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Two-step PTC effect in immiscible polymer blends filled with carbon black

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Recently conductive polymer composite materials (CPCMs) have been extensively studied based on the heterogeneous distribution of carbon black (CB) in multiphase polymeric blends. The selective dispersion of CB in one phase or at the interface of two polymers causes a decrease of the percolation threshold to a very low level, which contributes to being processed with ease, preserving the mechanical properties of the polymer and reducing as much as possible the cost of the final composite. Sumita *et al.* [1] proposed that the heterogeneous distribution of CB in immiscible polymer blends is mainly due to the difference in affinity of CB particles to each component of polymer blends, i.e., the difference in the interfacial free energy of the polymer/filler. Zhang *et al.* [2] reported the two-step percolation in the LDPE/EVA composite filled with CB. They thought that CB particles were predominately dispersed in LDPE first due to lower interfacial free energy and then began to be localized at the LDPE/EVA interface when the CB content in LDPE had approached a saturation limit. Accordingly the two-step percolation referred to the first corresponding to the percolation in LDPE and the second at the LDPE/EVA interface.

Among the conductive polymer composite materials, there is a kind of positive temperature coefficient (PTC) material [3], which is characterized by an increase in the resistivity with increasing temperature, especially at the melting point of the polymer. A sharp increase occurs due to an increase in average inter-particle distance of CB as a result of the large thermal expansion arising from the melting of the polymer crystallites.

In this paper, we have found the two-step PTC effect in filled immiscible semicrystalline polymer blends, to which we have given a reasonable explanation based on the conclusions made by the references [1, 2] mentioned above and in other papers [4–6].

High density polyethylene (HDPE) and polypropylene (PP) were used as the polymer matrix, and their melting temperatures (T_m) were 133 and 170 °C, respectively. The CB-filled and a mixture of CB and carbon fiber (CF) filled HDPE/PP composites were prepared by melt-mixing the materials in a Brabender mixer at 180 °C and 30 rpm for 10 min. The compound obtained was further compressed into 1.5 mm sheet in a vulcanizing press at 180 °C.

Fig. 1 shows the dependence of the log resistivity on HDPE content in the HDPE/PP blends. The resistivity at a given CB content changes with the composition in rather a complex manner. Usually, thermodynamic factors [1, 7, 8] are closely related to the filler arrangement in the polymer matrix. In view of this, the surface free energies of the materials at 180 °C, the mixing temperature employed in the present work, are listed in Table I. Using these values of γ^d and γ^p, the interfacial free energies of polymer/CB interface can be calculated by the equation [7, 9] below:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} - 2\left(\gamma_1^p \gamma_2^p\right)^{1/2}$$

The corresponding interfacial free energies of HDPE/CB, $\gamma_{\text{PE-CB}}$, as well as of PP/CB, $\gamma_{\text{PP-CB}}$, are calculated as follows: $\gamma_{\text{HDPE-CB}} = 2.2$ mJ/m^2, $\gamma_{\text{PP-CB}} = 4.1$ mJ/m^2. The results indicate that CB tends to disperse in the HDPE phase.

It is well known that a double-percolation [8] is the basic requirement for the conductivity of the composites, i.e., the percolation of CB in the CB-rich PE phase and the continuity of this phase in the blends, which hereby are defined as the first percolation and the second percolation. As shown in Fig. 1, when HDPE content is lower than 30 wt%, the PP forms the continuous phase and the PE forms the dispersed phase, therefore, a higher resistivity is obtained. With the increase of HDPE content up to 50 wt%, co-continuous phases are formed and a double-percolation effect is achieved in the blends, thus a notable decrease of the resistivity is observed. However, with further increase of HDPE

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TABLE I Surface free energy at 180 °C

Material	γ (mJ/m^2)	γ^{d} (mJ/m^2)	γ^{p} (mJ/m^2)
HDPE	25.9	25.9	0
PP	20.2	19.8	0.4
CB	42.2	41.9	0.3

$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}}$, γ: surface free energy, γ^{d}: dispersion component, γ^{p}: polar component.

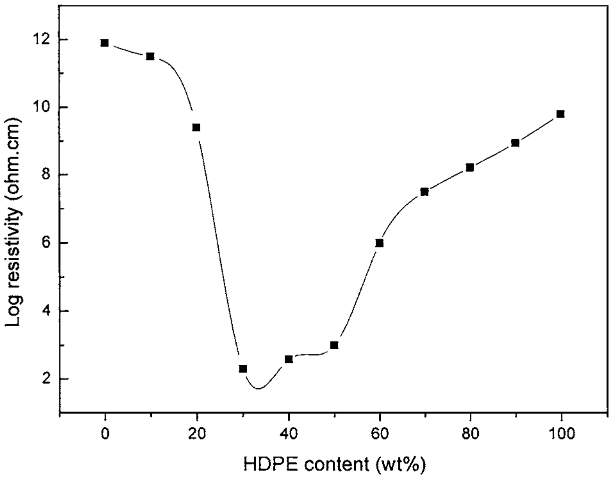

Figure 1 The dependence of the log resistivity on HDPE content in the 6 wt% CB-filled HDPE/PP blends.

content, the resistivity of the composite starts to increase gradually. This is due to the dilution of constant content of CB localized in the PE phase. The continuity of PE phase is of course preserved, but the CB percolation becomes looser and disappears beyond 60 wt% PE. In conclusion, the percolation value in the CB-filled miscible PE/PP blends is largely decreased in comparison with one in the CB-filled single HDPE composite depicted in Fig. 2.

Fig. 3 depicts the log resistivity of the 10 wt% CB-filled 40/60 PE/PP composite as a function of temperature. Two sharp resistivity jumps are observed. This phenomenon is remarkably different from that of any CB-filled single semicrystalline polymer composite [3], which exhibits only one sharp resistivity jump when heated to the T_{m} of the polymer. As temperature increases, the first resistivity jump occurs at about 133 °C, which is just the T_{m} of HDPE. With further increase of temperature up to about 160 °C, a slight decrease of the resistivity is observed, which is referred to as a negative temperature coefficient (NTC) effect that is attributed to the flocculated structure formed by CB due to the lower viscosity of PE phase above the T_{m} of PE. However, when temperature reaches the T_{m} of PP phase, the second resistivity jump occurs. We refer to these two resistivity jumps as the "two-step PTC effect."

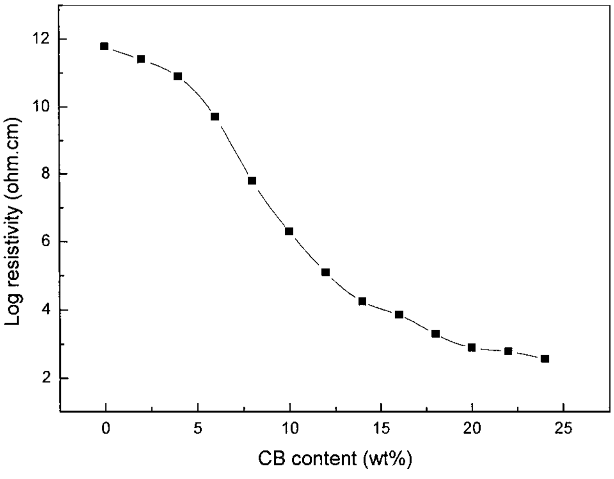

Figure 2 The dependence of the log resistivity on CB content in the CB-filled HDPE composite.

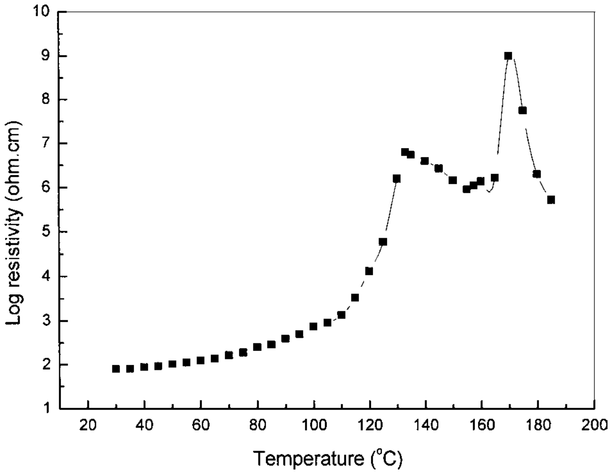

Figure 3 The dependence of the log resistivity on the temperature in the 10 wt% CB-filled 40/60 HDPE/PP blends.

As reported by the references [2, 6], CB has a great tendency to accumulate in the PE phase first, and then begins to be localized at the PE/PP interface when the CB content in the PE phase approaches a saturation limit. Therefore, the conductive paths are formed in the PE phase and at the PE/PP interface, respectively. When the temperature increases to the T_{m} of PE, the large volume expansion of PE due to the melting of PE crystallites breaks down the conductive paths in the PE phase, resulting in the happening of the first resistivity jump. As the temperature further increases to the T_{m} of PP, the second resistivity jump occurs, which is attributed to the volume expansion of PP, breaking down the conductive paths at the PE/PP interface. In short, the heterogeneous distribution of CB in the co-continuous PE/PP blends determines the occurrence of two-step PTC effect. In addition, the melting of HDPE and PP crystallites and the two resistivity jumps occur at the similar temperatures. Therefore, the large volume expansion due to the melting of HDPE and PP crystallites is responsible for the two-step PTC effect.

Fig. 4 shows the resistivity-temperature behavior of the 10/90 PE/PP blends filled with a mixture of 2 wt% CB and 2 wt% 2 mm-long CF, in which PP forms the continuous phase and PE forms the dispersed phase. This composite, if without CF, will show poor conductivity at the ambient temperature based on the above considerations. However, as CF is added, it is interesting to note that a low resistivity of the composite at the ambient temperature is achieved. It is highly likely that since the CF particles are substantially longer than the particles size of HDPE and PP [10], it is expected

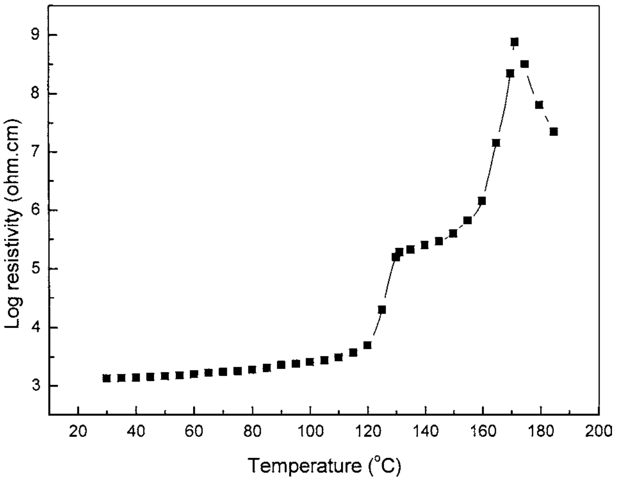

Figure 4 The dependence of the log resistivity on the temperature in the 10/90 HDPE/PP blends filled with 2 wt% CB and 2 wt% CF.

that the CF can span PP-rich domains and connect CB-rich HDPE domains that may not be otherwise connected. When the temperature is increased, a two-step PTC effect occurs. However, the composite does not show any NTC effects but rather a strong PTC effect between the T_ms of PE and PP, compared with Fig. 3. This novel phenomenon observed in Fig. 4 deserves exploring, which will be illustrated in a forthcoming paper.

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