PTC Effect of Polymer Blends Filled with Carbon Black

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SYNOPSIS

Low-density polyethylene/ethylene-propylene-diene terpolymer (LDPE/EPDM) blends and LDPE/ethylene-ethyl acrylate (EEA) blends were chosen as objects of study. Their positive temperature coefficient (PTC) phenomena and their distinctive aspects were described. The explanations were given from the structural characteristics of the blends. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Positive temperature coefficient (PTC) materials were extensively used and exploited in electricity and cable industries as self-controlled components of temperature or heat. However, improving various performances of PTC materials should be further studied.

There are two major types of carbon-black-filled polymers. One is crystalline polymers, such as polyethylene or ethylene-vinyl acelate. The other is noncrystalline polymers, such as SBR or silicone rubber. In the latter case, the peak temperature may be found in a wide temperature range, but because of its low PTC intensity it has little application. Much of the earlier work has been carried out with crystalline polymers. In this case the peak temperature is determined by the melting range of the polymer, and the resistivity may increase by many orders of magnitudes.[1] Then the NTC phenomenon appears, and this can be eliminated by crosslinks.

In this study, the PTC effects of blends of plastics and rubber or two kinds of plastics were studied. Much better PTC materials for practical use have been obtained by controlling the structures of the blends.

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EXPERIMENTAL

Materials

Low-density polyethylene (LDPE) with melt index of 2.0 and ethylene-propylene-diene terpolymer (EPDM), ethylene-ethyl acrylate copolymer (EEA) with melt index of 6.0 were selected as the ingredients of the blends. High-density polyethylenes with melt index of 0.2 and 2.0 were tested for comparison.

CSF carbon black was used as conductive filler. Its average size is 70 nm; surface area, 230 m^2/g; DBP value, 280 mL/100 g, and pH value, 7–9.

Sample

Different proportions of LDPE, EPDM (EEA), and carbon black were mixed on a two-roll mill at 130°C for 6 min. The crude sheet was then pressed in a mold at 160°C for 10 min. The sample was cooled down in air and became a 1-mm-thick sheet.

Resistivity

In order to measure volume resistivity of the sample at progressively elevated temperatures, we connected heating electrode of insulating resistance tester with a programmed temperature controller. A digital multimeter was used to measure lower resistivity. When resistivity exceeded 100 MΩ, an insulating resistance tester was used. The whole process was continuous, and it was very convenient and accurate. In order to reduce the contact resistivity, the two sides of the sample were bonded with copper foils.

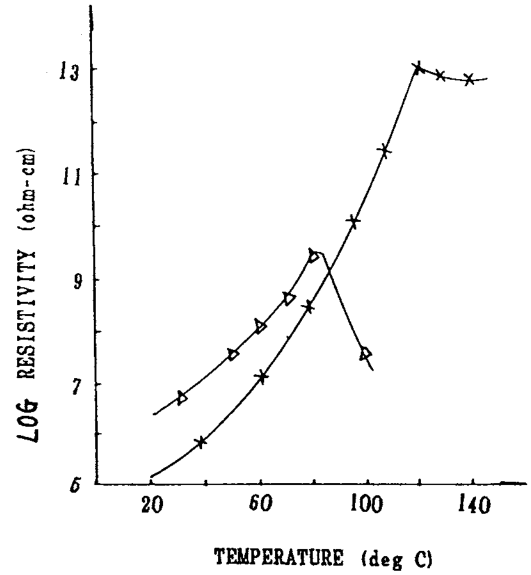

Figure 2 Effect of radiation crosslinking on PTC effect of LDPE/EPDM/0.2 CSF blends: (△) thermoplastic; (×) crosslinked for 15 Mrad.

RESULTS AND DISCUSSION

PTC Effect of LDPE/EPDM Blends

The influences of radiation crosslinking on PTC effects of LDPE and LDPE/EPDM blends are shown in Figures 1 and 2, respectively. The proportion of LDPE and EPDM content is 3 to 1. It can be seen that the PTC phenomenon of LDPE/EPDM blends has little difference compared with that of LDPE. It has even a slightly lower PTC intensity. But after crosslinking, the PTC intensity of the blends increases approximate 5 orders of magnitudes, while LDPE has only very little increase. This implied that the rubber phase has played a very important role.

In this composite, the carbon-black particles are mostly distributed to the rubber phase and the amorphous phase of LDPE.[2] There are two mechanisms during temperature rise. On the one hand, the thermal expansion coefficient of the rubber phase is greater than that of others. It expands continuously as temperature rises, thus increasing the distance between carbon-black agglomerates and the resistivity.[3] On the other hand, as temperature increases, the viscosity of the elastomer is greatly reduced, the mobility of the polymer segments increases, and more energy is added to the carbon-black dispersion.[1,4] The flocculated structure of carbon black is preferably generated, thus decreasing the resistivity. The competitive result of these two cases determines the PTC effect. After radiation crosslinking, the carbon-black agglomerates are more adsorbed to the network of the polymer matrix than previous and cannot move freely. At higher temperatures, especially in the vicinity of the melting point, molten LDPE phase and expansive rubber

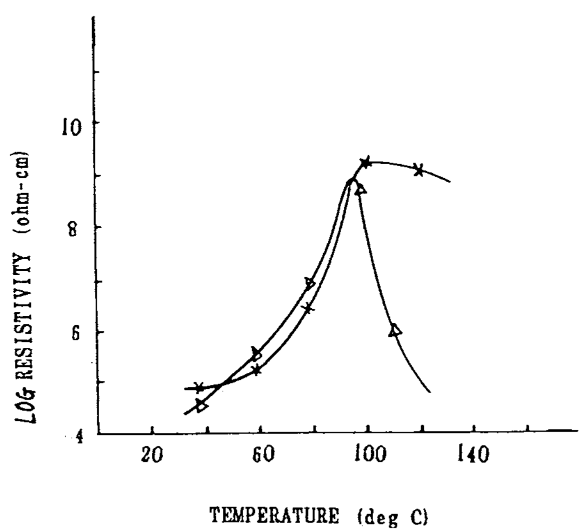

Figure 1 Effect of radiation crosslinking on PTC effect of LDPE (MI = 2)/0.18 CSF compound: (△) thermoplastic; (×) crosslinked for 15 Mrad.

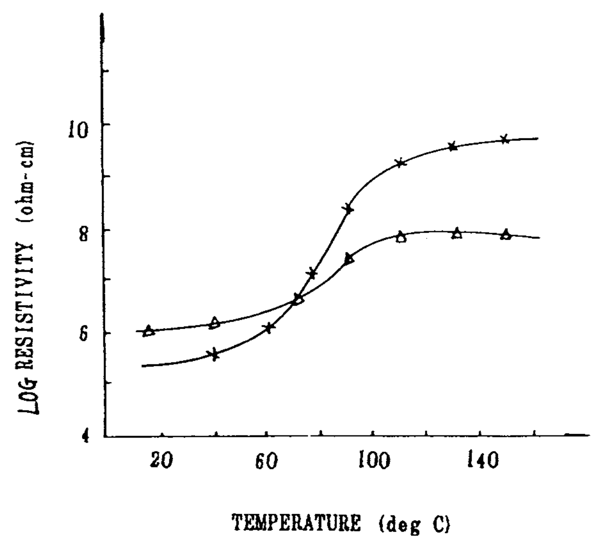

Figure 3 Effect of radiation crosslinking on PTC effect of LDPE/EEA/0.19 CSF blends: (△) thermoplastic; (×) crosslinked for 15 Mrad.

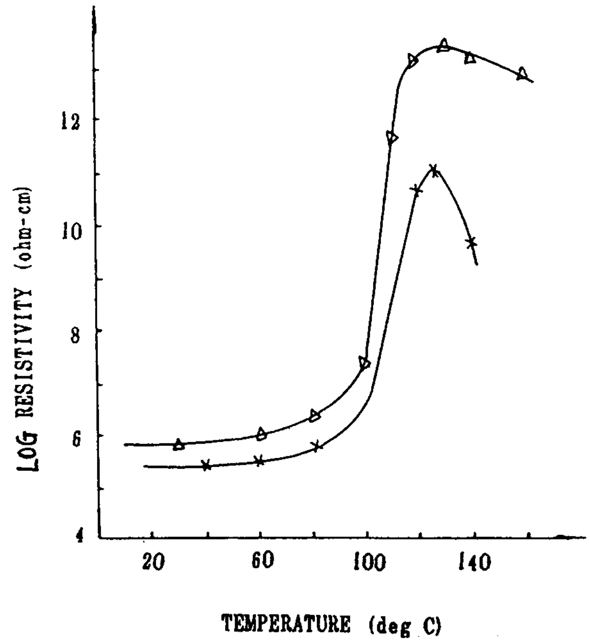

Figure 4 Resistivity/temperature plot for carbon black filled in different HDPE. (△) HDPE (MI = 0.2)/0.19 CSF; (×) HDPE (MI = 2.0)/0.16 CSF.

phase break up the carbon-black agglomerates rapidly, but no more dispersed particles can flocculate to build conductive structures, thus a significantly high PTC effect appears.

PTC Effect of LDPE/EEA Blends

Radiation crosslinking on PTC effect of LDPE/EEA blends are shown in Figure 3. The proportion of LDPE and EEA content is 3 to 1. It can be seen that the PTC intensity of the blends increases 3 orders of magnitudes after crosslinking, which lower than that of crosslinked LDPE/EPDM blends, because EEA has not as high an expansive rate as EPDM does. The LDPE/EEA blends have no NTC effect. This is due to the ethoxycarbonyl groups in EEA segments. The existence of polar groups in EEA increases the interaction between polymer matrix and carbon-black filler by some specific chemical interactions.[5]

Applied Value of the Blends

The PTC effects of different kinds of HDPE filled with carbon black are shown in Figure 4. The resistivities of HDPE increase many orders of magnitudes over temperature intervals of 10–20°C. Such pronounced increase in resistivity over narrow temperature intervals cannot be easily controlled in applications. In contrast, LDPE/EPDM blends have approximately linear changes of resistivity upon temperature increase. These can be used as automatically controlled heaters or sensors. The blends have better mechanical properties and low prices. It deserves further studies for future use.

CONCLUSION

The PTC effects of crosslinked LDPE/EPDM blends and LDPE/EEA blends have prominent distinctions compared with that of uncrosslinked systems. These are due to the existence of the second phase, EPDM or EEA, which has large expansive rate upon temperature increase. Such PTC materials are very promising in the future.[6]

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