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Two-Step Percolation in Polymer Blends Filled with Carbon Black

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Introduction. It is well-known that a composite consisting of conductive fillers and an insulating polymer becomes electrically conductive as the filler content exceeds a certain critical value, which is generally attributed to percolation phenomenon.[1] Moreover, the critical fraction corresponding to such a transition-like change in conductivity might shift to a much lower loading than expected theoretically with the incorporation of polymer blends as matrix resin due to the multiple percolation resulting from heterogeneous distribution of conducting fillers in one phase of the blended matrix and/or at the interface of the polymers.[2−4] From the practical point of view, a low conducting threshold offers the possibility that the composite's mechanical properties as well as processability are less deteriorated. However, very few efforts have been made to date to improve the reproducibility of conductive composites by using the above concept, i.e., multiple percolation in incompatible polymer blends.

In fact, the desired composites serving as candidates for many applications such as PTC (positive temperature coefficient) materials should have a filler concentration a bit higher than the upper limit of the percolation region,[5] as shown in the loading dependence of composite resistivity (Figure 1). The steeper the resistivity versus filler content curve, the more difficult to obtain reproducible composite, especially in the case of small changes in manufacturing or starting material. Chan and co-workers developed a method to prepare composite by blending a polymer with the granulates that had been made from a cross-linked mixture of carbon black and another polymer.[6] The resistivity of the composites of this kind decreases more gradually with a rise in filler fraction in comparison with conventional cases.

In this paper, we introduce a way that can bring about a relatively flat portion on the loading curve of composite resistivity so as to provide a wider processing window for composite manufacturing. In addition, an explanation of the experimental results is presented in terms of two-step percolation, a notion different from double percolation or multiple percolation.

Experimental Section. Low-density polyethylene (LDPE) and ethylene−vinyl acetate copolymer (EVA) with an identical melting flow index of 2.0 g/10 min were employed as matrix resins in this study. A China-made electrically conductive grade carbon black (CB) with an average diameter of 22−24 nm, surface area of 150 ± 5 m^2/g, and DBP (dibutyl phthalate absorption) value of 125 ± 10 mL/100 g, was used as conductive filler. Polymers and carbon black with desired proportions were melt mixed in a laboratory size Brabender plasticorder model XB20-80 under standard conditions of the experiment in each case at 160 °C and 20 rpm for 15 min. Carbon black was added when the polymers were melted. Having been removed and granulated, the blends with pre-embedded electrodes were compression

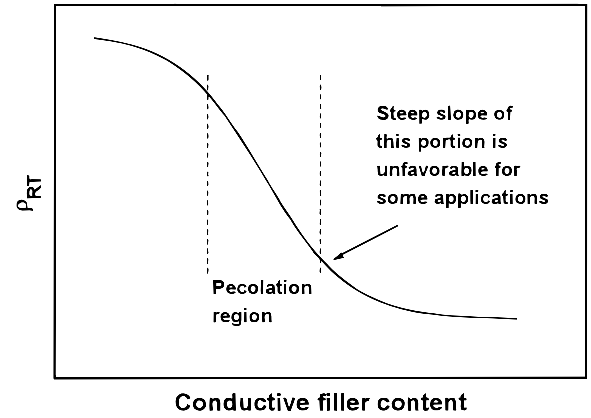

Figure 1. Schematic drawing of room-temperature resistivity ρ_{RT} vs filler content of a conductive polymer composite. The percolation region is defined as the space between the two peaks of the second derivation of ρ_{RT} with respect to filler content.

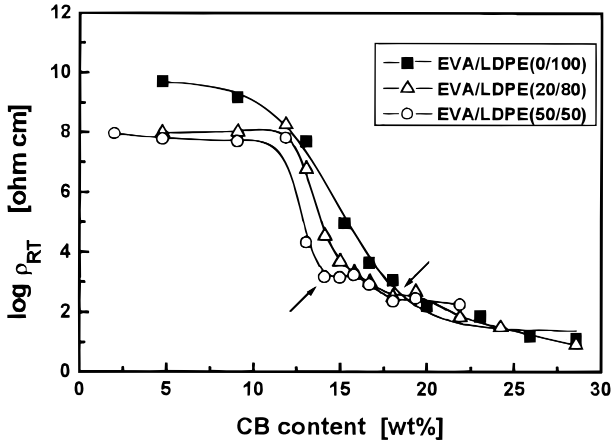

Figure 2. Room-temperature resistivity ρ_{RT} as a function of CB content. Arrows indicate the initial points of the terrace-like portions on the loading curves of EVA/LDPE systems.

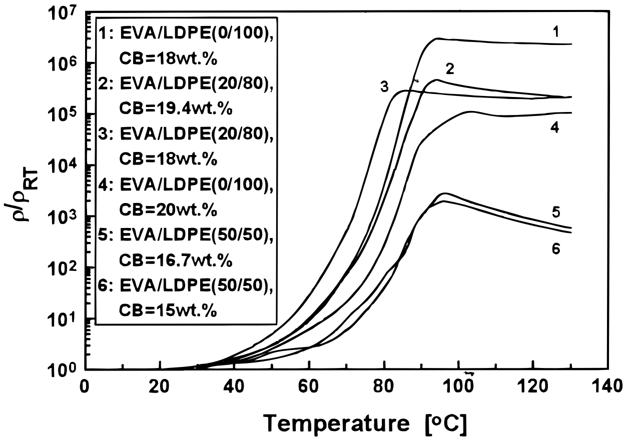

Figure 3. Ratio of resistivity to room-temperature resistivity ρ/ρ_{RT} as a function of temperature.

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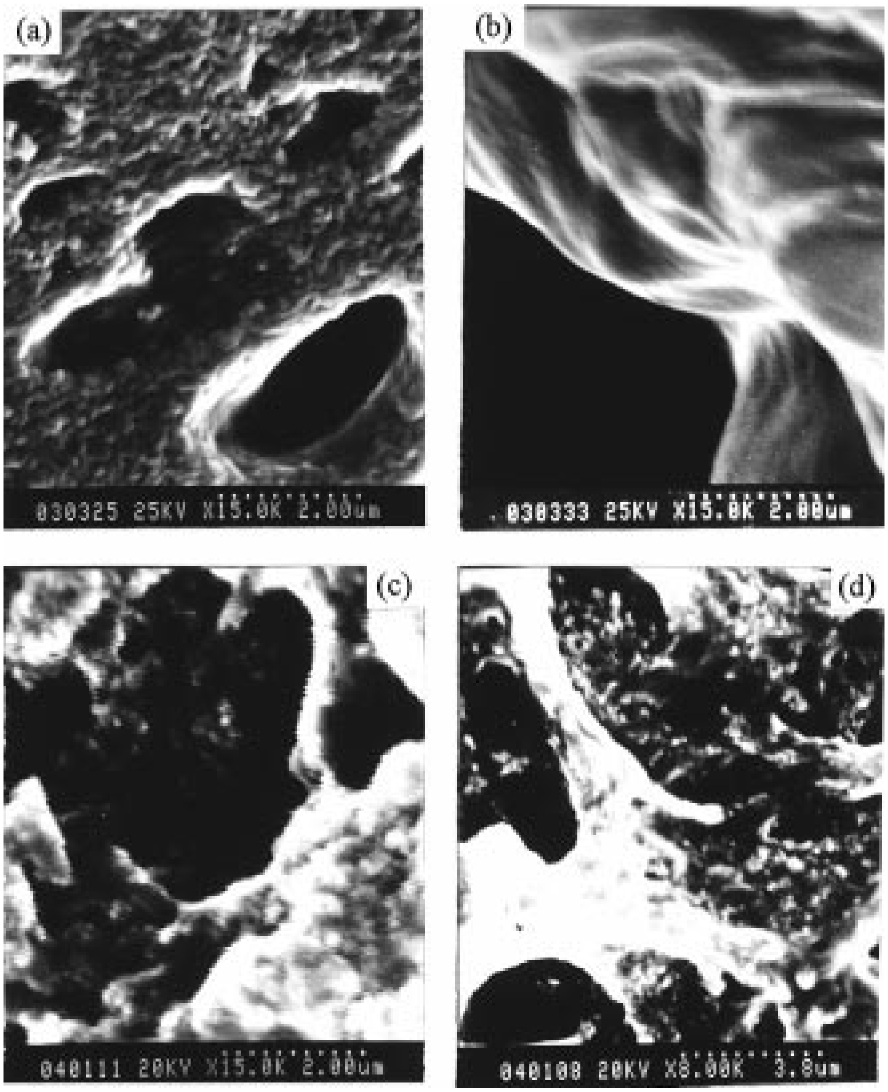

Figure 4. SEM photographs of CB-filled EVA/LDPE(50/50) composites. CB content: (a), (b) 12 wt %; (c), (d) 22 wt %; Etching details: (a), (c) EVA removed by decahydronaphthalene; (b), (d) LDPE removed by toluene.

molded at 140 °C and then cooled in air to room temperature, making sheets about 65 × 45 × 3 mm^3 in size. The sheet samples were rested overnight to release residual thermal stress before the subsequent measurements.

The composite samples for verifying PTC effects were cross-linked by irradiation with a ^{60}Co γ-ray source in air at room temperature. The radiation dose rate was 0.3 Mrad/h, and the radiation dose was 25 Mrad.

Room-temperature volume resistivity was measured with a four-lead system. The temperature dependence of composites resistivity was measured by heating the samples at a rate of 3 °C/min and cooling with air in an oven. All values of resistivity reported in this work are values of dc resistivity.

Morphology observation was performed by means of a HITACHI S-520 scanning electron microscope (SEM), prior to which composite samples were etched with toluene to remove the LDPE phase in the blends and decahydronaphthalene to remove the EVA phase, respectively, and then, the etched surfaces were vacuum-coated with a thin gold layer.

Results and Discussion. The influence of CB content on the room-temperature resistivity of the composites is illustrated in Figure 2, using the curve of individual LDPE as a reference. A zigzag drop in resistivity with filler content is observed for both CB-filled EVA/LDPE blends (being more evident for EVA/LDPE(50/50)), in sharp contrast with filled LDPE. The dependence of the former composites seems to be composed of two subsequent Z-shaped transitions and flattens midway at higher CB loading prior to the achievement of equilibrium resistivity, which approaches the value of filler itself when CB content further increases. Obviously, these short terrace-like parts on the percolation curves have engineering importance, as mentioned in the Introduction.

The resistivity to room-temperature resistivity ratio of selected composites is plotted as a function of temperature in Figure 3, from which PTC intensity (a parameter quantitatively characterizing the PTC effect and defined as the ratio of the maximum resistivity to room-temperature resistivity) can be seen clearly. With respect to the composites having filler fraction at the halfway gentle portions of the loading curves (Figure 2), there is no significant variation in their PTC intensities with a rise in CB content (Figure 3). This is quite different from the case of CB-filled LDPE when a similar increment of CB content is concerned and gives additional supporting evidence for the advantage of building up an intermediate terrace on the composite percolation curve.

Table 1. Surface Properties[a] at 160 °C

material	γ (mJ/m^2)	γ^d (mJ/m^2)	γ^p (mJ/m^2)
LDPE	25.9	25.9	0
EVA	26.6	25.0	1.6
CB	42.2	41.9	0.3

[a] $\gamma = \gamma^d + \gamma^p$, γ: surface free energy, γ^d: dispersion component, γ^p: polar component.

To reveal the mechanism involved, SEM observation of etched composites was carried out (Figure 4). It can be seen that in the case of lower filler content CB is predominantly located in the LDPE phase, which forms a continuous structure in the blends (Figure 4a) and there is no CB at the interface of EVA/LDPE or in EVA (Figure 4a,b). As filler loading increases, CB is dispersed in LDPE and at the interface zone (Figure 4c,d). In fact, the EVA phase also contains some CB aggregates (Figure 4d). That means the distribution status of CB in EVA/LDPE blends performs as a function of filler loading.

Usually, thermodynamic factors are closely related to filler arrangement in the matrix.[7] In view of this, the surface free energies of the materials at 160 °C, the mixing temperature employed in the present work, are listed in Table 1. By using these data and the harmonic mean method,[8] the corresponding interfacial free energies of LDPE and CB, $\gamma_{\mathrm{LDPE-CB}}$, as well as of EVA and CB, $\gamma_{\mathrm{EVA-CB}}$, are calculated as follows: $\gamma_{\mathrm{LDPE-CB}} = 4.1$ mJ/m^2, $\gamma_{\mathrm{EVA-CB}} = 5.2$ mJ/m^2. The results suggest CB tended to be dispersed in the LDPE phase under the prerequisite that the melt viscosity of the two polymers is comparable (the apparent viscosities of LDPE and EVA at current processing conditions are 1156 and 1210 Pa·s, respectively[9]), which coincides with the actual situation shown in Figure 4a,b. However, it is evident that the remaining photographs of Figure 4 still need another explanation.

Examination of the initial points of the terrace-like portions on the loading curves of CB-filled EVA/LDPE indicates the values are 18 wt % (for EVA/LDPE(20/80)) and 15 wt % (for EVA/LDPE(50/50)), respectively (Figure 2). Since CB is found to be distributed preferably in the LDPE phase at the lower loading regime, the above values can thus be approximately converted within LDPE, i.e., 21.6 wt % (11.7 vol %) and 26 wt % (14.5 vol %). In consideration of the fact that the maximum volume fraction, defined as the filler volume fraction of a rigid system with an infinite viscosity in which all the fillers are arranged in such a way that the interfiller spaces are completely filled with matrix, of CB in LDPE at the current processing conditions equals to 0.255[9] and covers the above estimated CB concentrations, the specific curve profiles of CB-filled blends shown in Figure 2 can be attributed to the volume restriction effect as follows.

With the addition of CB, CB aggregates were predominately dispersed in LDPE due to the lower interfacial free energy and then began to be located at the EVA/LDPE interface and/or in the EVA phase when the CB content in LDPE had approached a saturation limit. Consequently, composite resistivity became less sensitive to filler concentration in the latter course in a way similar to the beginning stage of incorporating CB into an insulating polymer, and electrical conduction was carried out mostly through the existing conduction networks in the LDPE phase. With a further rise in CB content, the composite resistivity continued to decrease until sufficient conduction paths throughout the polymers' interface were established. As a result, two-step percolation took place: the first corresponding to the percolation in LDPE and the second in EVA/LDPE interface. Accordingly, the percolation curves in Figure 2 exhibit two subsequent drastic drops in resistivity with filler content. It should be noted that each step of the percolation here belongs to the category of double percolation on the whole, but the combination of the two steps could not be simply interpreted by double percolation.

In summary, it can be concluded that such factors as polarity matching of polymers and conductive filler, similar melt viscosity of polymer components engaged in blending, and proper filler concentration are necessary for obtaining two-step percolation in binary polyblends, which provides versatile advantages for desired applications. Besides, blend composition of matrix resins also affects the conduction level of the terrace-like portion and shape of the percolation curve with two-step percolation characteristics.

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