

# The Positive Temperature Coefficient Phenomenon of Vinyl Polymer/CB Composites

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## SYNOPSIS

In this paper, the results of a systematic study of carbon black (CB)-filled conducting polymer positive and negative temperature coefficient (PTC/NTC) effects are reported. The conductivity of the composites jumps by several orders of magnitude at the critical value of carbon black. This critical value,  $\phi_c$ , decreases with the increase of melt index and degree of crystallinity of the polymer. The crystalline lamellae just "modify" the distribution of carbon black and make the dispersion heterogeneous. Radiation cross-linking enhances the PTC intensity and decreases the NTC effect of the materials. The electrical reproducibility of compounds is improved by the cross-linking structure that reduces the freedom of carbon black movement at high temperature. The NTC phenomenon is related to the carbon black coagulation that facilitates electrical conduction at high temperature. The larger the melt index, the more easily carbon black coagulates. A new model was set up to explain the results successfully. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer materials in their pure state are excellent electrical insulators. However, they can become semiconducting materials when they are doped with some kinds of conducting particles (carbon black, carbon fiber, metal powder). Positive temperature coefficient (PTC) material is one kind of them. The main feature of the PTC material is that its electrical resistivity increases with the increase of temperature when the filler concentration is moderate. Sometimes the material has the negative temperature coefficient (NTC) effect, i.e., that the resistivity decreases as the temperature increases. PTC materials can be used as self-regulating heaters, current limiters, and overcurrent protectors, but the NTC effect diminishes these functions.

Many scientists have studied the manufacture of PTC materials and investigated the process of electron transport since Frydman discovered the PTC phenomenon in 1945,<sup>1</sup> but they did not establish a

satisfactory theory to explain the mechanism. Percolation<sup>2,3</sup> and the quantum mechanical tunneling effect<sup>4-6</sup> are two good models to illustrate the electron transport process. Sherman<sup>7</sup> considered the two models as a whole, to apply the percolation theory to the situation that the conducting network sets up easily when the carbon black (CB) concentration is high and the resistivity is low. When the CB concentration is low and the resistivity is high, we can apply the tunneling effect theory.

Many people found that the critical value depends on the properties of the polymer matrix and filler, but it is ambiguous which factors are directly related. Sumita and Abe found that the critical value of the filler decreases with the melt index of the matrix, but he did not consider the influence of the degree of crystallinity on the value.<sup>8</sup> Similarly, Wessling's experiments showed that the critical value is also dependent on the molecular weight of the polymer matrix.<sup>9</sup>

Many crystalline polymer/CB compounds have the PTC effect, so some scientists suggest that the degree of crystallinity has influence on the effect, but this is contradicted by Meyer.<sup>10,11</sup> His experiments show that no correlation existed between PTC

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intensity and the degree of crystallinity. The resistivity of PTC materials changes abruptly near the melting point of the polymer matrices, at which the polymer matrices have the biggest thermal expansion coefficient; therefore, some people assume that the PTC effect is due to the difference of thermal expansion coefficients of matrix and filler. There are some experiments to prove the suggestion.<sup>12</sup> Meyer<sup>10,11</sup> found that some composites have the PTC effect, but thermal expansion coefficients of the matrices are small, so he opposed the assumption mentioned above.

Many experimental results showed that electrical reproducibility of the materials during heating-cooling cycles can be improved by doping different size CB<sup>13</sup> or by cross-linking<sup>3</sup>; the latter is especially effective. A few scientists investigated the NTC effect. Klasen and Kubat<sup>14</sup> suggested that the NTC phenomenon is due to the formation of the new conduction network of CB at high temperature; however, they did not explain the process in detail.

In this paper, we report the results of a study on the PTC effect of the polymer/CB composites. The influence of melt index and degree of crystallinity of the matrix on the critical value, the effect of CB content, radiation cross-linking, and CB agglomeration on the PTC/NTC phenomenon were investigated. A model was established to explain the results.

## EXPERIMENTAL

Polyethylene polymers were used as matrices. Their melt index (MI) and degree of crystallinity are shown in Table I. They were provided by Daqing Petrochemical Factory [PE(1)–PE(3)], Yanshan Petrochemical Co. [PE(4)–PE(6), PE(8)], and Mitsuishi Petrochemical Co. [PE(7)]. CSF-III carbon black (provided by Changchun Institute of Applied Chemistry) was used as the conducting filler; its average size is 700 Å; surface area, 230 m<sup>2</sup>/g; DBP value, 280 mL/100 g, and pH value, 7–9.

Compounds were made in a Brabender at 150°C [PE(1)–PE(3)] and at 140°C [PE(4)–PE(8)]. The CBs were added when the polymers were melted

and mixed for 5 min and roll-milled for 5 min at the same temperature for 24 h to make the CB particles have a good dispersion state. The samples were compression-molded to approximately 1.0 mm-thick sheets and some of them were irradiated with a <sup>60</sup>Co-rays. Electrical resistivity was measured with a digital multimeter when it was lower than  $2 \times 10^7$  and a ZC-36-type meter was used when the resistivity exceeded  $2 \times 10^7$ . The heating rate was 2°C/min and the samples were cooled in air.

## RESULTS AND DISCUSSION

### I. The Effect of Melt Index and Degree of Crystallinity on the Critical Value

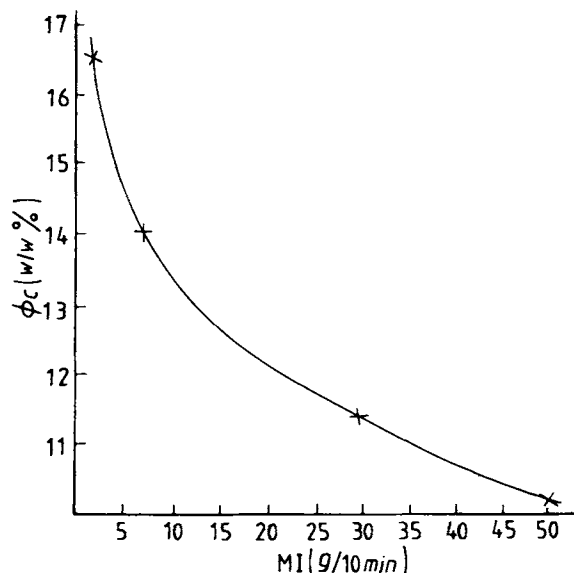
The resistivity of a composite conducting polymer depends critically on the weight fraction of the CB  $\varphi$ . For low values of  $\varphi$ , the resistivity of the composite is basically that of the polymer matrix. At some critical value  $\varphi_c$ , however, the resistivity drops precipitously by many orders of magnitude. This is known as the percolation threshold. Above  $\varphi_c$ , the resistivity then approaches monotonously the resistivity of the CB.

The plot of critical value  $\varphi_c$  (w/w %) of the CB vs. the melt index of the polymers is shown in Figure 1. The degrees of crystallinity of the matrices are nearly the same. We can see that  $\varphi_c$  decreases with the melt index of the matrices.

The transmission electron micrographs of CB show that several or tens of particles align to form aggregates when CB is at a free state.<sup>15</sup> The aggregates were broken up gradually by the shear force of the matrix while the compounds were prepared at high temperature. The longer the length of the process, the better the CBs distribute. When the preparation time remains constant, the degree of dispersion depends on the shear modulus of the polymers. At the same time, because of the force of van der Waals and the covalent bonds among some particles,<sup>16</sup> the CBs have a tendency to agglomerate. Decreasing of the shear modulus of the polymers preserved more of the CB aggregates and some CBs reaggregate easily in the preparation process. As

**Table I** Melt Index and Degree of Crystallinity of the Polyethylene Matrices Used

	PE (1)	PE (2)	PE (3)	PE (4)	PE (5)	PE (6)	PE (7)	PE (8)
Melt index (g/10 min)	2.0	2.0	2.0	2.0	2.0	8.0	30.0	50.0
Degree of crystallinity (%)	70.6	57.0	50.0	39.0	30.5	30.0	29.0	28.3



**Figure 1** Relation between the critical CB content and the MI of the polymer. The four matrices are of PE(5), PE(6), PE(7), and PE(8).

a result, a more segregated distribution of CB was formed, and this distribution facilitates the electrical conduction. Therefore,  $\phi_c$  decreases with the melt index of the matrices.

Figure 2 exhibits the effect of the degree of crystallinity of the polymer on the  $\phi_c$ . The melt indexes of the matrices are the same. From Figure 2 we can see that  $\phi_c$  decreases slowly with increase of the degree of crystallinity.

As is well known, the CB disperses in the amorphous region of the crystalline polymer and the filler could not penetrate the crystalline; therefore,  $\phi_c$  decreases as the degree of crystallinity increases. As mentioned above, the distribution of CB in the amorphous region is heterogeneous or segregated. Like crystalline areas, some amorphous regions remain unperturbed, and CBs just disperse around these regions. The increasing of the degree of crystallinity leads to a more heterogeneous distribution; however, the decrement of  $\phi_c$  is not directly proportional to the increment of the degree of crystallinity. The crystalline lamellae just "modify" the distribution of the CB, and this modified function is remarkable when the degree of crystallinity exceeds 40%.

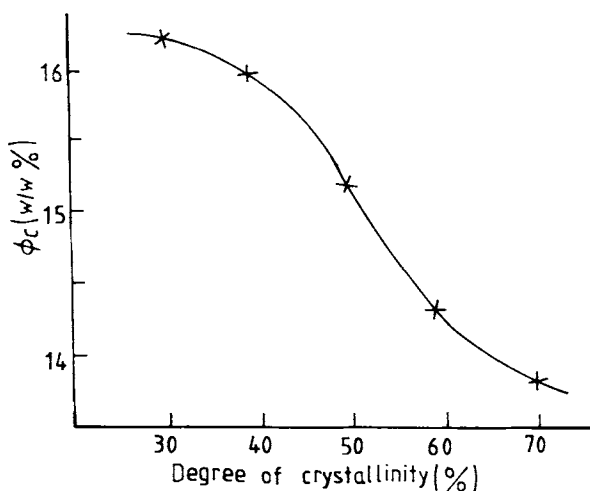
## II. The Effect of Cross-linking on PTC Intensity and Electrical Reproducibility

The effect of radiation cross-linking on PTC intensities (the ratio of peak resistivity to resistivity at

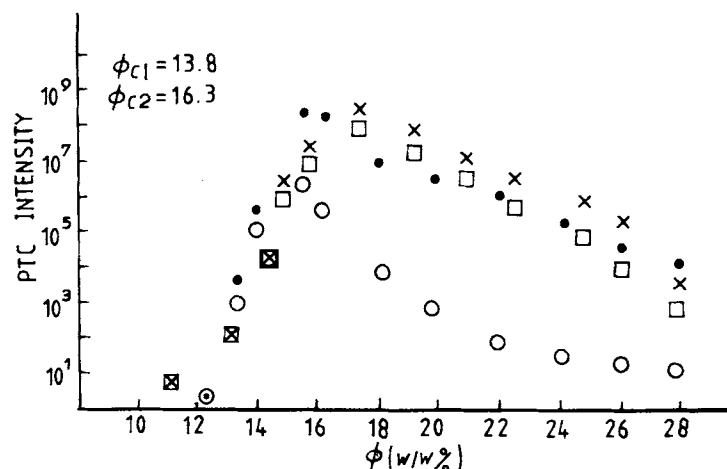
room temperature) vs. CB content (w/w %) for PE(1)/CB and PE(5)/CB composites are shown in Figure 3.

The maximum PTC intensities occur at the CB concentration that is slightly larger than the critical value, at which maximum PTC intensities appear according to Narkis et al.'s<sup>13</sup> results. For the PE(1)/CB composite, the radiation cross-linking enhanced the PTC intensity, especially at a high content of carbon black. The increase of the PTC intensity is caused by the reactions of free radicals of polymer with the chemical groups of CB.<sup>17</sup> The covalent bonds enhanced the binding force between polymer and CB. Figure 4 shows the resistivity-temperature curves of PE(1)/CB compounds for various radiation doses. The PTC intensities increase significantly up to the radiation dose at which PTC intensities remain almost constant, and most of the chemical groups of carbon black have been reacted with the free radicals of the polymer. For the PE(5)/CB compounds, however, the effect of cross-linking on the PTC intensities is faint. Perhaps this is because that the degree of crystallinity of PE(5) is smaller than of PE(1), so PE(5) has more branched chains that produce free radicals or are forced into the inter- and intraparticle void volume easily during the preparation of the compounds. Therefore, both the chemical and physical adsorptions of polymers on the carbon black surface are increased compared with the PE(1)/CB compound.

Narkis et al.'s results showed that the effect of peroxide cross-linking significantly increases the resistivity (which is caused by the deactivation of the CB surface) and reduces the PTC effect.<sup>18</sup> How-



**Figure 2** Plot of the critical CB content against the degree of crystallinity of the polymer. The five matrices are of PE(1)–(5).

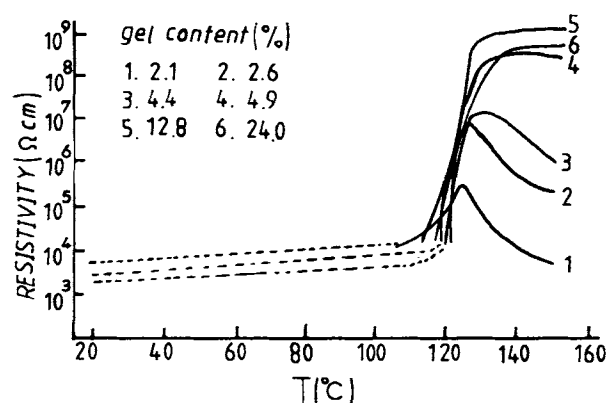


**Figure 3** The effect of radiation cross-linking on PTC intensities vs. CB content  $\phi$ : (○) PE(1)/CB thermoplastic; (●) PE(1)/CB cross-linked for 0.14 M Gy; (□) PE(5)/CB thermoplastic; (X) PE(5)/CB cross-linked 0.14 M Gy.

ever, the change of PTC intensity is not significant for radiation cross-linking materials. Perhaps it is because that most of the chemical groups reacted with the free radicals of polymer during the preparation process or that the CBs have no such chemical groups. The effect of radiation cross-linking on the PTC intensity depends on the properties of polymer and CB.<sup>17</sup>

The cross-linking structure not only enhances the PTC intensity of the compound, but also improves the electrical reproducibility and declines the NTC effect of the composites. For the PE(5)/CB composites, this effect is shown in Figure 5. It is obvious that PTC intensity decreases as the time of thermal cycling increases for the thermoplastic compound, in which the CB align easily to form conducting

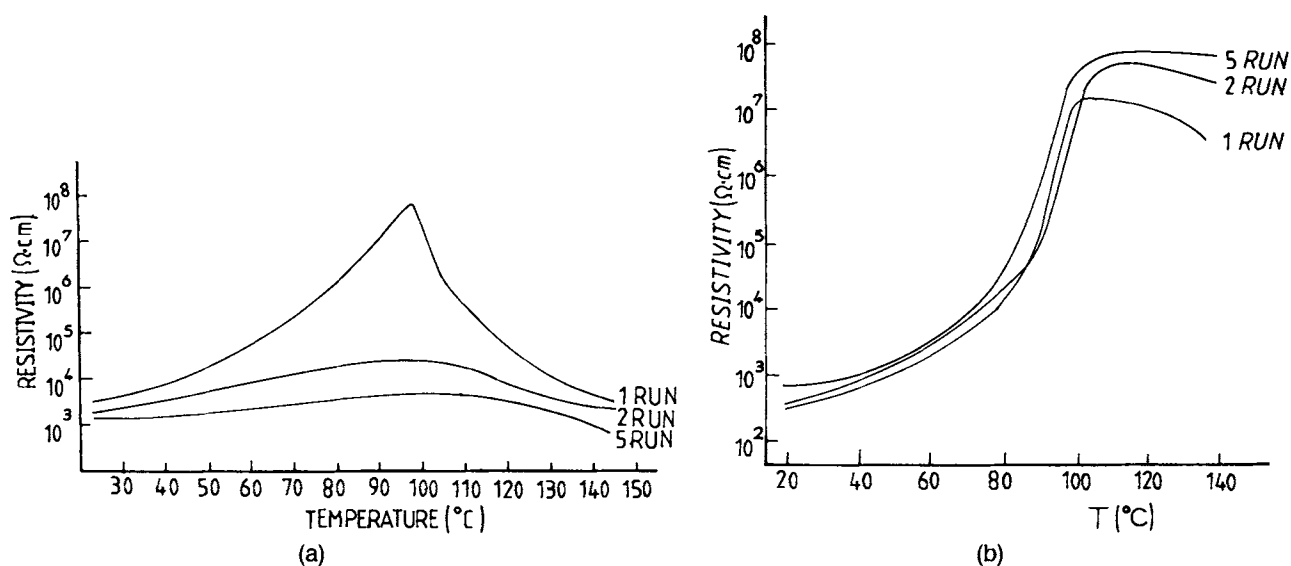
channels. However, the reproducibility is well improved and the NTC effect decreases for the cross-linked compound. These results are due to the effect that cross-linking enhances the shear modulus of polymers and that CBs are strongly attached to cross-linked polyethylene networks. This strong attachment to cross-linked networks is, thus, expected to reduce the freedom of movement of carbon particles at high temperatures, including at the melting region, which is of concern for the PTC/NTC phenomena, especially at noncrystalline region in which the CB is dispersed. This restricting function not only makes the CBs redistribute during the movement and expansion of the matrix at high temperature, but also takes the particles back to the original positions while the sample is cooled. We will prove the existence of this effect in the next part.



**Figure 4** Schematic representation of resistivity-temperature curves of PE(1)/20 CB (w/w %) samples for various degrees of cross-linking.

### III. The Effect of Carbon Particle Agglomeration on Electrical Resistivity

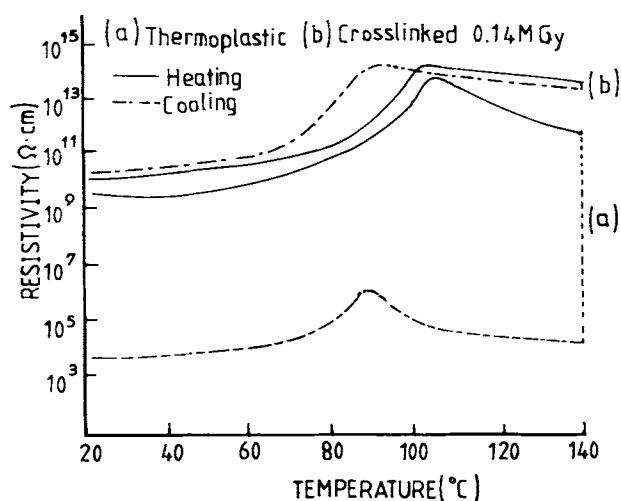
The PTC effect is caused by the melting of the crystallinity and the expanding of the polymer matrix; the NTC effect is due to the CB reagglomerating at high temperature. Figure 6 shows the  $\rho$ - $T$  curves of PE(5)/13.0% (w/w) CB compound at the first thermal cycle. For the thermoplastic compound, the resistivity is high in the course of heating because the CB content is lower than that at the critical value; CB cannot form the conducting networks at room temperature before the thermal cycle. When the sample was kept for a while at 140°C, the viscosity of the polymer matrix was lower, so the CBs align to form conducting networks that remain in



**Figure 5** Reproducibility of resistivity-temperature curves upon repeated temperature cycling for PE(5)/25 CB (w/w %): (a) thermoplastic; (b) cross-linked 0.14 M Gy.

the cooling process and the resistivity decreases abruptly.

Table II shows the forming time of the conducting networks at 120°C for various polymer matrices. The level at which CB concentration deviates from the critical value is  $\frac{1}{4}$ . The deviation level,  $X_d$ , is defined as  $(\varphi_c - \varphi)/\varphi_c$ , where  $\varphi$  is the CB content and  $\varphi_c$  is the critical value. From Tables I and II, we can conclude that the time decreases with the increase of melt index. We assume that the movement of carbon particles is controlled by the viscosity of the matrix. For the same polymer matrix, the time increases with the  $X_d$ .



**Figure 6** Resistivity-temperature curves during first heating/cooling cycle for PE(5)/13.0 (w/w %) CB compound.

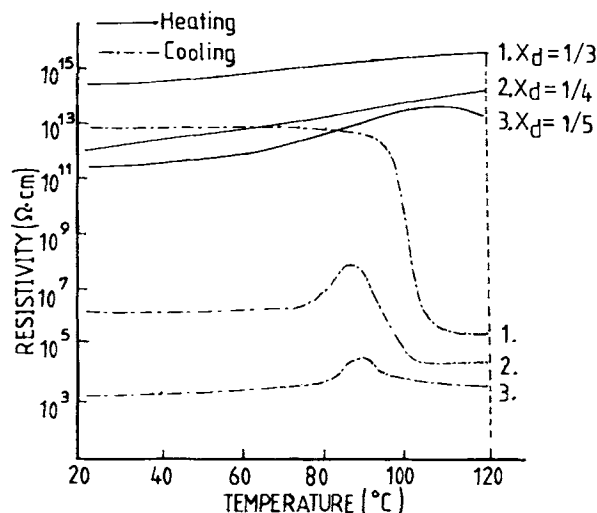
The stability of the conducting network that is formed by the agglomeration of carbon particles depends on both the degree of crystallinity of the polymer,  $D_c$ , and the  $X_d$  value. The network is stable if both  $D_c$  and  $X_d$  are small. Figure 7 shows the  $\rho$ - $T$  curves of the PE(5)/CB composites for various  $X_d$  during the first heating-cooling cycle. According to the results of the differential scanning calorimetry (DSC), the temperature of polymer PE(5) crystallization is from 98 to 85°C, at which region the resistivity changes abruptly in the cooling process. We suggest that the moving of the polymer chains, which is caused by the crystallization, breakdowns the conducting network that is formed at high temperature. The effect is more powerful for the composite in which  $X_d$  is large because the density of the conducting network that was formed at high temperature is low. However, it is not remarkable for the sample in which CB content is near the critical value.

From Figure 6(b) we found that the resistivity-temperature curves of heating and cooling nearly coincide for cross-linked PE(5)/13.0% (w/w) CB compound. It indicates that the carbon particles are bound significantly by the cross-linked networks.

As has been noted, we could conclude that the

**Table II** Formation Time of Conducting Network ( $\rho = 10^3 \Omega \text{ cm}$ ) at 120°C for Different Matrices ( $x_d = 1/4$ )

Matrix	PE (5)	PE (6)	PE (7)	PE (8)
Time (min)	45	30	15	10



**Figure 7** Resistivity-temperature curves during first heating/cooling cycle of PE(5)/CB composites for different CB content.

CBs cannot penetrate the crystalline lamellae, even at high temperature. As a result, the assumption that CBs distribute in the “crystalline region” at high temperature, which is proposed by many authors<sup>19</sup> to explain the abrupt change of resistivity near the melting point, is in doubt. We suggest that the precipitous change of electrical resistivity is due to the expansion and the movement of the crystalline lamellae or amorphous regions around which CB particles distribute. The enlargement of the distance between two particles causes the conducting network to be broken up. However, this model remains to be confirmed by further experiments.

## CONCLUSIONS

1. Carbon black-filled polyethylene composites have a strong PTC effect, and the critical value depends on both the melt index and degree of crystallinity of the polymers.
2. The maximum PTC intensity occurs at the CB concentration that is slightly larger than the critical value  $\varphi_c$ . The radiation cross-linking enhances both the PTC intensity and the electrical reproducibility of the CSF-III CB-filled polyethylene.

3. The NTC phenomenon is caused by the agglomeration of the carbon particles. The time needed for conducting networks to form is decided by the polymer matrix viscosity and the CB content. The stability of the network depends on the concentration of CB and the degree of crystallinity of the polymer.

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