ELECTRICAL PROPERTIES OF MULTI-WALLED CARBON NANOTUBE/HIGH-DENSITY POLYETHYLENE COMPOSITES

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Introduction

In recent years, the electrical conductive properties of carbon nanotubes (CNTs) filled polymer composites have attracted great attention. Due to their good electrical conductivity and high aspect ratios, CNTs could dramatically improve the electrical conductivity of polymers with a relatively low CNT loading. The electrical properties of CNTs filled various polymer matrix composites, such as polystyrene [1], epoxy [2], poly(vinyl alcohol) [3] and polycarbonate [4], were reported. However, the temperature dependence of electrical resistivity for CNT/ polymer composites is rarely studied.

The temperature-resistivity characteristics of carbon black (CB) [5-7] or other conductive particles [8] filled polymer composites were widely investigated. It was found that in the vicinity of melting point or glass transition temperature of the polymer, some conductive particles filled polymer composites could exhibit a positive temperature coefficient (PTC) effect, i.e., their resistivity increased sharply with increasing temperature. The CB filled polymer PTC composites have found important applications in self-controlled heaters, over-current protectors, sensors, etc. However, to reach the percolation concentration (the filler concentration at which a pathway of the conductive filler is formed through the matrix), PTC composites have to have high loading ratio of CB, which usually results in degradation of mechanical and processing properties of the polymer matrix. When temperature is above the melting temperature of the polymer matrix, the resistivity of the composite decreases rapidly with increasing temperature, a phenomenon known as negative temperature coefficient (NTC) effect, which has to be overcome for application as PTC electrical devices [9].

In this presentation, multi-walled carbon nanotubes (MWNTs) filled high-density polyethylene (HDPE) composites were prepared and electrical properties of the composites were studied. An obvious PTC effect was observed in MWNT/HDPE composites with relatively low MWNT concentration and the mechanism of PTC and NTC effects was discussed.

Experimental

The MWNTs produced by a CVD method [10] were used without further purification. The SEM image of the MWNTs is shown in Figure 1. The average diameter and length of the MWNTs are approximately 50 nm and 5~50 μm, respectively, and impurity of metal catalyst is less than 9 wt%. HDPE with a melt index of 0.3 g/10min was used as polymer matrix. MWNT/HDPE composites were prepared by the following method. The MWNTs were sonicated in alcohol for 30min. Then xylene solution of HDPE was added to MWNT dispersion under both sonication and agitation. The mixture was agitated for 24 hrs. After filtration, the composite was dried in a vacuum oven and molded to sample sheets of 0.2 mm in thickness.

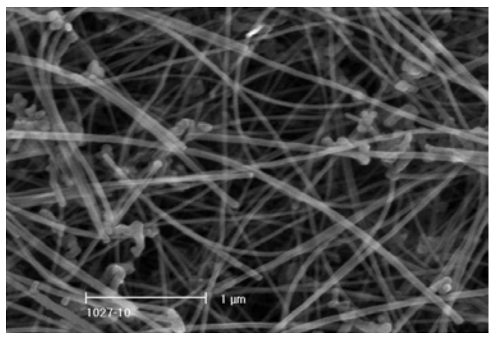

Figure 1 SEM image of the as-produced MWNTs.

The volume resistivities of the samples were measured using a digital multimeter for low resistance (<10MΩ) and an insulating resistance tester for high resistance (≥10MΩ). The resistivity-temperature characteristic of the composites was measured at consecutively elevated temperature with a heating rate of 5°C/min.

Results and Discussion

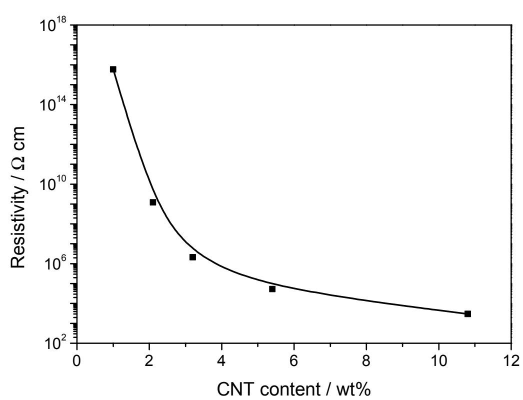

Figure 2 Electrical resistivity versus MWNT content curve for the MWNT/HDPE composites.

The volume electrical resistivity versus MWNT content curve for the MWNT/HDPE composites is shown in Figure 2. It can be seen that the resistivity change with MWNT content exhibits a percolation behavior. The percolation threshold lies in about 2 wt%, which is much lower than that for MWNT/HDPE composites fabricated by melt-mixing [11]. This may be attributed to the effect of sonication on the dispersion of CNTs. It is well known that the as-produced MWNTs exist in an entanglement state. When dry powder of MWNTs was directly mixed with molten HDPE, aggregates of MWNTs could not be well disentangled because the interaction between HDPE molecule chains and MWNTs was weaker than that between MWNTs [12]. When MWNTs were sonicated in alcohol, the MWNT entanglements turned loose or even disentangled because of the penetration of alcohol molecules. To blend HDPE with MWNTs in such a state, the dispersion of MWNTs could be better, thus the pathway of conductive filler was easy to form and the percolation threshold of the composite was lower.

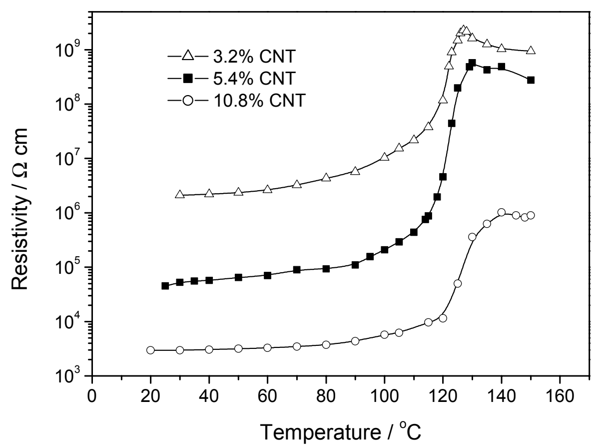

Figure 3 Resistivity-temperature curves of the MWNT/HDPE composites.

The temperature dependence of resistivity characteristic of MWNT/HDPE composites was examined. Figure 3 shows the resistivity-temperature curves for various MWNT content. It can be seen that in the vicinity of the melting temperature (T_m) of HDPE, resistivity of the composite increased sharply with increasing temperature. The PTC intensity (the ratio of peak resistivity to room temperature resistivity) for the MWNT/HDPE composite containing 5.4 wt% MWNT reached 1.1×10^4. The PTC mechanism of MWNT/HDPE composites, we suppose, is similar to that of CB composites, resulting from the breakdown of conductive network principally caused by the thermal expansion of matrix. From Figure 3 it can be seen that the NTC effect of MWNT/HDPE composites at temperature above T_m of HDPE is small. It is generally accepted that NTC effect is caused by the agglomeration of conductive particles. As can be imagined, in the PTC composites each conductive particle is surrounded by many polymer chains. The agglomeration of conductive particles would require polymer segments adjacent to them to move correspondingly. The larger the size of conductive particles, the more energy needed for agglomeration. The geometric size of CNTs is much larger than that of CB particles, so the agglomeration of CNTs is more difficult and thus only weak NTC effect is manifested. Agglomeration of fillers is the main cause of the instability of polymer PTC devices. Thus it can be expected that more stable polymer PTC devices may be fabricated from CNT/polymer composites.

Conclusions

MWNTs filled HDPE composites were prepared and electrical properties of the composites were studied. The MWNT/HDPE composites exhibit obvious PTC effect in the vicinity of T_m of HDPE and the NTC effect at temperature above T_m of HDPE is relatively small. The composites are promising for using as high performance polymer PTC materials with good processing properties.

Acknowledgements

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