

Electrical Behavior of Carbon Black-Filled Polymer Composites: Effect of Interaction Between Filler and Matrix

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SYNOPSIS

The effect of interaction between carbon black and polymer on electrical behavior was studied using the ESR method. The polymer matrices used were HDPE, LDPE, and ethylene/vinyl acetate (EVA). Two kinds of carbon blacks (CB), high structure CSF-III and low structure FEF, were used as a conductive filler. Compared to that of the HDPE/FEF compound, the positive temperature coefficient (PTC) intensity is lower and electrical reproducibility is worse for the HDPE/CSF-III compound; however, it can be improved significantly by radiation cross-linking. On the other hand, the cross-linking has no practical effect on the PTC intensity of the LDPE/CSF-III compound while it can be achieved by mixing the compound for a longer time. The great PTC intensity was obtained in the HDPE/EVA/CSF-III compound, and it is greater than that of HDPE/CSF-III or EVA/CSF-III. We explain these results using the concept of interaction between the filler and matrix. The absorption of the polymer on the carbon black surface may be physical or chemical; the latter is caused by the free-radical reaction between the polymer and carbon black, and it can occur during the radiation or preparation process of the compound. These "bound polymers" are essentially important for materials to have a great PTC intensity and good reproducibility. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Semiconducting polymeric mixtures are becoming common in many applications,¹ such as in heating, prevention of static electricity accumulation, electrodes, electrically conductive coatings and adhesives, and positive temperature coefficient (PTC) materials.² Conductivity in polymers can be provided by incorporation of conductive fillers (carbon blacks, carbon fibers, and metallic powders) into the polymeric matrix.

The sudden resistivity increase with the temperature is described by a PTC, whereas the resistivity decrease is described by a negative temperature coefficient (NTC). The PTC phenomenon is a negative factor in cable engineering;³ however, it is being put to good use in a number of other applications such as in self-controlled heaters, current limiters, or sensors.

The lack of electrical reproducibility and the NTC effect are two main drawbacks to the application of the PTC materials, and many scientists have investigated the mechanism of electron transport and studied the stability and practicality of these materials.^{4,5} Narkis et al.'s results showed that reproducibility was improved using different-sized carbon blacks as a filler or by cross-linking.^{6,7} However, the cross-linking sacrifices somewhat the PTC intensity, especially that of the peroxide. Both the properties of the polymer, such as melt index,^{8,9} degree of crystallinity,⁹ molecular weight,¹⁰ and of the carbon black, such as surface area, chemical groups, and DBP value,^{6,7} have strong influence on the electrical conductivity.

Some authors have studied the mechanical properties and electrical conductivity of carbon black-filled rubber.^{11,12} They assumed that the reinforcement and the electrical resistivity of the materials are interrelated to the interactions between the filler and rubber; the interactions may be physical or chemical. Some cure conditions (temperature, time, and pressure) have a strong effect on the resistivity;

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Table I Specification of Polymer Matrices Used and Mixing (Molding) Temperature of Compounds

Polymer	Melting Index (g/10 min)	Density (g/cm ³)	Melting Point (°C)	Degree of Crystallinity (%)	Mixing Molding Temperature (°C)
HDPE	1.2	0.954	130.8	60.6	150
LDPE	2.0	0.925	107.1	37.4	140
EVA ^a (VA 18%)	2.5	0.943	89.6	21.2	110

^a EVA, ethylene/vinyl acetate.

however, the results were different or contradictory.^{13,14} The studies of interaction between the filler and matrix are still lacking in carbon black-filled vinyl polymer.¹⁵ The present article reports the effect of this interaction on the PTC/NTC phenomenon of different carbon black-filled vinyl polymers.

EXPERIMENTAL

The matrices of the three kinds of polymers listed in Table I and two kinds of carbon blacks listed in Table II were used in this study. Polymer and carbon black were mixed at high temperature for 5 min, roll-milled for 5 min at the same temperature after 24 h, and, subsequently, compression-molded to about a 0.5 mm-thick film. All the sample preparation processes were the same except the mixing and molding temperatures, which are shown in Table I.

The electrical resistivity was measured in the thickness direction of the composite films. Copper paste was used to ensure good contact of the sample surface with the electrodes of the conduction tester. Low resistivity was measured with a multimeter and a ZC-36 type megger was used for high resistivity. The temperature dependence of the composites was measured by heating at 2°C/min and cooling by air. All resistivities reported in this work are dc resistivities. Carbon black concentrations are always expressed by the weight fraction.

Table II Physical and Chemical Properties of Carbon Blacks Used

	Average Size (nm)	Surface Area (m ² /g)	DBP Value (mL/100 g)	pH Value
CSF-III	70	230	280	7.0-9.0
FEF	50	41-50	95-110	7.0-9.5

Samples were irradiated in ⁶⁰Co- γ -ray at a rate of 8.0×10^3 Gy/h in air, and the degree of cross-linking was determined by a gel content, namely, the polymer fraction that did not dissolve in boiling xylene for 72 h at 155°C. The ESR spectra of the samples were obtained from a Bruker ER 200D EPR after irradiation at room temperature in the atmosphere.

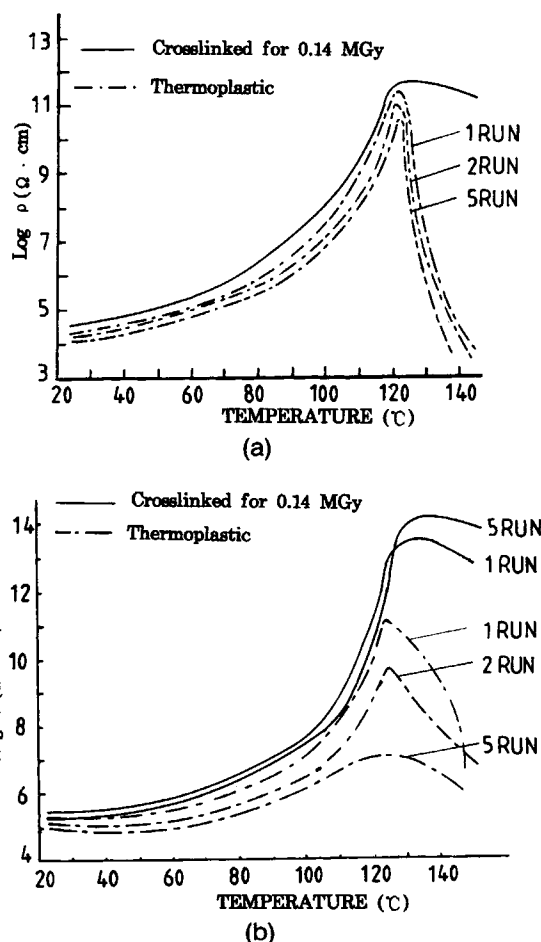


Figure 1 The effect of radiation cross-linking on the PTC intensity and electrical reproducibility of carbon black-filled HDPE composites: (a) HDPE/0.16 CSF-III; (b) HDPE/0.20 FEF.

RESULTS AND DISCUSSION

Carbon Black-filled HDPE Composites

The effect of radiation cross-linking on the PTC intensity and electrical reproducibility of two carbon black-filled HDPE composites are shown in Figure 1. We chose the carbon black concentration at which the composites have the maximum PTC intensity. Figure 1 shows that the PTC effect and electrical reproducibility of HDPE/CSF-III are improved significantly by the cross-linking. The result is different from that of Narkis et al.,^{6,7} which showed that the PTC effect is slightly declined by the radiation cross-linking. However, the resistivity-temperature curves of the thermoplastic HDPE/FEF composite nearly coincide for different runs, and the PTC intensity is greater than that of the HDPE/CSF-III composite. In particular, cross-linking has no practical effect on the PTC intensity.

The disparity of the PTC intensity and reproducibility for thermoplastic HDPE/CSF-III and HDPE/FEF composites is caused by the difference of the carbon blacks. Figure 2 shows the transmission electron micrographs of the blacks. From Table

II and Figure 2, we can see that CSF-III has a larger surface area and a greater DBP value; the particles tend to align and form aggregates that contain several or tens of particles at the free state. This tendency may be caused by the van der Waals force or the covalent bands between particles. For the HDPE/CSF-III composite, the reagglomeration of carbon particles at high temperature facilitates the conductivity, so that the compound has a low PTC intensity and poor reproducibility for the irreversible movement of the blacks. Such a behavior may not be valid for FEF black, which has a low structure and the tendency mentioned above is lacking. As a result, the expansion of the matrix makes some conducting channels breakup. Although the carbon particles reaggregate about 120°C, this alignment is reversible and it is broken up in the next thermal run. Thereby, for the FEF-filled polymer composite, the PTC intensity is greater and electrical reproducibility is better.

Compared to the thermoplastic counterpart, the increase of the PTC intensity of the cross-linked HDPE/CSF-III compound indicated that some free-radical reactions between filler and matrix may exist during the irradiation of the compound.

The nature and role of unpaired electronic spins in carbon blacks still appear to be in doubt. Donnet and his associates¹⁶ postulated an aroxylic structure for "carbon black radicals":

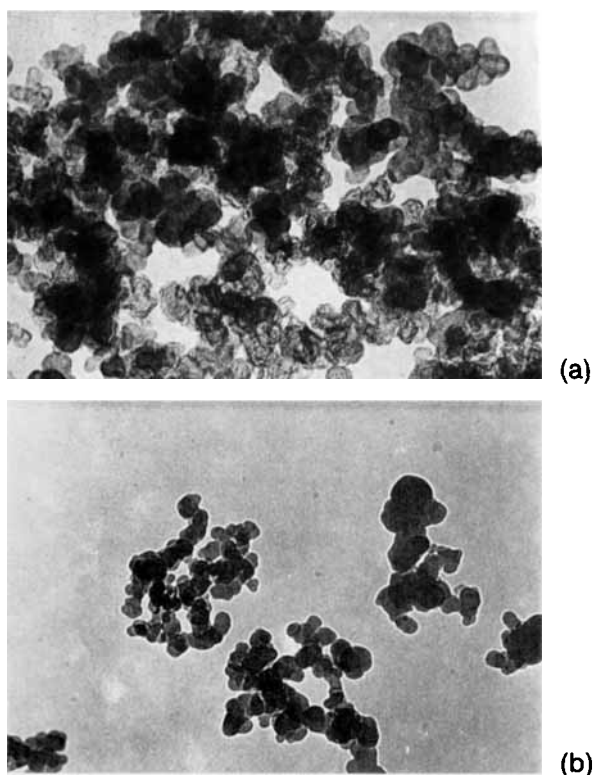
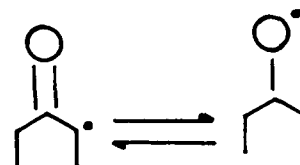


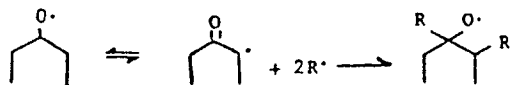
Figure 2 Transmission electron micrographs of carbon blacks ($\times 50$ K): (a) CSF-III black; (b) FEF black.



Starting with this hypothesis, they were able to explain a number of seemingly contradictory observations regarding the reactivity of the carbon black "radicals," particularly, the fact that spin concentrations are frequently unchanged after reaction of the black with free radicals. On the other hand, the radicals in the irradiated polyethylene have been investigated by many scientists.¹⁷

Figure 3 shows the ESR spectra of the samples. We found that the lifetime of the radicals in polyethylene was about several days, and the radical intensity became very weak 2 days after irradiation. From the spectral shape and the lifetime of the radicals, we can conclude that most of the radicals are alkyl, whereas the allyl and peroxy radicals are very scarce in polyethylene. The crystallinity of the

polyethylene has an effect on the intensity and lifetime of the radicals^{17,18}; the differential radical intensity between HDPE and LDPE in Figure 3 is due to the difference in the crystallinity. According to the DSC results, carbon black has no practical effect on the degree of crystallinity; therefore, the reduction of the alkyl radical concentration of HDPE/CSF-III, compared to that of HDPE, is not due to the change of crystallinity. We assume that the free radicals of polymer and carbon black can react as follows:¹²



This reaction reduces the alkyl radicals; however, it does not change the unpaired spin concentration of the carbon blacks. As a result, the alkyl radical concentration of the HDPE/CSF-III composite is smaller than that of HDPE.

Figure 3(g) and (h), respectively, shows the ESR spectra of HDPE and HDPE/CSF-III 2 months after irradiation. The radicals of HDPE vanished and the carbon black radical remained, since the free radical of carbon black is very stable.¹⁵ This experimental result supports our assumption proposed above. However, the reaction of free radicals between the polymer and carbon black may not exist in the HDPE/FEF composite, since such a free radical is not available in the carbon black [Fig. 3(a)].

Our previous works⁹ showed that the cross-linking networks of polymer restrict the freedom of movement of carbon black. The free-radical reaction enhanced the binding force between polymer and black. The restricting function and the binding force not only make the carbon blacks redistribute and to be restrained from coagulating at high temperature, but also take them back to the original dispersion state while the sample is cooled. Therefore, the PTC effect and reproducibility were improved significantly, and the NTC phenomenon vanished practically for the cross-linked HDPE/CSF-III compound. The PTC intensity of the sample increases slowly with the thermal cycle; this is due to the further cross-linking of polymer or the reaction of the polymer with carbon black. For the HDPE/FEF compound, only the NTC effect is removed due to the cross-linking structure.

Carbon Black-filled LDPE Composites

Previous experimental results⁹ showed that the effect of radiation cross-linking on the PTC intensity

of the LDPE/CSF-III compound is not remarkable, and the reason remains to be determined.

Figure 3(e) is the spectrum of cross-linked LDPE and Figure 3(f) is that of cross-linked LDPE/CSF-III compound. Contrasted with LDPE, it can be seen that the alkyl radical peak of LDPE/CSF-III decreases slightly. The ESR spectrum of the LDPE/CSF-III composite 2 months after irradiation was similar to that of HDPE/CSF-III. Consequently, we suggest that the reaction between the polymer and carbon black is weak while the sample is irradiated. The radical reaction between the matrix and filler mentioned above occurred during the processing of the composite. As is well known, the degree of crystallinity of LDPE is small and it has more branched chains. These branched chains can produce free radicals that may react with the carbon

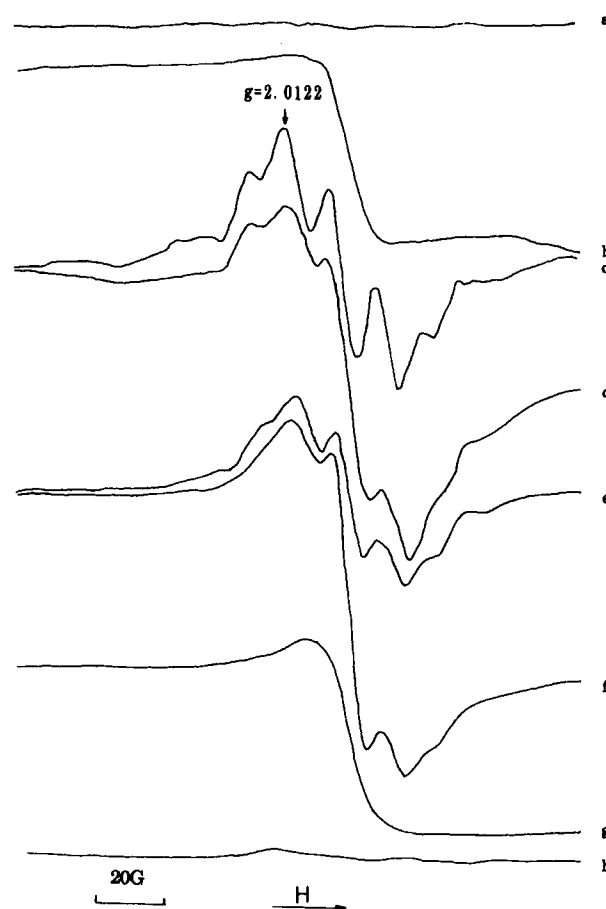


Figure 3 ESR spectra of the samples for cross-linked 0.20 MGy. The weights of the carbon black or matrix for all samples were equal. The spectra (a)–(f) were obtained 30 min after irradiation, and (g) and (h), 2 months after irradiation: (a) FEF black; (b) CSF-III black; (c) HDPE; (d) HDPE/CSF-III; (e) LDPE; (f) LDPE/CSF-III; (g) HDPE/CSF-III; (h) HDPE.

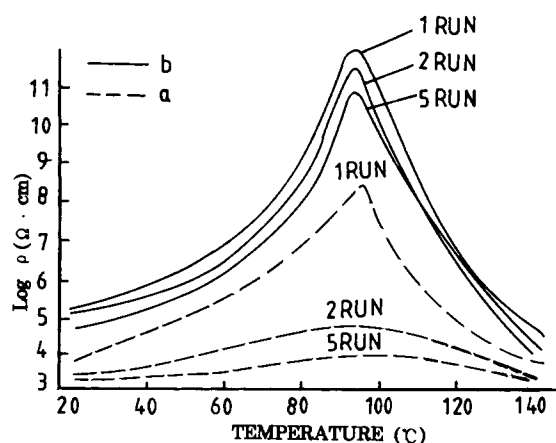


Figure 4 Resistivity-temperature curves upon heating and cooling. Five runs for LDPE/0.20 CSF-III compounds: (a) mixed for 5 min; (b) mixed for 15 min.

black or be forced into a particle void volume during the preparation process of the compound. These chemical or physical absorptions enhanced the PTC intensity and improved the reproducibility, as discussed in the previous section. Therefore, the radiation cross-linking has no significant effect on the PTC intensity of LDPE/CSF-III.

Figure 4 shows the resistivity-temperature curves of LDPE/CSF-III composites for different mixing times. It indicates that both the PTC effect and the reproducibility are improved significantly when the sample has been mixed for a long time. We attribute the improvement to the increasing absorption of the polymer on the carbon black surface. This absorption forms a "bound polymer" around the blacks, and it obstructs the conduction of particles, so that the room-temperature resistivity increases with the mixing time when the carbon black concentration is constant.

Carbon Black-filled EVA and EVA/HDPE Blend

Table III shows the effect of carbon black concentration on the gel content of cross-linked polymers.

Table III The Effect of Carbon Black on the Gel Content of Polymers (Radiation Dose, 0.14 MGy)

Polymer Matrix	HDPE				LDPE				EVA				
CB concentration (w/w %)	5	10	15	20	5	10	15	20	5	10	15	20	25
Gel content (%)	58	60	63	70	30	34	40	42	33	40	65	67	70

For HDPE and LDPE, the gel contents increase slowly with the carbon black concentration, so that we assume that carbon black must be attached to the cross-linking networks of the polymer by the interaction between them. This effect is more remarkable for the EVA/CSF-III compound, whose gel content increases greatly in relation to the carbon black concentration at which the gel content remains almost constant. According to the study results about the surface group chemistry of carbon black, the basic oxide can absorb some acidic group,¹⁹ the carboxy of EVA, and this reaction increased significantly the gel content of the matrix.

The PTC curves of cross-linked carbon black-filled vinyl polymer compounds are shown in Figure 5. The matrices are HDPE, EVA, and HDPE/EVA, respectively. In the case of the cross-linked HDPE/EVA/CSF-III compound, the PTC intensity exceeds 10^{10} , and it is greater than that of either HDPE/CSF-III or EVA/CSF-III. This phenomenon occurs because the interaction between EVA and black is stronger than that of HDPE/CSF-III and the modulus of HDPE is greater at high temperature than that of EVA, which are essentially important for compounds to have a great PTC intensity and good reproducibility.

CONCLUSIONS

The radiation cross-linking may improve significantly the reproducibility and practically decline the NTC effect for carbon black-filled vinyl polymers. The PTC intensity of the cross-linked HDPE/CSF-III compound is greatly increased due to the free-radical reaction between the polymer and carbon black during the irradiation process. This behavior has practically vanished or declined for the HDPE/FEF or LDPE/CSF-III compound. The former is because such a free radical is not available for FEF black and the latter is caused by that the free-radical reaction between the polymer and carbon black occurs during the preparation process of the compound, since there are more branched chains in LDPE and they produce easily free radicals by me-

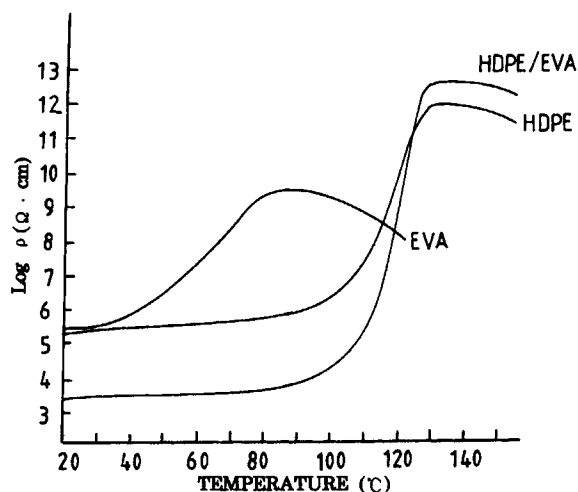


Figure 5 Resistivity-temperature curves of CSF-III-filled vinyl polymers for cross-linked 0.14 MGy. The carbon black contents are 0.16, 0.20, and 0.18 for HDPE, EVA, and HDPE/EVA, respectively.

chanical force. The PTC effect and the electrical reproducibility are improved for the compounds that were mixed for a long time during the preparation process. The increment of the "bound polymer," which is the physical and chemical absorption of the polymer on the carbon black surface, makes the room-temperature resistivity of the compound increase. The HDPE/EVA/CSF-III compound has great PTC intensity. This is because of the stronger interaction of EVA with black and the bigger modulus of HDPE at high temperature, which are essentially important for compounds to have a great PTC intensity and good reproducibility.

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