

Positive-Temperature-Coefficient/Negative-Temperature-Coefficient Effect of Low-Density Polyethylene Filled with a Mixture of Carbon Black and Carbon Fiber

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ABSTRACT: Low-density polyethylene (LDPE) filled with carbon black (CB) and carbon fiber (CF) composites were prepared by a conventional melt-mixing method. The effects of a mixture of CB and CF on the positive-temperature-coefficient (PTC) effect and the negative-temperature-coefficient (NTC) effect, as well as the percolation threshold, were examined in detail. A synergy effect between CB and CF occurred, in that continuous conductive pathways formed within the CB/CF-filled composite. The percolation threshold was moved to a reduced filler content with the addition of CF to an LDPE/CB composite. A model was proposed to explain the difference in the PTC behavior of composites containing CB and CF and composites containing only CB or CF. In addition, the NTC effect was weakened with a mixture of CB and CF, and a relatively small radiation dose was required to eliminate the NTC phenomenon in LDPE/CB/CF composites. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 41: 3094–3101, 2003
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INTRODUCTION

The dispersion of a conductive filler, such as carbon black (CB) or carbon fiber (CF), or a metal powder into an insulative polymer matrix can yield a conductive polymer composite.^{1,2} These composites can exhibit a positive-temperature-coefficient (PTC) effect. The main feature of the PTC effect is that with heating, the conductive system shows a sharp resistivity increase around the melting region of the semicrystalline polymer

matrix.³ However, above this region, a more conductive network may be formed, and a lower resistivity will be observed.⁴ This phenomenon is called a negative-temperature-coefficient (NTC) effect. The ratio of the maximum resistivity to the room-temperature resistivity is defined as the PTC intensity. PTC materials have widespread commercial applications, including sensors, self-regulating heaters, and switching materials.^{5,6}

A comprehensive theory describing the PTC/NTC phenomenon has not been fully established yet, although many researchers have tried to explain it. Kohler⁷ suggested that a conductive filler forms a network of conductive chains at a temperature below the melting temperature (T_m); as the

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polymer is heated, the sudden expansion that takes place at the crystalline T_m results in the breakup of the conducting chains with a consequent anomalous increase in resistance. However, Kohler was not able to explain the steep decrease in the resistance above T_m , when the volume of the polymer continues to increase with temperature. Ohe and Natio⁸ assumed a more uniform distribution of interparticle gaps at low temperatures, near T_m , but the distribution becomes more random; although the average gap width may not be changed considerably, the presence of a significant number of interparticle gaps large enough to hinder an electron-tunneling mechanism gives rise to the destruction of many conductive paths through polymer composites. However, this theory does not interpret why the distribution becomes more random at higher temperatures. Meyer⁹ posited that thin crystalline films of a polymer are much more conductive than amorphous films of the polymer and that there is a thin crystalline film between conductive particles. In the vicinity of T_m , the melting of the film causes the change in the resistivity. Al-Allak¹⁰ recognized that the cooperative effects of the changes in the crystallinity and volume expansion of a polymer are key factors responsible for the PTC effect.

A desired PTC performance includes a low room-temperature resistivity, a high PTC intensity, a low NTC intensity, a high electrical reproducibility, and a high PTC transition temperature, together with a low conductive filler content. The percolation threshold achieved is related to the filler type. If CB¹¹ serves as a conductive particle, a considerable content is needed to achieve the percolation threshold; this probably results in much difficulty in preparing polymer/CB composites containing more than 30 wt % CB with simple mixing techniques. However, when CF¹² is used as a filler instead of CB, a relatively small amount is required. Usually, a composite filled with a fiber has a lower percolation threshold than one filled with spherical conductive particles. Fillers with high aspect ratios may also increase the tendency of continuous networks forming in polymer matrices.

In general, CB-filled semicrystalline polymer composites cannot be used as thermistors in over-temperature and overcurrent protection because of their NTC effect and poor reproducibility in thermal cycling. To overcome these disadvantages, researchers have proposed and developed many methods of eliminating the NTC effect,

such as using mixtures of two CBs with polyethylene,¹³ adding rubber as a mechanical stabilizer to CB-filled composites,¹⁴ and using a very high viscosity polymer as one component in a composite,¹⁵ as well as crosslinking the semicrystalline polymer.¹⁶

Both single-polymer/single-filler and double-polymer/single-filler systems have been studied by many researchers, but little interest has been focused on a single polymer filled with a mixture of double fillers. In this study, we explored the influence of the synergy effect between CB and CF on the PTC/NTC effect in low-density polyethylene (LDPE) composites filled with a mixture of CB and CF fillers.

EXPERIMENTAL

Materials

The LDPE was a commercial resin (18D, Daqing Petrochemical Co., China) with a melt index of 2 g/10 min and a density of 0.921 g/cm³. The CB was acetylene black (Chun'an Chemical Co., China) with an average particle size of 40–50 nm, a surface area of 60–70 cm²/g, a dibutyl phthalate absorption (DBP) value of 300–320 mL/100 g, and a pH value of 5.0–7.0. The CF (T300, Jilin Carbon Co., China) was based on high-strength polyacrylonitrile. It was a short fiber with the following characteristics: diameter = 7 μm, density = 1.6 g/cm³, and volume resistivity = $6 \times 10^{-3} \Omega \text{ cm}$ at 25 °C.

Blending of the Composites

The composites were prepared in a Brabender internal mixer at T_m of the polymer. The mixing procedure involved adding the polyethylene into a preheated rotating mixer and then allowing the addition of CB and CF into the melting polymer matrix. These blends were further mixed in a two-roll mill for short periods at a temperature only slightly above the polymer T_m . The blends were compression-molded in the vulcanized press, cooled down in air to room temperature, and made into sheets with a radius of 1 cm and a thickness of 1.5 mm. The sheet samples were rested overnight so that residual thermal stress would be released before the subsequent measurements.

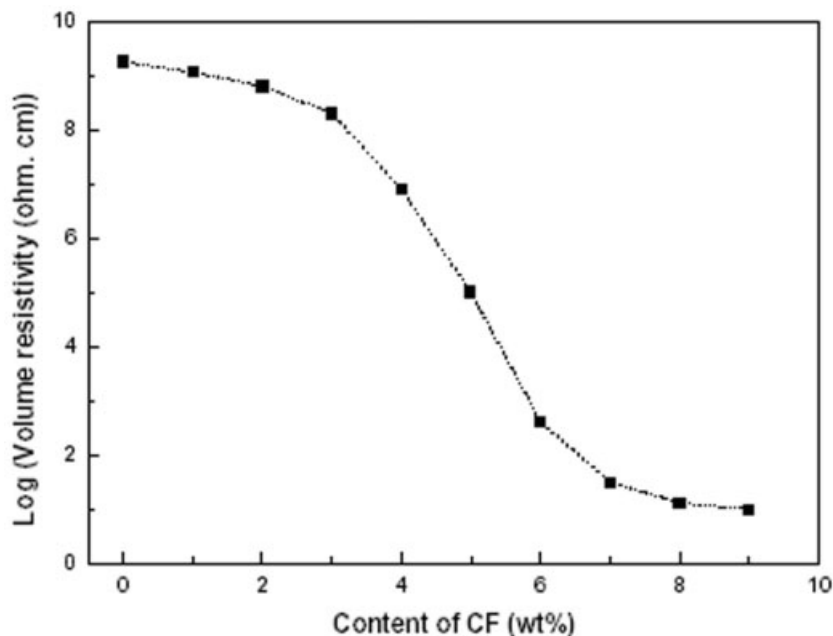


Figure 1. Effect of adding CF on the volume resistivity in composites containing 14 wt % CB. The measurements were made with an applied voltage of 500 V for the high-resistivity materials and 50 V for the more conductive materials.

Irradiation

The samples were sealed in glass tubes *in vacuo* and irradiated with ^{60}Co γ -rays at room temperature at different radiation doses. They were held for 1 day after irradiation crosslinking for the elimination of postradiation effects.

Morphology

We conducted morphology studies to observe the dispersed state of CB and CF in the composites with an optical microscope (Leica, Japan) equipped with a digital camera (Nikon, Japan). Before our observations, we polished the samples to obtain smooth surfaces.

Resistivity Testing

The electrical resistivity was measured with a digital multimeter when it was lower than $2 \times 10^7 \Omega$; a high-resistance meter was used when the resistivity exceeded $2 \times 10^7 \Omega$. Different applied voltages were used on different samples, depending on the level of resistivity of the sample. Highly conductive samples caused short circuiting of the equipment when the applied voltage was too high. Therefore, the voltage was adapted to the resistivity; it was 500 V for poorly conduc-

tive composites and 50 V for conductive composites. According to ASTM D 4496 and D 257, the resistivity was converted into the volume resistivity (ρ_v) with the following formula: $\rho_v = \pi r^2 R_v / d$ (where r is the radius of the testing electrode, d is the thickness of the sample, π is a constant, and R_v is the measured resistance).

Melt Index

Melt-index measurements were performed with an XRZ-400-1 melt-index instrument. The addition of conductive fillers to the polymer matrix caused a change in viscosity of the polymer, which was reflected by the polymer melt index.

RESULTS AND DISCUSSION

Effect of the Blend Fillers on the Percolation Threshold

Figure 1 shows the effect of adding CF on the volume resistivity of a composite containing a constant CB content of 14%. At a low concentration of CF, the resistivity gradually decreases with increasing CF contents. However, at 7 wt %, a considerable reduction in resistivity, around $10^7 \Omega \text{ cm}$, can be observed. This stepwise change in

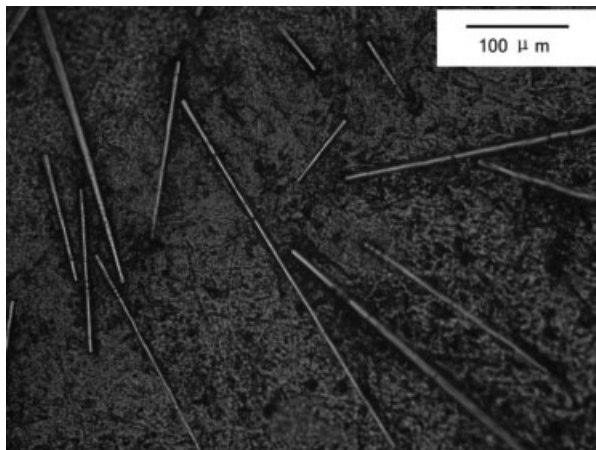


Figure 2. Optical micrograph of a composite filled with 14 wt % CB and 7 wt % CF. The addition of CF provided long conductive paths that improved the interparticle contacts, and CB improved the interfiber points of contact within the network.

resistivity is due to the formation of an interconnected structure of CB and CF and can be regarded as an electrical percolation threshold. It can obviously be seen from an optical micrograph of a composite containing 14 wt % CB and 7 wt % CF (Fig. 2) that CF is randomly oriented and that CB and CF form interconnecting structures; a certain degree of CB–CF interactions and/or entanglements is shown. This simply means that at

concentrations of 14 wt % CB and 7 wt % CF, very large quantities of electrons are permitted to flow through the composite because of the creation of interconnecting conductive pathways. When the CF content is beyond 7 wt %, the resistivity of the composite decreases continuously, but the rate of the decreases is very low.

It can be observed in Figure 3 that in the LDPE/CB composites, 32 wt % CB is needed to achieve the percolation value; however, with the addition of CF, the percolation threshold is reduced in a steplike manner, and the level of electrical conductivity is improved. This phenomenon is related to the different roles of CB and CF in the formation of conductive pathways. It is well known that CF provides charge transport over large distances, whereas CB provides charge transport over small distances. The incorporation of CF into LDPE/CB composites provides long conductive paths to bridge uncontacted CB particles and aggregates or connect short conductive paths, thereby enhancing the continuity of conductive pathways within the network. The CB particles and aggregates serve to improve interfiber points of contact. A mutual bridge for CB and CF is called a synergy effect,¹⁷ as illustrated in Figure 4, which demonstrates that the connectivity of a CB network is improved by the addition of CF to an LDPE/CB composite. Without CF, a higher concentration of CB is required to estab-

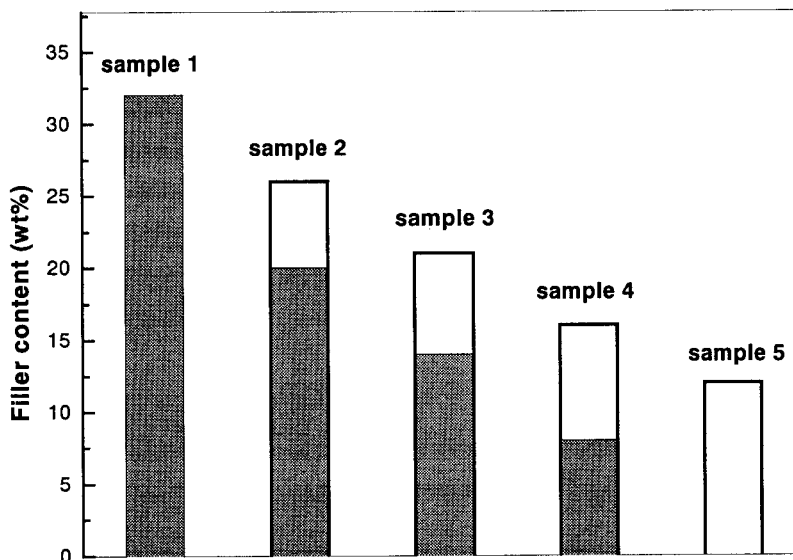


Figure 3. Percolation threshold achieved for LDPEs filled with carbon fillers of different types. The dark bars represent the CB content, and the white bars represent the CF content.

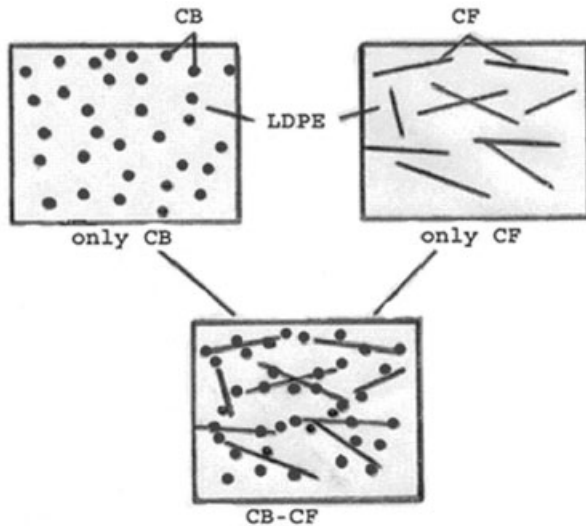


Figure 4. Scheme of the overlapping electrically conductive networks formed by CBs and CFs.

lish a conductive path throughout the entire composite.

Effect of the Blend Fillers on the PTC Effect

As mentioned earlier, CF provides long conductive pathways through CB particles and aggregate

gates and thereby improves the connectivity of a CB network, whereas CB not only provides charge transport over relatively small distances but also improves the interfiber contact by CB particle/aggregate bridges. This synergy effect is favorable for the PTC performance. As shown in Figure 5, the PTC intensity is enhanced, the PTC transition temperature is shifted to a higher temperature, and the ratio of resistivity to temperature is lower before the transition temperature for LDPE/CB/CF composites, in comparison with LDPE/CB and LDPE/CF composites.

An increase in resistivity with temperature is probably the result of cooperative effects of two sides: (1) charge transport over small distances is hindered and (2) charge transport over large distances is hindered. Figure 6(a) shows continuous conductive pathways at the ambient temperature in LDPE/CB/CF composites. With increasing temperature, the interparticle/aggregate distance of CB is increased gradually by the volume expansion of the polymer matrix, so charge transport over a small distance is destroyed. However, the force induced by the expansion of the polymer matrix drives CB particles and aggregates to approach the fiber end [Fig. 6(b)], so the contact situation between CB and CF is changed, and electron transport from CB to CF occurs; conse-

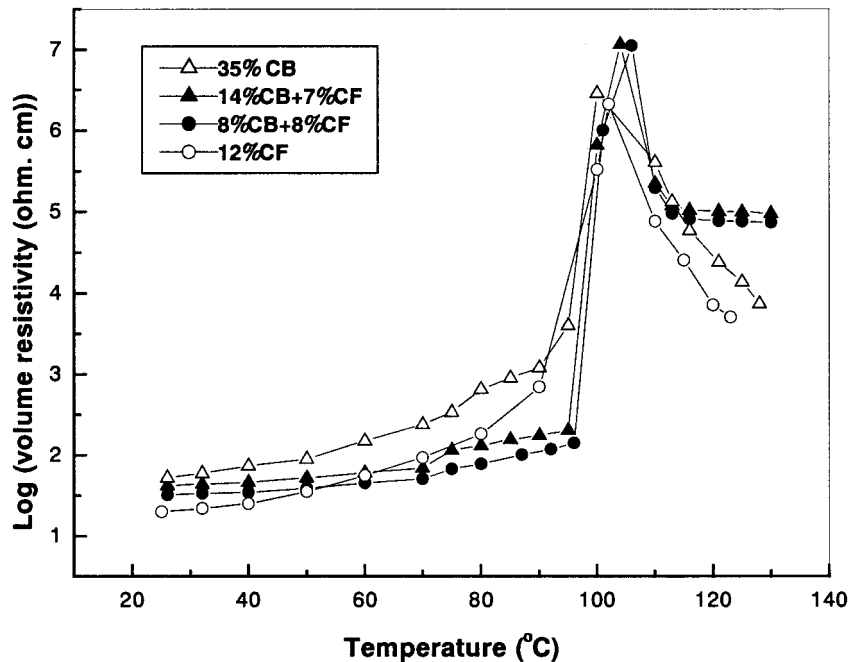


Figure 5. Dependence of the volume resistivity on the temperature in CB-filled, CF-filled, and CB/CF-filled composites.

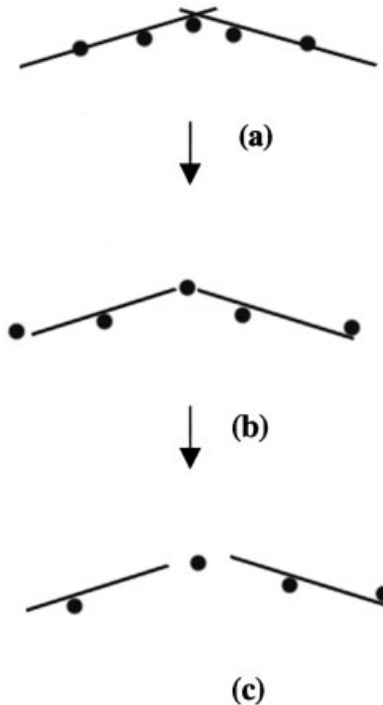


Figure 6. Schematic model of the destructive process of conductive pathways with increasing temperature in LDPE/CB/CF composites.

quently, new percolation paths are constructed, which can somewhat compensate for conductivity losses resulting from increased distances between CB particles and aggregates. Therefore, the resistivity of composites containing CB and CF is not as sensitive to temperature changes as that of composites containing only CB or CF before the transition temperature. With a further increase in the temperature, the polymer volume expands to a certain extent, and charge transport over large distances is destroyed [Fig. 6(c)]. In this case, resistivity increases drastically, and this leads to an extremely large PTC intensity. Therefore, the CB/CF-filled composites exhibit a stronger PTC effect and a higher PTC transition temperature than composites filled only with CB or CF.

Effect of the Blend Fillers on the NTC Effect

The NTC effect following PTC behavior can clearly be observed in Figure 5. The occurrence of NTC behavior is primarily associated with the aggregation effect of the filler. With an increase in the temperature, the viscosity of the polymer matrix is reduced gradually, and more and more

Table 1. Melt Indices of LDPEs Mixed with Different Filler Contents

Composition and Content (wt %)	Melt Index (g/10 min)
32 CB	0.65
14 CB + 7 CF	0.14
8 CB + 8 CF	0.11

energy is obtained for conductive fillers; this intensifies their tendency to aggregate. This consequently results in the formation of new paths and a conductivity increase, which gives rise to the PTC effect.

As shown in Figure 5, the NTC effect of CB/CF-filled composites is lower than that of composites only filled with CB. The resistivity in LDPE/CB/CF composites starts to drop moderately at the PTC transition temperature up to 115 °C or so, and it subsequently remains unchanged. This is thought to be due to the fact that the addition of CF causes an increase in the melt viscosity of the CB/CF-filled system.^{18–20} Table 1 shows the melt indices of LDPEs mixed with different filler compositions. The melt indices of LDPEs mixed with 14 wt % CB/7 wt % CF and 8 wt % CB/8 wt % CF are much lower than that of an LDPE mixed with 32 wt % CB. It is well known that CF possesses a certain aspect ratio, and it is regarded as a rigid and conductive chain formed by many CB particles. Therefore, more thermal energy is needed for the motion of CF than for that of CB. At an elevated temperature, CF will restrict the mobility of the polymer chains to a certain extent; this is equal to somewhat increasing the viscosity of the polymer matrix. Therefore, the decrease in the melt index is believed to be caused by the high aspect ratio of CF. Table 2 indicates that the change in the melt index at a given fiber content is dependent on the aspect ratio of the filler. Sim-

Table 2. Comparison of the Melt Indices of LDPEs Filled with CB and/or CF with Various Aspect Ratios

Composition and Content (wt %)	Aspect Ratio of CF	Melt Index (g/10 min)
21 CB	—	0.76
14 CB + 7 CF	100	0.43
	250	0.26
	500	0.11

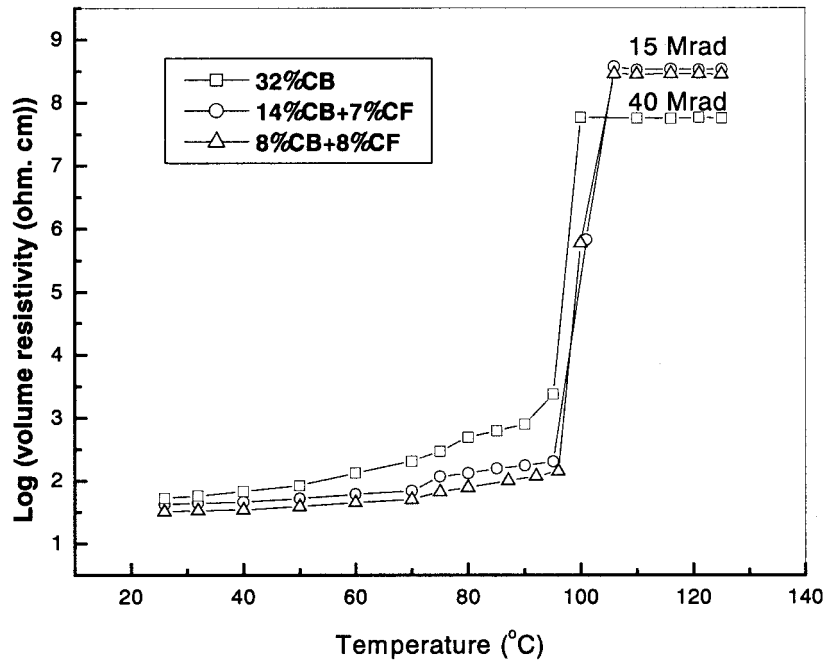


Figure 7. Dependence of the volume resistivity on the temperature after irradiation crosslinking.

ilar results were reported by Kitano and Kataoka¹⁹ for polyethylene melts filled with glass fibers. This indicates that the larger the aspect ratio is, the higher the viscosity increase is at a given fiber content. On the basis of this consideration, the tendency to flocculate for CB particles and aggregates in LDPE/CB/CF composites at elevated temperatures is somewhat depressed, and this impairs the NTC effect to a certain extent.

Effect of Irradiation Crosslinking on the PTC/NTC Effect

The presence of the NTC phenomenon may have an adverse effect on desired switching properties. Structure stabilization and a significant reduction in the movements of conductive fillers can be achieved by the introduction of crosslinking. The absence of the NTC effect in the crosslinked semi-crystalline polymer composites is attributed to an increase in the viscosity of the polymer matrix, which leads to a significant reduction in the mobility of the conductive fillers in the composites. Crosslinking is, therefore, expected to greatly improve the electrical reproducibility and at least partially eliminate the NTC phenomenon.

It can be observed in Figure 7 that radiation not only eliminates the NTC phenomenon but

also improves the PTC intensity. As a matter of fact, two processes having opposite effects on the conductivity exist at elevated temperatures: the interruption of conductive paths due to a large volume expansion of the polymer and the reformation of new conductive paths due to a tendency of fillers to aggregate. Therefore, the PTC intensity is determined by the net result of the two processes before crosslinking. The higher the temperature is, the more mobile the fillers are and, therefore, the more likely aggregation and agglomeration are. The effect of the polymer volume expansion on the resistivity is partially counteracted by the aggregation/agglomeration effect of the fillers, so the PTC intensity decreases relatively. After irradiation crosslinking, the conductive fillers are strongly attached to crosslinking networks, and the latter effect might not be taken into consideration, so the PTC effect is improved by the introduction of irradiation crosslinking. In addition, as shown in Figure 7, the NTC effect can effectively be eliminated with crosslinking with a 40-Mrad dose for LDPE/CB composites; however, a relatively small radiation dose, that is, 15 Mrad, is required for LDPE/CB/CF composites. This has further confirmed that the addition of CF to the LDPE/CB system increases the viscosity of the system, this being equal to a slight crosslinking.

On the basis of this consideration, a relatively small radiation dose is enough to stabilize the distribution of the conductive filler.

CONCLUSIONS

CB and CF play different roles in the formation of conductive pathways within LDPE/CB/CF composites. CF provides long conductive paths to bridge uncontacted CB particles and aggregates or short conductive paths. CB serves to bridge the interfiber points. These mutual bridges for CB and CF are called a synergy effect, which enhances the continuity of conductive pathways, thereby reducing the percolation threshold.

The occurrence of the PTC effect in composites containing CB and CF is the result of cooperative effects resulting for two reasons: (1) the percolation paths of CB formed by charge transport over small distances are interrupted and (2) the percolation paths of CF formed by charge transport over large distances are interrupted. This determines higher PTC transition temperatures and PTC intensities in CB/CF-filled composites. The addition of CF to LDPE/CB composites increases the viscosity of the composites; it is not as easy for a conductive filler in LDPE/CB/CF composites to aggregate or agglomerate as one in LDPE/CB composites at an elevated temperature, and the NTC intensity is reduced to a relatively low level. In addition, a relatively small radiation dose is required to effectively eliminate the NTC effect in

LDPE/CB/CF composites, in comparison with that needed for LDPE/CB composites. The crosslinked composites exhibit a higher PTC intensity than their noncrosslinked counterparts. This is thought to be due to the fact that the effect of the filler aggregation and agglomeration is eliminated by irradiation crosslinking.

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