at 90 °C for 1 h to evaporate the solvent completely. (6) After the samples formed into films, they were all cut into two pieces, one was pasted by silver slurry electrode (10–10 mm squares) for the tests of electrical conductive properties, another one without electrode was for the tests of optical transparent properties.

Optical transparency of transparent conductive films was measured by UV–Vis Spectrophotometer (Lambda 35). Morphology of samples was characterized by field emission scanning electron microscope (Sirion 200). The resistivity of samples was tested by Multimeter (UT51).

3 Results and discussion

For each kind of nanocomposites, a series of films with varying volume fractions of MWCNTs were prepared and the volume conductivities were tested. The percolation thresholds were estimated by the scaling relation:

$$\sigma \propto \sigma_p (f - f_c)^t \tag{1}$$

where σ_p is the conductivity of the insulating LDPE polymer, f is the volume fraction of MWCNT fillers, f_c is the percolation threshold, and t is the critical exponent. The best fits of the conductivity data to the log–log plots of the power laws give the results as Fig. 1 and Table 1. It could be seen that nanocomposites filled with T.1 showed the highest percolation threshold while nanocomposites filled with T.3 showed the lowest percolation threshold. Such result was in contrary to some reported works: thinner CNTs or higher aspect-ratio CNTs would lead to lower

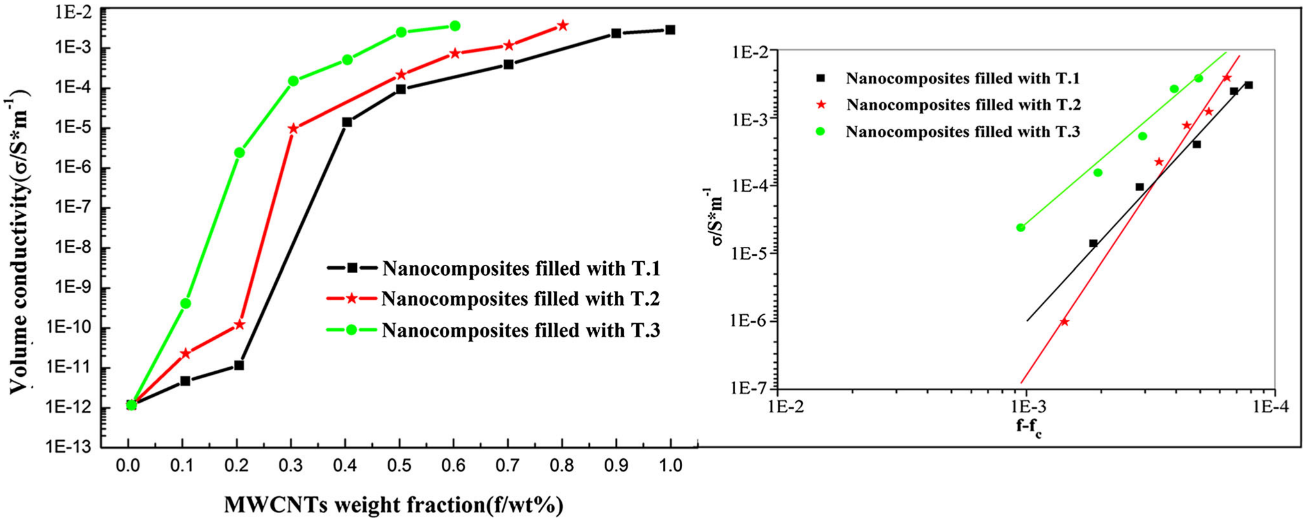

Fig. 1 Dependence of volume conductivities on the MWCNTs weight fraction of nanocomposites filled with T.1–T.3 respectively and the log–log plots

Table 1 Percolation threshold of nanocomposites filled with T.1–T.3 respectively

Sample	Filled with T.1	Filled with T.2	Filled with T.3
Percolation threshold (wt%)	0.212	0.156	0.104

Table 2 Volume conductivities of nanocomposites filled with 1 wt% of T.1, 0.8 wt% of T.2, and 0.6 wt% of T.3 respectively

Sample	With 1 wt% T.1	With 0.8 wt% T.2	With 0.6 wt% T.3
Volume conductivity (S m^{-1})	3.12×10^{-3}	4.03×10^{-3}	4.92×10^{-3}

percolation threshold [24, 25]. This might be contributed by the following reason: during the same preparation procedures, the thinner MWCNTs were more easily to be cut or broken, and the shortened MWCNTs were more difficult to form conductive passes in the matrix [26].

From Fig. 2, it could be clearly seen that with the similar electrical conductivities, nanocomposite film filled with T.1 showed the best transparency while the film filled with T.3 showed the worst. Due to the size effect [27], thinner MWCNTs network in the matrix could lead to a lower rate of light scattering, thus even the amount of T.1 was higher than that of T.3, and the loss of transparency was still lower.

Thereby, take the results of Fig. 2 and Table 2 into consideration, it could be drawn that MWCNTs with thinner diameters were more suitable for transparent conductive nanocomposites.

For the purpose of understanding the relationships between MWCNTs' lengths and the properties of films, nanocomposites filled with MWCNTs of similar diameters but different lengths (T.1 and T.4) were studied and compared.

Still, a series of films with varying volume fractions of MWCNTs were prepared and the volume conductivities were tested. The percolation thresholds were also estimated by the scaling relation and the best fits of the conductivity data to the log–log plots of the power laws give the results as Fig. 3 and Table 3. It could be seen that nanocomposites filled with T.1 showed much lower percolation threshold. Such result was in accord with our previous work [28]: if the thicknesses (d) of nanocomposites films were comparable to the lengths (l) of MWCNTs, higher value of d/l would result in higher percolation threshold. And it was also in accord with some reported works: higher aspect-ratio CNTs would lead to lower percolation threshold [24, 25].

As shown by Fig. 4 and Table 4, the nanocomposite films filled with the same amount of T.1 or T.4 had similar transparency. But the nanocomposite film filled with 1 wt% of T.1 had a much higher electrical conductivity than that of nanocomposite film filled with 1 wt% of T.4.

Consequently, taking all of the results presented above together, it could be concluded that MWCNTs with longer lengths and thinner diameters were more suitable for transparent conductive nanocomposites. And in this study, the nanocomposites filled with T.1 showed the best properties.

Finally, we further investigate the morphology and optical transmittance of nanocomposites filled with 1 wt% of T.1. Figure 5 was the Field Emission Scanning Electronics Microscope image of the cross section of the sample and Fig. 6 showed that the sample had an optical transmittance of 62.8 % at the light wavelength of 600 nm (Average wavelength of visible light from ~400 to ~800 nm). Thus, considering the high electrical conductivity and intrinsic flexibility of such nanocomposites, it could be used in a wide range of applications mentioned in the "Introduction".

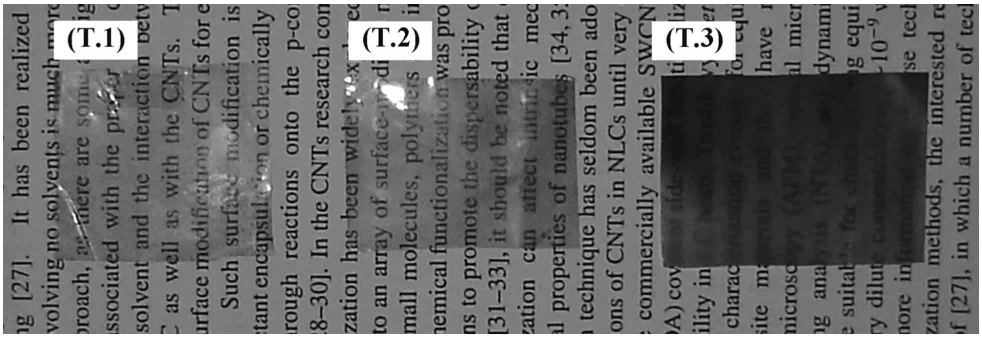

Fig. 2 Comparison of the transparency of nanocomposites filled with 1 wt% of T.1 (*left*), 0.8 wt% of T.2 (*middle*), and 0.6 wt% of T.3 (*right*)

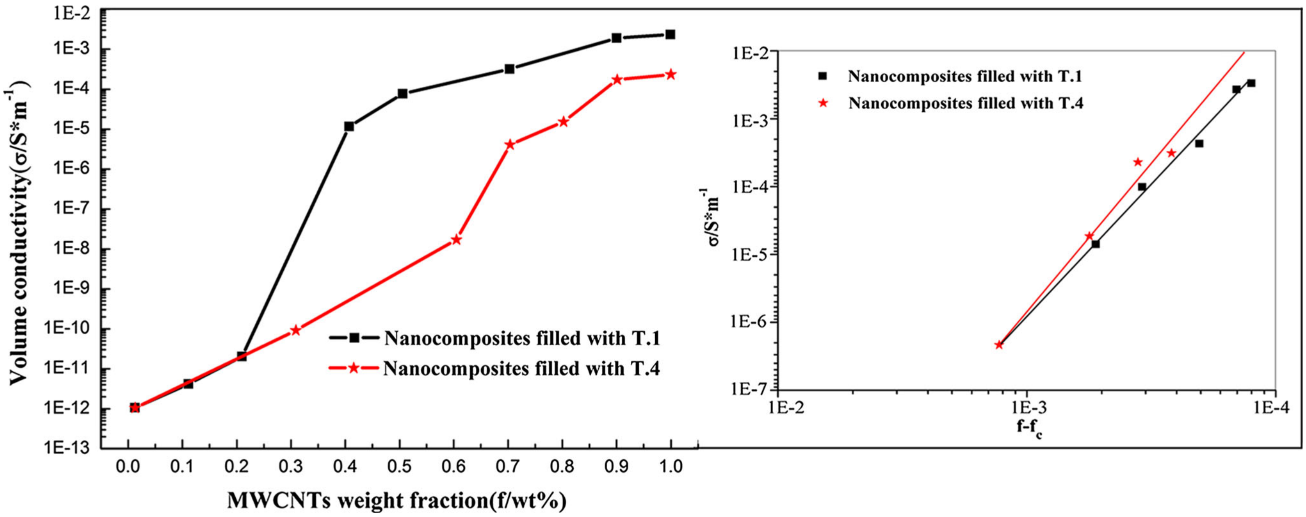

Fig. 3 Dependence of volume conductivities on the MWCNTs weight fraction of nanocomposites filled with T.1, T.4 respectively and the log–log plots

Table 3 Percolation threshold of nanocomposites filled with T.1, T.4 respectively

Sample	Filled with T.1	Filled with T.4
Percolation threshold (wt%)	0.212	0.623

Table 4 Volume conductivities of nanocomposites filled with T.1, T.4 respectively

Sample	With 1 wt% T.1	With 1 wt% T.4
Volume conductivity (S m^{-1})	3.12×10^{-3}	3.01×10^{-4}

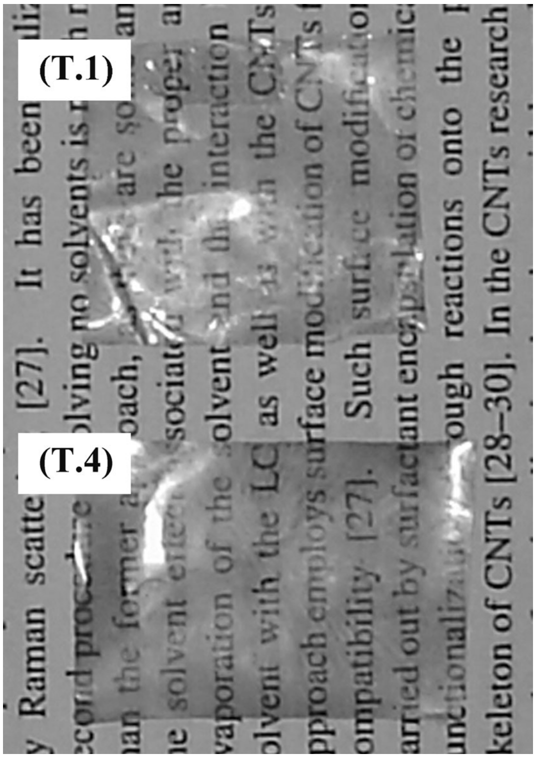

Fig. 4 Comparison of the transparency of nanocomposites filled with 1 wt% of T.1 (*above*), and 1 wt% of T.4 (*below*)

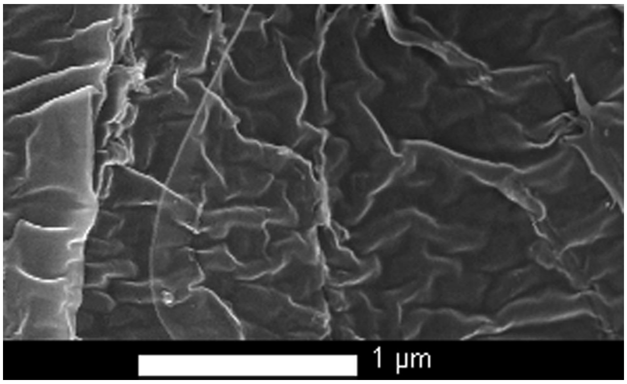

Fig. 5 FESEM image of nanocomposites filled with T.1 (1 wt%)

4 Conclusion

In conclusion, by comparison of a series of MWCNTs/LDPE nanocomposites with different MWCNTs, it could be concluded that MWCNTs with thinner diameter and longer length were more suitable for the fabrication of flexible transparent conductive nanocomposites. Thinner MWCNTs lead to higher transparency due to the size effect and longer MWCNTs resulted in higher conductivity for

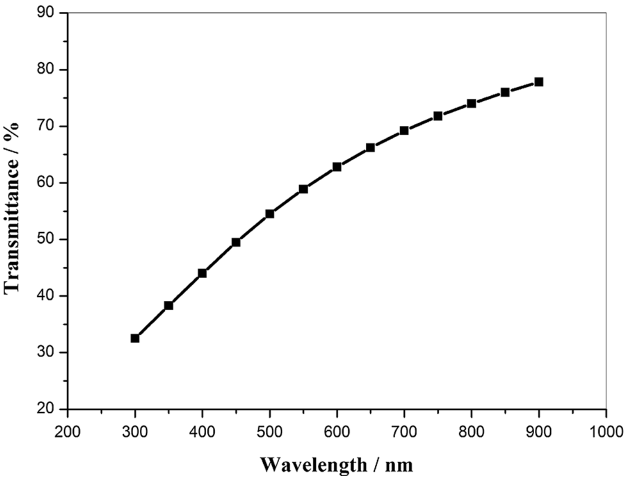

Fig. 6 Optic transmittance of nanocomposites filled with T.1 (1 wt%)

their favorable tendency to form conductive passes in the matrix. Eventually, the good transparent conductive properties (volume conductivity of 3.12×10^{-3} S m^{-1} and optical transmittance of 62.8 % at the light wavelength of 600 nm) of such nanocomposites could be a good candidate for the current transparent conductive materials.

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