# High-Density Polyethylene/Carbon Black Conductive Composites. I. Effect of CB Surface Modification on Its Resistivity–Temperature Behavior

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**ABSTRACT:** The effect of the interaction between a polymeric matrix and conductive particles of carbon black (CB), especially the interaction enhanced by oxidizing CB (o-CB), on the resistivity–temperature behavior of its composites was studied. The results reveal that the interaction between ethylene-vinyl-acetate and CB is stronger than that between high-density polyethylene and CB. The room temperature resistivity of the o-CB filled system subsequent to thermal cycles increases to a lower extent in comparison with those filled with virgin CB. Moreover, the resistivity decrease of composites filled with o-CB needs a longer time than that of the virgin CB filled system during isothermal annealing, meaning that the resistivity–temperature behavior of the former is much more stable than that of the latter. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 3112–3116, 2002; DOI 10.1002/app.10049

**Key words:** resistivity–temperature behavior; surface modification; carbon black; polymeric positive temperature coefficient composites

## INTRODUCTION

The resistivity–temperature behavior of semicrystalline polymeric composites filled with carbon black (CB) exhibits a positive temperature coefficient (PTC) effect in the polymer melting region.[1,2] It is well known that the PTC effect strongly depends on the specific type of conductive filler and characteristics of the polymers including the chemical structure, crystallization, processing conditions, and thermal history to which they were exposed. However, these PTC materials show poor reproducibility of resistivity during a long period of time or when undergoing thermal cycles, which is due to the varying dispersion of CB particles in the composites. In essence, the dispersion is driven and controlled by dispersion forces and the interfacial interaction between the polymer and CB.[3] Gubbels et al.[4] successfully reduced the percolation threshold of CB filler in incompatible polymer blends through controlling the interfacial energy. Wessling[5] and Miyasaka et al.[6,7] involved the reducing percolation threshold through the dynamic boundary model and surface tension, respectively. Many authors[8,9] also studied the effects on the PTC behavior but seldom reported the reproducibility

of electrical properties in view of the interfacial interaction function.[8] On the other hand, it is necessary to avoid as much as possible the negative TC (NTC) effect, which is induced by rearrangement of conductive fillers in low viscous polymer melts, following the PTC anomaly.

The present article reports on the study of the effect of the interaction between polymers and fillers on the reproducibility of the resistivity–temperature behavior of vinyl polymer composites filled with CB during thermal cycles by using oxidized CB (o-CB).

## EXPERIMENTAL

Composites were prepared by mixing high-density polyethylene (HDPE2480, Qilu Petro. Co.) or ethylene vinyl acetate (EVA) with CB (acetylene black, Chun'an Chemical Co.) or o-CB in a Bandury mixer at 170°C for 15 min and then mixing again on a two-roll mill under the same conditions. Plates molded at 170°C for 10 min were tailored into $1.0 \times 2.0 \times 0.2$ cm$^3$ samples. The o-CB was prepared by oxidizing acetylene black with 65% (aq.) nitric acid for 12 h and then washing with distilled water. The measurements of the resistivity–temperature behavior were conducted with a computer-controlled apparatus of design.[10] Characterization of the isothermal resistivity–time behavior was carried out in a temperature-controlled hot box.

## RESULTS AND DISCUSSION

We defined the ratio of the maximum resistivity ($\rho_{max}$) to the room temperature resistivity ($\rho_{RT}$) as
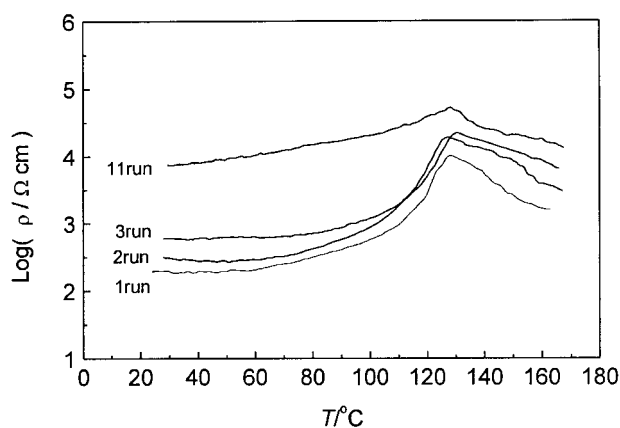


**Figure 1** The resistivity–temperature behavior of HDPE/EVA (2 : 1)/CB (65/35) composites during thermal cycles.
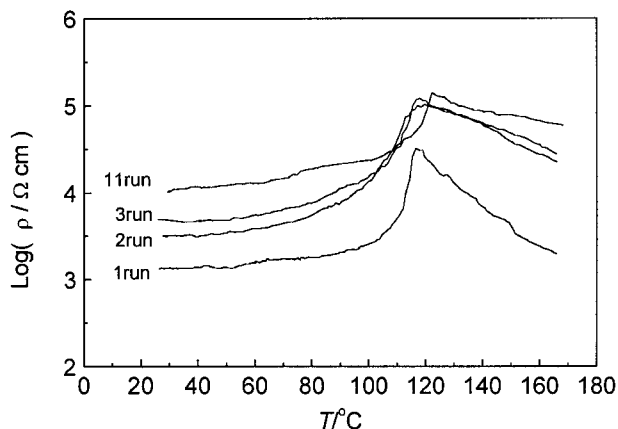


**Figure 2** The resistivity–temperature behavior of HDPE/EVA (2 : 1)/o-CB (65/35) composites during thermal cycles.

the PTC intensity ($I_{PTC} = \rho_{max}/\rho_{RT}$). It can be found that the resistivity of the virgin CB and o-CB filled systems at temperatures below the PTC–NTC transition point shifts upward with the increase of thermal cycles, meaning the decrease of the PTC intensity, as shown in Figure 1 and Figure 2. The increase of the $\rho_{RT}$ for the o-CB filled systems is believed to be the result of a decrease in the intrinsic conductivity of CB for high volatility.[11] For a polymeric matrix containing a polar component (e.g., EVA), the resistivity–temperature behavior of this conductive composite is different from those consisting of HDPE, because of the enhanced interaction between CB and EVA, especially for the system filled with o-CB. After 11 cycles only a slight PTC anomaly is observed for the virgin CB filled system whereas a relatively higher PTC intensity for the o-CB filled system can be found.

It is well known that the PTC characteristic of the conductive composites deals with the thermal history that they underwent. In other words, the PTC behavior of these materials would change when undergoing heating and cooling cycles under various applied conditions. The $\rho_{RT}$ is considered as a fatal parameter to determine the availability of the composites. Hence, it is very important to study the $\rho_{RT}$ during or after thermal cycles. In our study the thermal process was set from room temperature to 170°C at 2°C/min. Figure 3 shows the plots of the resistivity at 30°C for each run versus the number of thermal cycles. It can be found that after six runs the resistivity and PTC intensity approach is unchanged for all composites. Similarly, Figure 3 also indicates the PTC
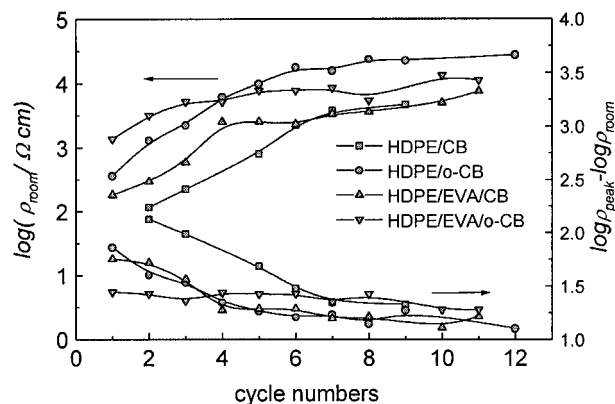
**Figure 3** The variance of the room temperature resistivity and PTC intensity for composites filled with CB or o-CB during thermal cycles.

intensity variation versus the number of thermal cycles of the composites. The $I_{PTC}$ decreases markedly before six runs for CB filled composites, but it appears unchanged after six runs. Especially for the HDPE/EVA composites filled with o-CB, the $I_{PTC}$ is almost unchanged during all the cycles. It is suggested that the stability of the electrical properties results from the interaction between the polar polymer component and the CB, in particular o-CB.

The interfacial interaction between the polymer and CB fillers could exert a marked influence on the dispersion state of CB particles in the composites. Moreover, CB particles are easily moved away from their original positions because of the rejection function of spherulites during their formation and growth.[12] Although the agglomeration and alignment of CB are irreversible under elevated temperature, they could be broken up in the next thermal cycles. When undergoing further thermal cycles, the dispersion of CB particles approaches a uniform state in the matrix that is driven by interfacial energy.

Polymer–CB interaction involves factors such as the absorption of polymer chains on the surface of the CB and the chemical reactions of CB with the polymer. The oxidation could change the surface structure and the surface energy of the CB particles. It is well known that many polar groups exist on the surface of CB particles, which have a weak interaction with nonpolar HDPE of about a few kilocalories per mole of polymer.[13] The CBs are wetted mainly by the physical absorption of HDPE, and the chemical reaction or covalent bonds could exist between the surface of the CB (especially o-CB) and the polar polymeric matrix

(EVA).[14] The enhanced interaction in this composite restricts not only the aggregation of CBs but also the mobility of the absorbed polymer chains. Thus, the slight variation of the resistivity of the composites as shown in Figure 2 is believed to be the result of the reduced aggregation of o-CBs compared to that of virgin CB as shown in Figure 1.

Concerning the relationship between the resistivity decrease during isothermal annealing and the agglomeration of CB particles, the resistivity–temperature behaviors at two different temperatures were investigated. The results presented in Figure 4 show a much more obvious decrease of the resistivity with time for the virgin CB filled system than that for the o-CB filled system. The resistivity decrease with time relevant to the resistivity relaxation can be expressed by[15]

$$(\rho - \rho_\infty) = (\rho_0 - \rho_\infty)\exp\left(-\frac{t}{\tau}\right) \tag{1}$$

where $t$ is time and $\rho_0$ and $\rho_\infty$ represent the resistivity at $t = 0$ and $t = \infty$ (equilibrium state), respectively. The relaxation time ($\tau$) can be given as

$$\tau = \tau_0 e^{(\Delta E/RT)} \tag{2}$$

where $\tau_0$, $\Delta E$, $R$, and $T$ are a constant, activation energy, gas constant, and absolute temperature, respectively. The $\Delta E$ could be calculated at two different temperatures by the following equation:
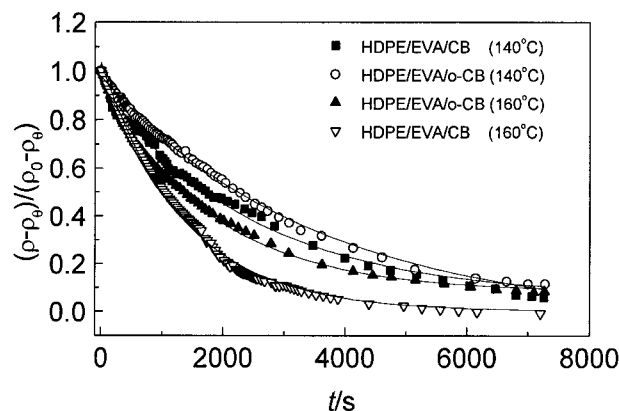


**Figure 4** The resistivity–time behavior of HDPE/EVA composites filled with CB or o-CB during isothermal heating.

**Table I  Relaxation Time and Activation Energy of Composites at 140 and 160°C**

| Composites | HDPE/EVA/CB | HDPE/EVA/o-CB |
|---|---|---|
| Relaxation time (s) at | | |
| 140°C | 2435.3 | 3468.4 |
| 160°C | 1358.9 | 1786.1 |
| Activation energy (kJ) | 43.4 | 49.3 |

$$\Delta E = \frac{R \ln \frac{\tau_1}{\tau_2}}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (3)$$

The results given in Table I show that filling with o-CB increases the activation energy of the composites. Based on Figures 3 and 4 and Table I, we owe the resistivity decrease with time to the agglomeration of CB particles in the polymer, which are involved in the different activation energies of the composites.

The resistivity increase of the samples undergoing thermal cycles is related to the variation of the dispersed state of CB particles in the composites. In other words, thermal cycles reduce the conductive pathways that are generally determined by the volume fraction. The percolation phenomenon of a polymeric matrix containing conductive fillers depends on the volume fraction of filler. Figure 5 presents the resistivity percolation curves for each composite. We used the con-
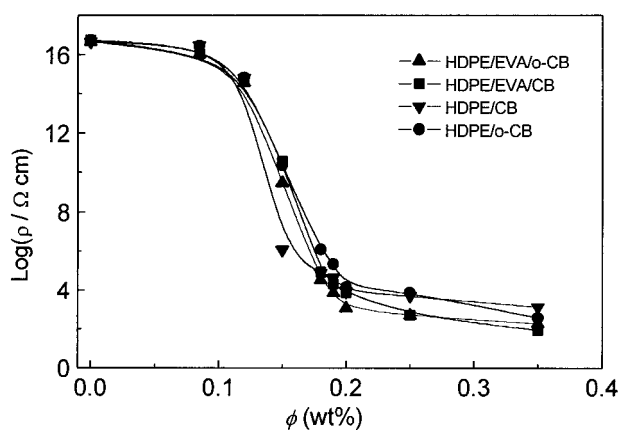


**Figure 5** The resistivity versus the CB content (percolation curves) of HDPE and HDPE/EVA (2 : 1) composites filled with CB or o-CB.
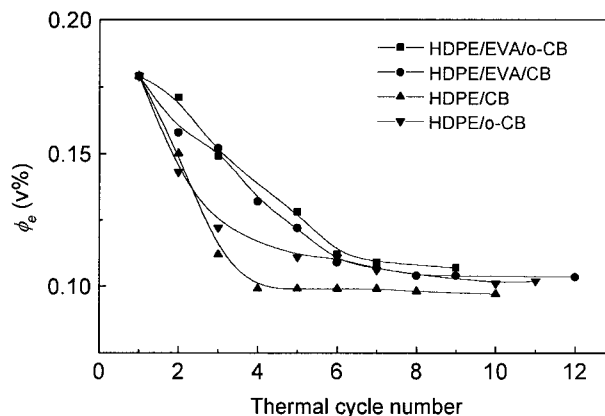


**Figure 6** The effective volume fraction of CB in the composites after thermal cycles.

version of the variation of resistivity during thermal cycles according to percolation curves to obtain the relationship between the effective volume fraction of CB devoted to the formation of conductive pathways and the number of thermal cycles as presented in Figure 6. It is obvious that the effective volume fraction decreases with the increase of the number of thermal cycles for HDPE filled with CB, as well as o-CB. In comparison, HDPE/EVA composites filled with CB, especially with o-CB, exhibit a slight decrease of them. Thus, we believed that the much better stability of the electrical properties for HDPE/EVA filled with CB or o-CB than that for HDPE filled with CB is attributed to the interaction enhanced by the better adhesion of the interface between CB and EVA. As a result, the interaction between the HDPE matrix and CB, in particular o-CB, is promoted. Additionally, when the CB (or o-CB) content is less than 35%, the PTC intensity increases according to our previous work.[14] However, the PTC intensity decreases because of the uniform dispersion of CB particles in the composites after thermal cycles, as shown in Figure 3.

## CONCLUSION

The interaction between CBs and polymeric matrices played a major role in the electrical properties. Oxidization of CB and the addition of a polar polymeric component increased the activation energy of the composites. The variation of the resistivity–temperature behavior during thermal cycles was believed to be the result of the dispersion of CB particles in the matrix that was driven

by the activation energy. An improved reproducible resistivity of the composites was obtained through increasing the activation energy.

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