



Selective location and conductive network formation of multiwalled carbon nanotubes in polycarbonate/poly(vinylidene fluoride) blends

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ABSTRACT

Multiwalled carbon nanotubes (MWCNTs)-filled polycarbonate (PC), poly(vinylidene fluoride) (PVDF) and PC/PVDF conductive composites were fabricated using melt mixing, respectively. The dynamic process of MWCNTs conductive network formation in the composites was *in situ* traced by recording the variation of electrical resistivity with time during annealing treatments. As a result, the percolation threshold for the MWCNTs-filled PC/PVDF system was much lower than those of MWCNTs-filled individual polymers and the MWCNTs were selectively located in the PC phase of PC/PVDF composite, which had been verified by scanning electron microscopy measurements. The activation energy of conductive network formation for PC/PVDF/MWCNTs composite was close to that of the PC/MWCNTs system, which further confirmed that MWCNTs were dispersed mainly in the PC phase. Furthermore, the assembly velocity of MWCNTs in the polymer melt increased with annealing temperature.

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1. Introduction

Plastics are usually considered as insulating materials. However, extensive studies have been carried out to fabricate conductive composites by incorporating conductive fillers such as carbon black (CB), vapor grown carbon fibers (VGCFs) or carbon nanotubes (CNTs), into insulating polymers. The improved electrical and mechanical properties of these conductive composites make them competitive candidates for many electronics applications, such as electro magnetic interference (EMI) shielding, electrostatic charge dissipation and antistatic charge dissipation applications [1]. To understand the conductive network formation in composites, the concept of “percolation” has been used to describe the critical point for a starting decrease of electrical resistivity with the increase of fillers content and the critical fillers content is named the percolation threshold, which depends on not only the loading amount of the fillers, but also on the dispersion state of fillers in the matrix and the preparation conditions such as the molding temperature and time [2–10].

Recently, much attention has been paid to the double percolation concept, in which an electrically conductive material with very low fillers content is achieved by creating a co-continuous structure in the blend [11–14]. The reduction of percolation threshold in the double percolation system could be explained by the difference in the affinity of fillers to the polymer components,

which results in the fillers selectively located in one of the two polymer phases or at their interface [15,16]. The electrical properties of the conductive composites strongly depend on double percolation, i.e., the percolation of fillers in the fillers-rich phase, and this phase changes from discrete domains into a continuous structure in the blends [3,15], which are defined as the first percolation and the second percolation, respectively. However, there have been few reports dealing with the selective location and double percolation for CNT-filled polymer systems.

In our previous work [17], an *in situ* method has been developed to investigate the dynamic process of conductive network formation by recording the variation of electrical resistivity with time when the high-density polyethylene (HDPE)/isotactic polypropylene (iPP)/VGCF composite was annealed isothermally in the molten state. Therein, the percolation time (t_p) is characterized as a certain annealing time, in which the electrical resistivity starts to decrease drastically, and we refer this process as dynamic percolation, and the dynamic process of conductive network formation can be traced by dynamic percolation curves. Recently, we used the above *in situ* method to trace the self-assembly process of VGCFs in the poly(vinylidene fluoride) (PVDF) melt. It was found that the conductive network formation of the composites was related to the interaction between PVDF molecules and VGCFs [18]. Also, Wu et al. [19–21] used CB as a self-diagnostic probe to trace polymer dynamics in CB-filled polymer composites by dynamic percolation measurements, in which a dynamic percolation measurement was provided to achieve not only the real-time tracing of the dynamic process of conductive network formation but also

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the *in situ* detecting of the dispersion state of conductive fillers in polymer blends.

Multiwalled carbon nanotubes (MWCNTs) have been extensively used as fillers in various application fields because of their extremely high aspect ratio, high electrical and thermal conductivity, and excellent mechanical properties. Many efforts have been made to introduce MWCNTs into a polymer matrix to obtain a high performance conductive composite. Polycarbonate (PC)/PVDF is well known as an immiscible blend [22,23], and the heterogeneous distribution of MWCNTs is expected to occur in such a two-phase blend system. In this paper, MWCNTs-filled PC, PVDF and PC/PVDF composites were fabricated using melt mixing. The heterogeneous distribution of MWCNTs in PC/PVDF blends was observed, and the dynamic process of conductive network formation in the composites was investigated systematically.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF) (FR901, from 3F Co. China), and polycarbonate (PC) (IR2200, from Idemitsu Kosan Co. Ltd. Japan) were used as matrices. Multiwalled carbon nanotubes (MWCNTs) were supplied by the Chengdu Institute of Organic Chemistry, and synthesized from natural gas via catalytic chemical vapor deposition, with diameters of 20–30 nm and length of 10–30 μm .

2.2. Sample preparation

Polymers and MWCNTs were dried at 80 °C for 24 h under vacuum before use. The mixing of PVDF/MWCNTs and PC/MWCNTs was carried out using a Haake Rheomix R600 for 15 min at 190 °C and 250 °C, respectively. The preparation of PC/PVDF/MWCNTs composites was carried out by the following two methods: one-step method: PVDF was first mixed with PC at 250 °C for 5 min, and then MWCNTs were added to mix for the additional 15 min; two-step method: MWCNTs were first mixed with melted PVDF at 250 °C for 5 min, followed by adding PC into the PVDF/MWCNTs mixture. One-step method of the preparation of PC/PVDF/MWCNTs composites was adopted throughout this paper, except for special statement. The resulting PVDF/MWCNTs samples were melted at 190 °C for 2 min, and compressed under a pressure of 15 MPa for 3 min to obtain the sheets with a thickness of 1.5 mm with a cooling rate of 50 °C/min. The PC/MWCNTs and PC/PVDF/MWCNTs sheets were prepared at 250 °C in the same way. And the corresponding composites were listed in Table 1.

2.3. Characterization

The electrical resistivity at room temperature was measured in the thickness direction of the composite films using a Keithley 6517 picoammeter Voltage Source. One data point was the average value of eight experimental points. To trace the conductive net-

Table 1
Specimens prepared under the different processing conditions.

Numbers	Sample 1	Sample 2	Sample 3	Sample 4
Composites	PC/ MWCNTs	PVDF/ MWCNTs	PC/PVDF/ MWCNTs ^a	PC/PVDF/ MWCNTs ^b

^a Obtained by first mixing PC and PVDF at 250 °C for 5 min, and then MWCNTs were added to mix for the additional 15 min.

^b Obtained by first mixing PVDF and MWCNTs at 250 °C for 5 min, followed by adding PC into the PVDF/MWCNTs mixture.

work formation in the polymer melt, the variation of electrical resistivity with time was measured with a GZ-1 picoammeter equipped with a direct current voltage source when the composite sheets were annealed in the molten state. Specimens with a diameter of 30 mm were cut from the center area of the molded sheet and were fixed between two parallel copper electrodes. Nitrogen gas was introduced during measurement to prevent oxidation of the samples. The applied voltage for the measurement was 1 V. The variation of the electrical resistivity over time was recorded using a computer with a time interval of 5 s.

Scanning electron microscopy (SEM) observation was performed using a Hitachi S-4700 scanning electron microscope. The as-prepared specimens were fractured in liquid nitrogen and coated with platinum (Pt) before observation.

3. Results and discussion

3.1. Percolation and selective location

Fig. 1 shows the dependence of volume resistivity on fillers volume fraction for MWCNTs-filled PVDF, PC and PC/PVDF blends. The percolation threshold is 1.6 vol% for the PC/MWCNTs and 1.4 vol% for the PVDF/MWCNTs. However, it is interesting to find that the percolation thresholds of MWCNTs-filled PC/PVDF blends are about 0.95 vol% for PC/PVDF (50/50) composites and about 0.80 vol% for PC/PVDF (30/70) composites, which are obviously lower than those of MWCNTs-filled individual polymers. The reduction in percolation threshold is explained by the double percolation theory, in which MWCNTs selectively locate in the PC phase (proved by SEM, Fig. 2) to form the continuous conductive network and the MWCNTs-filled PC phase also connects to form conductive phase in the MWCNTs-filled PC/PVDF blends.

Fig. 2 shows SEM micrographs of PC/PVDF (50/50) blends filled with 1.34 vol% MWCNTs, which were prepared by the one-step method. It can be seen that MWCNTs are preferentially located in the PC phase (Fig. 2c), rather than in the PVDF phase (Fig. 2b). The preferential accumulation increases the relative MWCNTs concentration in the PC phase, resulting in the formation of a conductive network at a low total MWCNTs content. This heterogeneous distribution of fillers in the two phases is because of the difference in the affinity of the fillers to each component of the polymer blends. In fact, many studies have also shown that carbon fibers (for example, CB and VGCF) are prone to heterogeneously distribute in immiscible polymer blends, which results in a reduction in percolation threshold [11,14,24–27].

In order to further explore the different affinity between MWCNTs/PC and MWCNTs/PVDF, the two-step method was

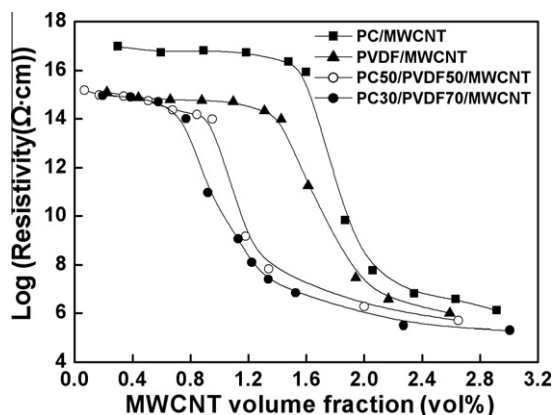


Fig. 1. Dependence of volume resistivity on fillers volume fraction for MWCNTs-filled PC, PVDF, PC/PVDF (50/50) and PC/PVDF (30/70) composites.

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