

# Resistivity–Volume Expansion Characteristics of Carbon Black-Loaded Polyethylene

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**ABSTRACT:** The resistivity and volume expansion of carbon black (CB)/high-density polyethylene (HDPE) composite with different CB volume fractions at different temperatures were measured simultaneously. A model based on Meyer's theory is proposed to explain the positive temperature coefficient resistance (PTCR) effect. The relationship between resistivity and volume expansion was determined. It was found that the phase change is the main cause of the PTC effect in the crystalline polymer PTC materials. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 53–58, 2000

**Key words:** carbon black; high-density polyethylene; volume expansion; positive temperature coefficient resistance

## INTRODUCTION

As carbon black or metal fillers are loaded in a polymer matrix over their critical volume fractions, the composites become electrical conductor at room temperature<sup>1</sup> and exhibit a strong positive temperature coefficient (PTC) effect on approaching the melting point of the matrix.<sup>2</sup> Because of the industrial importance of PTC materials, considerable work has been done on developing a valid theory for the composite PTC mechanism. To date, three models have been proposed by Kohler,<sup>3</sup> Ohe,<sup>4</sup> and Meyer<sup>5,6</sup> to interpret the PTC phenomenon.

Kohler<sup>3</sup> suggests PTC mechanism is a function of the differences in thermal expansion of the materials. He proposes that, as the material is heated, the conductive particles are separated,

and thus increase the resistance. The cause of the anomaly of resistance increases is assumed to be the sudden expansion of the polymer at the crystalline melting point. However, this theory does not explain the very small rise in resistance exhibited by such filled polymers when they are strained to an amount equivalent to that found at the crystalline melting point, nor does it explain why filled amorphous polymers do not, in general, show an increase in resistance upon heating. Furthermore, according to this theory, the resistance rise should be a direct function of the volume change; however, many experiments show that the volume expansion can only be used to explain the PTC effect partially.

Ohe<sup>4</sup> suggests a complex mechanism where the resistivity of the materials is mainly due to the difficulty of electron tunneling through intergrain gaps between the conductive particles. He proposes that the PTC phenomenon can be explained by the change of intergrain gaps distribution rather than the thermal expansion of the poly-

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mer. He suggests that at low temperatures the distribution of the intergrain gaps is comparatively uniform, and the gap width is small enough for extensive tunneling to occur. However, at high temperatures he feels that distribution becomes random due to thermal expansion, although the average gap width is not greatly changed. Ohe's theory is mathematically the most developed. However, there is no explanation yet for why there shall be a change from a uniform to a non-uniform distribution of carbon black in the polymer matrix close to the melting point.

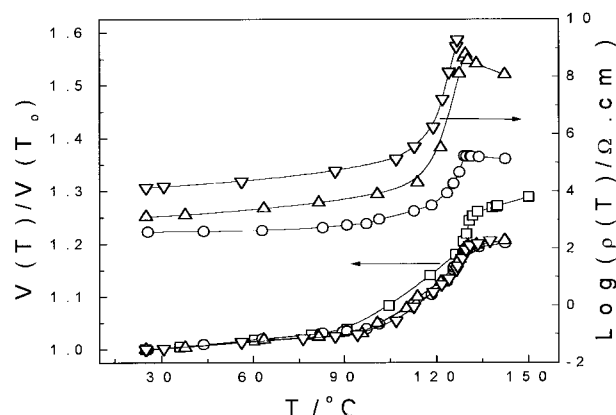
The theory of Meyer<sup>5,6</sup> depends on the assumption that thin (300 Å) crystalline films of polymer are significantly better conductors than amorphous films of the polymer. It has been shown, by microscopic investigation, that when a crystalline polymer is melted and loaded with finely divided conductive particles, upon cooling the particles are swept by advancing crystallite fronts into the amorphous regions between crystallites. Some authors<sup>7,8</sup> also suggest that the CB particles are mostly restricted to the amorphous phase. The high conductivity of such materials is assumed to be due to tunneling through the thin crystallites in a fashion similar to Schottky emission. This theory explains most of the properties displayed by PTC materials. However, it rests on an assumption that thin films of crystalline polymers are highly conductive. Although this has been demonstrated by Myoshi,<sup>9</sup> it has been disputed by other authors.

Despite considerable effort, there is yet no consensus of the mechanism of the PTC effect. However, all of these theories suggest that the volume expansion plays an important role in the PTC effect. Furthermore, the known methods determining the relationship of resistivity-temperature, voltage-current, and dielectrics-temperature usually do not involve the volume expansion directly, and the experiments on the volume expansion of the composites have been rarely reported.<sup>5</sup>

In this article, we simultaneously measured the volume expansion and resistance of HDPE/CB composites with temperature. A model based on Meyer's theory was proposed to explain the PTC effects quantitatively.

## EXPERIMENTAL

The composite's matrix was high-density polyethylene (HDPE 2480, density = 0.942 g/cm<sup>3</sup>, MI



**Figure 1** Simultaneously measured resistivity-volume expansion-temperature relation of the composites: (□) HDPE; (○) 16.0  $V_t$  % CB; (△) 11.9  $V_t$  % CB; (▽) 9.93  $V_t$  % CB.

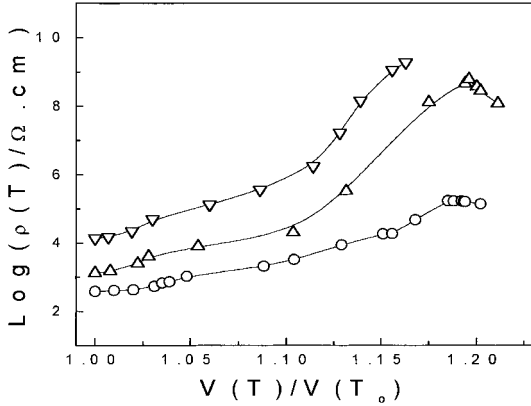
= 0.14 g/10 min, Qilu Petro. Co., China). The conductive filler was CB (acetylene black, average diameter = 43 nm, Chun'an Chemical Co., China). Other components include antioxidant, anti-copper agent, BaSt<sub>2</sub> and ZnO. They were mixed in a Bandury type mixer at 170°C for 15 min, then milled in roll-mill at the same conditions, and subsequently molded to get 2.0 mm thick sheets. Samples were cut into 3.0 × 1.0 × 0.2 cm<sup>3</sup> in size.

Crystallinity of the composites was investigated by a Perkin-Elmer DSC-7. The scanning rate was 10°C/min.

To eliminate the different thermal history and exclude the air in the sample, each sample was put into silicone oil, then heated to 160°C at 2.0°C/min, and subsequently cooled to room temperature at 2.0°C/min. The resistance and volume expansion of samples were simultaneously measured with temperature by using a special device.<sup>10</sup> Resistance was measured with a digital multimeter (M8908+). Copper net was used for electrical contacts. Volume change with temperature was determined by a dilatometer. The heating rate was 0.5°C/min.

## RESULTS AND DISCUSSION

Figure 1 shows the simultaneously measured resistivity and volume of CB/HDPE composites in different CB volume fractions with temperature. The resistivity-temperature and volume-temperature relations all show an abnormal increase during the melting ranges. It suggests that the



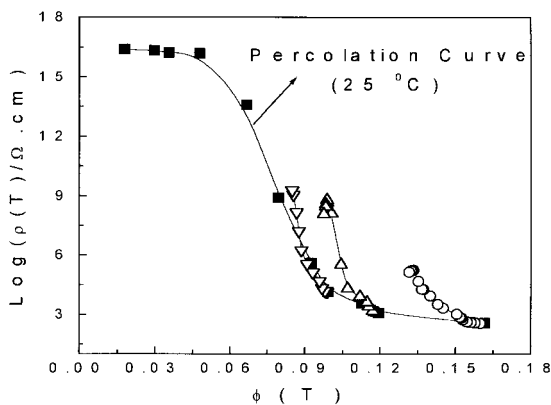
**Figure 2** Plot of resistivity against the volume expansion: (○) 16.0  $V_t$  % CB; (Δ) 11.9  $V_t$  % CB; (▽) 9.93  $V_t$  % CB.

volume expansion of composites is an important reason for the PTC effect. By eliminating the parameter  $T$ , the dependence of resistivity on volume expansion was given in Figure 2. In the range of small volume expansion, resistivity shows linear dependence on volume expansion. However, in the larger volume expansion region, the linear rule is deviated. This may be reasonably attributed to the melting effect of the crystalline phase.

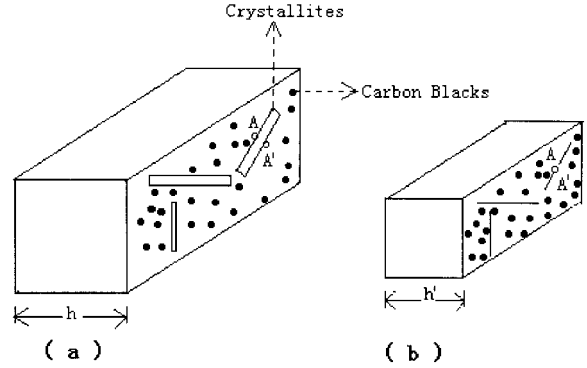
The CB volume fraction at temperature  $T$  is given by eq (1), supposing that the CB particles disperse evenly in the polymer matrix.

$$\phi(T) = \phi(T_0) \times [V(T_0)/V(T)] \quad (1)$$

where  $\phi$  is the CB volume fraction in the CB/HDPE composites, and  $V$  is the volume of CB/HDPE composites.



**Figure 3** Plot of resistivity against the CB volume fraction compared with percolation curve: (○) 16.0  $V_t$  % CB; (Δ) 11.9  $V_t$  % CB; (▽) 9.93  $V_t$  % CB.



**Figure 4** Schematic representation of conductive model: (a) the composite and (b) the “compressed-composite.”

The  $\rho(T) - \phi(T)$  relation and the percolation curve ( $25^\circ\text{C}$ ) are given in Figure 3. This shows that the volume expansion is not the only reason of the PTC effect.

### A MODEL FOR THE PTC EFFECT IN CRYSTALLINE POLYMERS

For the CB/HDPE composites, we supposed that: (1) CB fillers are restricted to the amorphous phase and scattered between crystallites; (2) thin crystalline films of polymer are significantly better conductors than amorphous films; (3) resistivity ( $\rho$ ) of a specific CB filled noncrystalline polymer is determined by the CB volume fraction ( $\phi$ ) and distribution ( $\psi$ ) in polymer matrix. That is,

$$\rho = f(\phi, \psi); \quad (2)$$

and (4) upon heating, the CB distribution in a crystalline region remains unchanged below the melting point because the viscosity is very high.

Supposed that the crystalline films have much lower resistance than that of amorphous films, and correspondent points A, A', as showed in Figure 4(a), can be put together, as showed in Figure 4(b). Then the composite's resistance ( $R$ ) will not be greatly changed, and shall be almost equal to the resistance ( $R'$ ) of a “compressed composite” (defined in Fig. 4).

$$R' \cong R \quad (3)$$

If the volume fraction of crystalline phase in the composite is  $\phi_c$ , and the crystallites are dis-

tributed evenly in the composite, we can have the following equation.

$$\frac{V}{V'} = \frac{S}{S'} = \frac{h}{h'} = 1 - \phi_c \quad (4)$$

$V$ ,  $S$ , and  $h$  are volume, cross-section area, and thickness of the composite, respectively;  $V'$ ,  $S'$ , and  $h'$  are volume, cross-section area, and thickness of the ‘‘compressed composite,’’ respectively.

As the ‘‘compressed composite’’ can be seen as an amorphous materials, combining eq. (4) and assumption 3 and 4, the resistivity of the composite ( $\rho$ ) can be written as:

$$\rho = \rho' = f(\phi') = f(\phi/(1 - \phi_c)) \quad (5)$$

where  $\rho'$  is the resistivity of the ‘‘compressed composite,’’ and  $\phi'$  is the CB volume fraction of the ‘‘compressed composite.’’

Because CB is supposed to disperse in the amorphous phase,  $\phi/(1 - \phi_c)$  is just the CB volume fraction in the amorphous phase. According to eq (5), we can say that the resistivity of a composite is a function of the CB concentration if distribution ( $\psi$ ) in the amorphous polymer phase remains unchanged.

When the temperature rises from the room temperature  $T_0$  to temperature  $T$ , the composite will undergo a linear thermal volume expansion in the low-temperature range. In the higher temperature range, however, this linear relation between volume and temperature is not present because of the melting of the crystalline phase. Considering these two facts, the resistivity,  $\rho(T)$ , at temperature  $T$  can be written as:

$$\begin{aligned} \rho(T) &= f\left(\frac{\phi(T_0)}{1 - \phi_c(T_0)} \times \frac{V_a(T_0)}{V_a(T)}\right) \\ &= f\left(\frac{\phi(T_0)}{1 - \phi_c(T_0)} \times \frac{1}{1 + K_a(T - T_0) + \frac{\alpha(T)}{\alpha(T) - 1}} \right. \\ &\quad \times \left. \left[ \frac{V(T)}{V(T_0)} - 1 - K(T - T_0) \right] \right. \\ &\quad \times \left. \frac{1}{1 - \phi_c(T_0)} \right) \end{aligned} \quad (6)$$

where  $\phi(T_0)$  is the CB volume fraction in the composite at the temperature  $T_0$ ;  $V(T)$  is the volume of the composite at the temperature  $T$ ;  $V_a(T)$  is the amorphous phase’s volume in the

composite at the temperature  $T$ ;  $K$  is the linear thermal volume expansion coefficient of the composite;  $K_a$  is the linear thermal volume expansion coefficient of the amorphous phase; and  $\alpha(T)$  is defined as the ratio of the crystalline phase’s density  $D_c(T)$  to the amorphous phase’s density  $D_a(T)$ . Supposed that the linear thermal volume expansion coefficients of the crystalline and amorphous phase of a specific polymer are  $K_{cs}$ ,  $K_{as}$ , respectively, the  $\alpha(T)$  can be written as:

$$\begin{aligned} \alpha(T) &= D_c(T)/D_a(T) = [D_c(T_0)/D_a(T_0)] \\ &\quad \times \{[1 + K_{as} \times (T - T_0)]/[1 + K_{cs} \times (T - T_0)]\} \end{aligned} \quad (7)$$

Taking the volume expansion into consideration, eq (6) shall be modified as:

$$\begin{aligned} \rho(T) &\times \frac{\sqrt[3]{V(T)}}{\sqrt[3]{V(T_0)}} \\ &= f\left(\frac{\phi(T_0)}{1 - \phi_c(T_0)} \times \frac{1}{1 + K_a(T - T_0) + \frac{\alpha(T)}{\alpha(T) - 1}} \right. \\ &\quad \times \left. \left[ \frac{V(T)}{V(T_0)} - 1 - K(T - T_0) \right] \right. \\ &\quad \times \left. \frac{1}{1 - \phi_c(T_0)} \right) \end{aligned} \quad (8)$$

If defining the real resistivity  $\rho_r(T)$  and real CB volume fraction  $\phi_r(T)$  as:

$$\rho_r(T) = \rho(T) \times \frac{\sqrt[3]{V(T)}}{\sqrt[3]{V(T_0)}} \quad (9)$$

$$\begin{aligned} \phi_r(T) &= \frac{\phi(T_0)}{1 - \phi_c(T_0)} \\ &\times \frac{1}{1 + K_a(T - T_0) + \frac{\alpha(T)}{\alpha(T) - 1}} \\ &\quad \times \left[ \frac{V(T)}{V(T_0)} - 1 - K(T - T_0) \right] \\ &\quad \times \frac{1}{1 - \phi_c(T_0)} \end{aligned} \quad (10)$$

Equation (8) can be further simplified as:

$$\rho_r(T) = f(\phi_r(T)) \quad (11)$$

**Table I The DSC Results of Different CB Volume Fraction Composites**

CB volume fraction ( $V_t$ %)	0	9.93	11.9	16.0
peak temperature $T_p$ (°C)	128.9	126.7	126.5	126.3
onset temperature (°C)	122.0	120.0	120.3	120.0
crystallinity $\beta$	50%	49%	49%	49%

In essence,  $\phi_r(T)$  is the CB volume fraction in the amorphous phase at temperature  $T$ .

As for the CB/HDPE composite used in this experiment, the typical constants at room temperature ( $T_0 = 25^\circ\text{C}$ ) are as follows<sup>11</sup>

$$D_c(T_0)/D_a(T_0) = 1.00/0.85 = 1.117;$$

$$K_{cs} = 3 \times 10^{-40} \text{C}^{-1}, K_{as} = 13 \times 10^{-40} \text{C}^{-1}$$

$$K_a = 7.0 \times 10^{-40} \text{C}^{-1};$$

$$K = 6.0 \times 10^{-40} \text{C}^{-1} \text{ (the linear slopes in Fig. 1)}$$

$$\phi_c(T_0) = \phi_{\text{HDPE}} \times \beta$$

where  $\phi_{\text{HDPE}}$  is the HDPE's volume fraction in the composite, and  $\beta$  is the crystallinity of the composite.

As shown in Table I, CB has no significant effect on the crystallinity of HDPE, and the crystallinity  $\beta$  is about 0.5 for all CB/HDPE composites. Thus, Through eqs. (9), (10), and the constants given above, the curves,  $\log(\rho(T)) \sim \phi(T)$ , in Figure 3, can be transferred to the curves,  $\log(\rho_r(T)) \sim \phi_r(T)$ , as showed in Figure 5.

In Figure 5, PTC curves of different CB volume fraction overlap and also agree with the modified percolation curve. This shows that the resistivity depends solely on the CB concentration in the amorphous phase. The mechanism of PTC can be regarded as the dilution of CB concentration, which is caused by the volume expansion and the melting of the crystalline phase.

For further discussing the volume expansion effect on the PTC, we define a parameter  $Z$ :

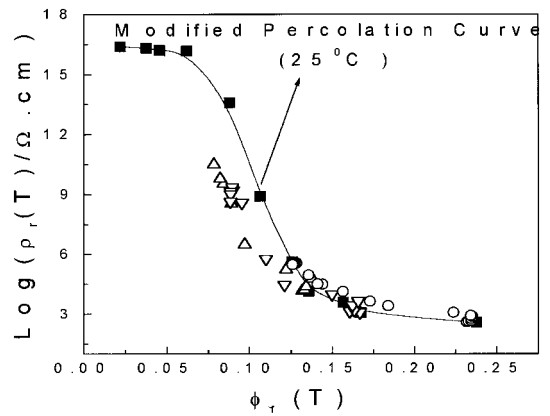
$$Z(T) = [K_a(T - T_0)] / \left\{ K_a(T - T_0) + \frac{\alpha(T)}{\alpha(T) - 1} \times \left[ \frac{V(T)}{V(T_0)} - 1 - K(T - T_0) \right] \times \frac{1}{1 - \phi_c(T_0)} \right\} \quad (12)$$

Clearly,  $Z = 1$  means that the PTC is caused by the thermal volume expansion, whereas  $Z = 0$  means it is caused by the phase change in the composites. For our experiments, at the melting point ( $T = T_p$ ),  $Z(T_p) \approx 0.08$ . This suggests that the thermal volume fraction only plays a minor part in the PTC phenomenon. This will explain why there is only a very small rise in resistance exhibited by crystalline PTC materials when they are strained to an amount equivalent to that found at the crystalline melting point, and why filled amorphous polymers do not in general show an increase in resistance upon heating, because in this two cases no phase transition is involved.

Obviously, negative temperature coefficient (NTC) phenomenon cannot be explained by the above discussion. However, the NTC phenomenon can be appropriately attributed to the change of the CB distribution ( $\psi$ ) in the composite. Further, our model is developed on the basis of Meyer's assumption, but it is macroscopic and phenomenological. In particular, it does not account for changes in the real microstructure or in conduction mechanisms.

## CONCLUSION

The resistivity and volume of CB/HDPE composite with different CB volume fractions at different temperature are measured simultaneously. A model based on Meyer's theory is proposed to explain the PTC effect. Thereby, a quantitative



**Figure 5** Plot of real resistivity against the real CB volume fraction compared with modified percolation curve: ( $\Delta$ ) 9.93  $V_t$  % CB; ( $\nabla$ ) 11.9  $V_t$  % CB; ( $\circ$ ) 16.0  $V_t$  % CB.

relationship between resistivity and volume expansion is obtained. It is found that in the crystalline polymer PTC materials the phase change is the main cause of the PTC effect.

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