

# Studies on the Electrical Conductivity of Carbon Black Filled Polymers

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## SYNOPSIS

The conductivity mechanism for a carbon black (CB) filled high-density polyethylene (HDPE) compound was investigated in this work. From the experimental results obtained, it can be seen that the relation between electrical current density ( $J$ ) and applied voltage across the sample ( $V$ ) coincides with Simmons's equation (i.e., the electrical resistivity of the compound decreases with the applied voltage, especially at the critical voltage). The minimum electrical resistivity occurs near the glass transition temperature ( $T_g$ ) of HDPE (198 K). It can be concluded that electron tunneling is an important mechanism and a dominant transport process in the HDPE/CB composite. A new model of carbon black dispersion in the matrix was established, and the resistivity was calculated by using percolation and quantum mechanical theories. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Electrical conductivity is important in many rubber and plastic compounds, including antistatic applications, wire and cable sheathing, shielding against electromagnetic interference, and positive temperature coefficient materials.<sup>1</sup> Elastomers and plastics are insulators to which conductivity is imparted by the addition of conductive fillers. With regard to the physical processes involved in the conduction of electricity, various authors have proposed different mechanisms.<sup>2,3</sup> However they have not set up a satisfactory theory to illustrate the electron transport process in the composites. It appears that many physical processes can be involved and that the dominant process depends on the composition of the composite and the conditions of measurement. Percolation and the quantum mechanical tunneling effect are two good models to illustrate the electron transport process. Sherman<sup>4</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 concentration is high. A few models were set up to calculate the resistivity of metal-filled polymers in which the particles have a regular geometry.<sup>4</sup> For carbon black filled polymers, however, it is difficult to simulate the resistivity–filler fraction relation because of the strong interaction between the carbon black particles. In this work, the conductivity mechanism of carbon black (CB) filled high-density polyethylene (HDPE) compound was investigated. A new model of carbon black dispersion in the matrix was established, and the resistivity was calculated by using percolation and quantum mechanical theories.

## Experimental

High-density polyethylene was used as the matrix. Its melt index was 2.0 g/10 min, degree of crystallinity, 70.6%; density, 0.954 g/cm<sup>3</sup>; and melting point was 130.8°C. CSF-III carbon black (provided by Changchun Institute of Applied Chemistry) was used as the conducting filler; its average size was 50 nm; surface area, 230 m<sup>2</sup>/g; DBP value, 280 mL/100 g, and pH value 7 to 9. Compounds were made in a Brabender at 150°C. The carbon black was

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added when the HDPE melted, was mixed for 5 min, and was roll-milled for 5 min at the same temperature after 24 h to disperse the carbon black particles well. The samples were compression molded to approximately 1.0-mm-thick sheets. The high-temperature (300 K) electrical resistivity was measured with a digital multimeter when it was lower than  $2.0 \times 10^7 \Omega$ , and a ZC-36-type meter was used when the resistivity exceeded  $2.0 \times 10^7 \Omega$ . The low-temperature (100–300 K) electrical resistivity was measured by using a YEW2553 (Yokogawa Co.) constant-current instrument and a WX4302 (Graphtec Co.) voltage automatic recorder. To retain the electrical reproducibility of the samples,<sup>5,6</sup> all compounds were irradiated with  $^{60}\text{Co}$ - $\gamma$ -rays at a rate of  $8.0 \times 10^3 \text{ Gy/h}$  in air. The radiation dose was 0.14 MGy. Carbon black concentrations are always expressed by the weight fraction.

## RESULTS AND DISCUSSION

For the carbon black filled polymer system, the electrical resistivity of the matrix exceeds  $10^{15} \Omega \cdot \text{cm}$ , while that of carbon black is about  $10^1$ – $10^2 \Omega \cdot \text{cm}$ . To have a higher electrical conductivity, the electrons must transport through the insulating film between carbon black aggregates. The thickness of the film (1.0–10.0 nm) is smaller than the carbon black diameter (20.0–100.0 nm). Therefore, the electron transport process in carbon black filled polymer is similar to that of two metallic electrodes separated by an insulating film. The action of the insulating film is to introduce a potential barrier between the electrodes which impedes the flow of electrons between the electrodes. For a rectangular barrier with image forces included, Simmons established a relation between tunnel current density ( $J$ ) and voltage across film ( $V$ ):

$$J = (6.2 \times 10^{10} / \Delta W^2) \{ \varphi_I \exp(-1.025 \Delta W \varphi_I^{1/2}) - (\varphi_I + V) \exp[-1.025 \Delta W (\varphi_I + V)^{1/2}] \}$$

$$\text{where } \varphi_I = \varphi_0 d_0 - (V/2W)(W_1 + W_2) - [5.75/K(W_2 - W_1)] \times \ln[W_2(W - W_1)/W_1(W - W_2)]$$

and when  $V < \varphi_0$

$$W_1 = 6/K\varphi_0$$

$$W_2 = W[1 - 46/(3\varphi_0 KW + 20 - 2VKW)] + 6/K\psi_0$$

when  $V > \varphi_0$

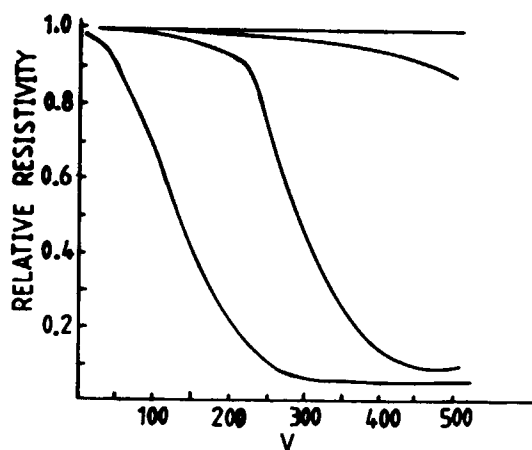
$$W_1 = 6/K\varphi_0$$

$$W_2 = (\varphi_0 KW - 28)/KV$$

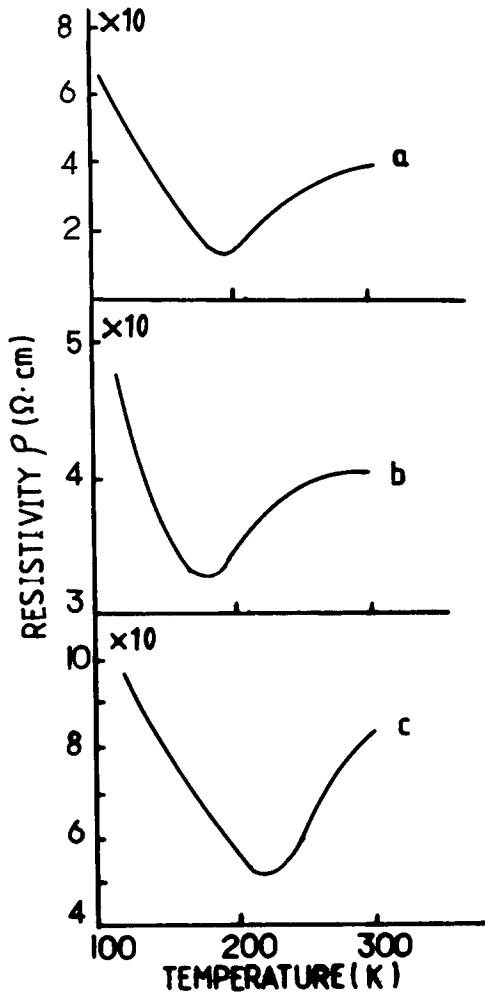
where  $V$  is the voltage across film;  $\varphi_0$  is the height of the rectangular barrier;  $W$  is thickness of insulating film;  $\Delta W = W_2 - W_1$ ; and  $K$  is dielectric constant.

From Simmons's equation, it can be seen that the current density ( $J$ ) decreases with the applied voltage. The critical voltage, which is defined as the voltage at which  $J$  decreases sharply, increases with the thickness of insulating film  $W$ .

Figure 1 shows the relative resistivity–voltage curves of carbon black filled HDPE compound. (The electrical resistivity of the HDPE/0.05 CB compound is defined as 1, and the resistivities of other compounds correspond with the value of HDPE/0.05 CB.) The curves may be divided into three regions when the carbon black fraction is moderate. In region 1, as the voltage increases, the resistivity remains almost constant at a value equal to that of an insulator up to a certain voltage, which may be called the critical voltage. In region 2, the resistivity decreases sharply with the increasing of voltage; whereas in region 3, the resistivity remains almost constant with voltage. It can be seen that the critical



**Figure 1** Relative resistivity–voltage curves of carbon black filled HDPE compounds. Carbon black fraction is (a) 5%, (b) 10%, (c) 15%, (d) 20%.



**Figure 2** Resistivity-temperature curves of HDPE/CB compounds for various CB fractions: (a) 0.15, (b) 0.18, (c) 0.25.

voltage strongly depends on the carbon black fraction. With the increase of carbon black fraction, the width between two conducting carbon black aggregates decreases; meanwhile the conductivity of the compound increases. Therefore, the critical voltage decreases with the increase of carbon black fraction. The curves shown in Figure 1 are similar to that of Simmons's calculated results,<sup>3</sup> indicating that the critical voltage increases with the width between two conducting particles for a certain barrier potential. Although the voltage across the sample is macroscopic in our experiment, the result is in accord with Simmons's equation qualitatively, as the macroscopic voltage is just different from microscopic voltage in magnitude. From the experimental results, the conclusion may be drawn that the electron tunneling effect is a dominant transport process in HDPE/CB composites.

Figure 2 shows the resistivity-temperature curves of HDPE/CB compounds for various CB fractions. It indicates that the minimum resistivity occurs when the temperature is near 200 K. According to quantum theory, the increase of temperature will facilitate electron transport and make conductivity increase; on the other hand, the carbon black aggregates are separated by the polymer matrix, and the width between carbon black aggregates ( $W$ ) will increase with temperature, especially at the glass transition temperature of high-density polyethylene (198 K), at which the polymer thermal expansion coefficient is bigger. Hence the increase of  $W$  will cause an increase in the resistivity of composites. Therefore, the resistivity of the composites is controlled by the two aforementioned opposite factors, and the minimum resistivity will occur at an appropriate temperature.

For carbon black filled polymers, it is difficult to calculate the resistivity accurately because of the complexity of carbon black geometry and the uncertainty of the carbon black dispersion state. There are many dispersion factors to affect the electrical resistivity in HDPE/CB compounds. We can assume, however, that the width between conducting carbon black aggregates plays an important role.

According to Sherman's result,<sup>4</sup> the resistivity of a conductive filler filled polymer can be expressed by

$$\rho = [2.11 \times 10^{-3} WL / (m^*/m)^{1/2} \varphi^{1/2} \alpha_{ct}] \times (1 - Z\Psi/2f) \exp[T_1 / (T + T_0)] \quad (1)$$

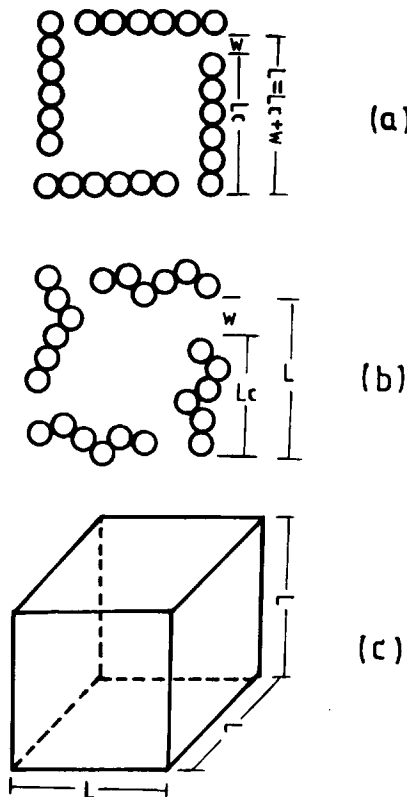
For the carbon black filled polymer system, when  $T = 300 \sim 500$  K,

$$[T_0 = 2^{1/2} \alpha_{ct} h \varphi_0^{5/2} / \pi^2 e^2 W^2 m^{1/2} k \gg T$$

Equation (1) can be written as

$$\rho = [2.11 \times 10^{-3} WL / (m^*/m)^{1/2} \varphi^{1/2} \alpha_{ct}] \times (1 - Z\Psi/2f) \exp \pi^2 (2m^* \varphi)^{1/2} W / h \quad (2)$$

where  $\rho$  is electrical resistivity,  $\Psi$  is the volume fraction of CB,  $Z$  is the coordination number of the lattice,  $f$  is the packing fraction appropriate to the lattice geometry selected,  $L$  is the unit cell length,  $W$  is the tunnel gap length,  $h$  is Planck's constant,  $m$  and  $m^*$  are electron mass and electron effective mass, respectively,  $\varphi$  is the effective tunnel barrier potential, and  $\alpha_{ct}$  is the effective tunnel junction cross-sectional area.



**Figure 3** The model of carbon black dispersion in matrix. (a) Two dimensional,  $q = 1$ , (b) two dimensional,  $q < 1$ , (c) three dimensional.

Equation (2) can only be applied to the system in which the carbon black fraction is smaller than the critical fraction (the critical filler fraction is defined as that at which all the conductive fillers contact each other to form conducting networks).

As shown in the literature, the polymer matrix can be absorbed on a carbon black surface to form "bound polymer" due to the physical or chemical interactions between matrix and polymer.<sup>5</sup> The conducting carbon black aggregates are separated by the bound polymer, so the aggregates can never quite contact each other. Hence, Eq. (2) can be applied to HDPE/CB compounds.

Here we assume that the carbon black particles form rodlike aggregates, which disperse around the crystallinity or amorphous regions of polymer matrix. These aggregates form three-dimensional networks (Fig. 3). Their mean length is denoted by  $L_c$ , their mean cross-sectional area by  $\alpha_c$ , and an effective mean cross-sectional tunnel area by  $\alpha_{ct}$ . The unit cell length is  $L$ . The temperature-dependent tunnel gap length  $W$  is given by  $W = L - L_c$ . Then the carbon black volume fraction can be expressed by

$$\Psi = 3 \cdot (4/3) \pi r^3 n / (2nrq + W)^3 \quad (3)$$

where  $r$  is the radius of carbon black,  $q$  is the dispersion parameter ( $q$  is defined as the projection of the diameter of CB on the side of a unit cell, divided by the diameter), and  $x$  is the number of CB particles in one side of the unit cell. In Eq. (3),  $3 \cdot (4/3) \pi r^3 x$  is the carbon black volume in a unit cell, and  $(2nrq + W)^3$  is the volume of the unit cell.

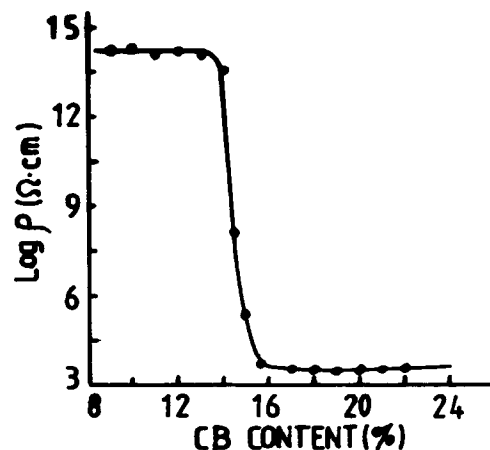
Equation (3) can be written

$$W = r[(4\pi x)^{1/3} / V_c^{1/3}] - 2xrq \quad (4)$$

For the HDPE/CB composite,  $m^*/m = 0.05$ ,  $\alpha_{ct} = (1/10)\alpha_c$ ,  $Z = 6$ ,  $f = 0.5$ ,  $\varphi = 1$  eV (ref. 4), and the radius of CSF-III carbon black ( $r$ ) is 25 nm. Here we assume  $n = 6$  and  $q = 0.82$ ; then the resistivity-carbon black fraction can be calculated by using Eq. (2) and Eq. (4). Figure 4 shows the calculated result (solid line), which agrees well with the experimental data (points shown in Fig. 4).

## CONCLUSION

1. Electron tunneling is an important mechanism and a dominant transport process in HDPE/CB compounds. The electrical resistivity of the compounds decreases with the increase of applied voltage, especially at the critical voltage.



**Figure 4** Resistivity-carbon black fraction characteristic of HDPE/CB compound. (—) Theoretical, (●) experimental.

2. For HDPE/CB compounds, the increase of temperature facilitates the electron transport; meanwhile the conductivity will decrease due to the expansion of the matrix. The minimum resistivity can be found near the glass transition temperature of high-density polyethylene (198 K).
3. Sherman's calculations can be applied to HDPE/CB compounds on the assumption that carbon black aggregates are separated by the bound polymer and the aggregates can never contact exactly. With a new model of carbon black dispersion in the matrix, the electrical resistivity was calculated using Sherman's equation.

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## REFERENCES

1. A. I. Medalia, *Rubber Chem. Technol.*, **59**, 432 (1986).
2. P. Sheng, E. K. Sichel, and J. I. Gittleman, *Phys. Rev. Lett.*, **40**, 1197 (1978).
3. J. G. Simmons, *J. Appl. Phys.*, **34**, 1793 (1963).
4. R. D. Sherman, L. M. Middleman, and M. Jacobs, *Polym. Eng. Sci.*, **23**, 36 (1983).
5. H. Tang, Z. Y. Liu, J. H. Piao, X. F. Chen, Y. X. Lou, and S. H. Li, *J. Appl. Polym. Sci.*, **51**, 1159 (1994).
6. H. Tang, J. H. Piao, X. F. Chen, Y. X. Lou, and S. H. Li, *J. Appl. Polym. Sci.*, **1795**, 48 (1993).

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