

# Study on Time-Dependent Resistance of Carbon Black-Loaded High-Density Polyethylene Composites During the Isothermal Course

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**ABSTRACT:** Carbon black (CB)-loaded high-density polyethylene composites were prepared using conventional blending. The resistance and temperature (R-T) relations under constant heating rates and the resistance and time (R-t) relations at different isothermal temperatures have been studied. The results of the R-T and differential scanning calorimetry (DSC) curve demonstrated a correlation between the positive temperature coefficient/negative temperature coefficient transition and the melting course. At isothermal temperatures below  $T_{PTC/NTC}$ , the resistance displayed a sharp increase and thereafter a mild decrease with time. The time to reach the highest resistance became shorter with rise in the isothermal temperature. The ratio between highest resistance and initial resistance was maximum at  $T_{peak}$  of the DSC curve. When the isothermal temperature was higher than  $T_{PTC/NTC}$ , the resistance attenuated with time. The attenuation fits to a first order exponential decay function. The calculated time constant  $\tau$  decreased with rise in isothermal temperature. The attenuation discrepancy under different isothermal temperatures reduced as the heating rate before the isothermal courses was higher. A model based on polymer chain diffusion and CB movements at high temperature is proposed. The model can explain the results obtained in R-T and R-t measurements. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2258–2263, 2001

**Key words:** filled polymer composites; conductive polymer composites; positive temperature coefficient/negative temperature coefficient; resistance relaxation

## INTRODUCTION

The most attractive characteristic of carbon black-filled polyethylene composites (CB/PE) is a jump-like increase in the electrical resistance with the

rise in temperature when approaching the melting point of the polymer matrix. This is usually called a positive temperature coefficient (PTC) effect.<sup>1</sup> The PTC effect has been primarily explained by an abrupt volume expansion of the polymer matrix during melting. The abrupt volume expansion leads to a spatial gap increase between neighboring CB aggregates within the CB conductive network, which hence hinders the electronic tunneling and hopping,<sup>2</sup> and increases the electrical resistance. However, this explanation is not so convincing because it does not take into account the changes in

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the polymer crystallinity and the interactions between CB and PE. The PTC effect is usually characterized under a linear heating or cooling (a constant heating or cooling rate). For the same sample, different heating or cooling rates and heating cycling usually give different resistance-temperature (R-T) curves. As the temperature is further increased after the polymer matrix is completely melted, a decrease instead of the increase in the resistance is usually observed, which is consequently defined to be a negative temperature coefficient (NTC) effect. Similarly, the NTC behavior is also found heating rate and heat cycling dependent.

The heating rate and cycling dependence of both PTC and NTC implies that the resistance changes with temperature may involve a resistance relaxation with time. Investigation of the resistance relaxation behavior becomes necessary for a further understanding of the mechanism behind the electrical properties of polymer PTC composites. This paper reports the experimental results of isothermal resistance relaxation with time of high-density polyethylene (HDPE)-20wt%CB, and analyzes these results. A model based on CB aggregate movements and polymer chain diffusion is proposed to explain the experimental results.

## EXPERIMENTAL

The composite samples were prepared as follows: conventional compounding of CB (acetylene black, Chun'an Chemicals, China) and HDPE (2480, Qilu Petro. Co., China) at 170°C for 10 min in an internal mixer of Bandury type, compression molding at 170°C for 5 min under 15 MPa to form a plate with 2 mm in thickness, mounting copper nets onto two sides of the plate as electrodes. All samples studied contain the same amount of CB (22 wt %). The samples were finally cut into rectangular pieces with dimensions of  $20 \times 20 \times 2 \text{ mm}^3$  and  $10 \times 30 \times 2 \text{ mm}^3$  for R-T and resistance-time (R-t) measurements, respectively.

The R-T relationship during heating at 2°C/min was carefully measured on a computerized system set up in our laboratory. The system combines a digital multimeter (7150 Plus, Solatron Instrument, Schurberger, England) and a high resistance meter (ZC36, Shanghai Instrument Co.,  $10^{-14}$  amperes) for a wide range of the resistance measurements, and also a heating (cooling) section including an accurate temperature controlling and monitoring.

The R-t measurements were undertaken in a modified dilation meter made in our laboratory. A sample of  $10 \times 30 \times 2 \text{ mm}^3$  was positioned in an ampoule bottle full of silicone oil. Two copper wires were elicited from the copper-net electrodes of the sample to the digital multimeter through a capillary tube. The capillary tube surface was marked in a fine scale for volume expansion measurements. The silicone oil acted as the heating as well as volume expansion medium. On electrically heating, the temperature of the sample immersed in the silicone oil was controlled by a conventional temperature relay. The volume change of the heated sample was determined by the difference in the volume of the silicone oil with and without the sample. The heating rate was estimated by temperature over time and was found very slow (0.20–0.50°C/min) so that the heating process was thought equilibrium. The whole system could record the temperature, the volume of the sample and time simultaneously.

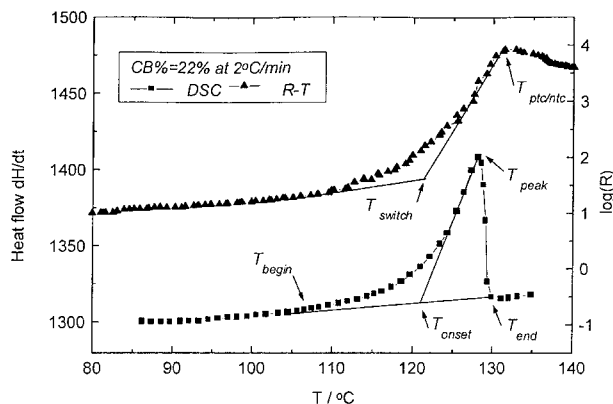
Some samples of  $20 \times 20 \times 2 \text{ mm}^3$  were also characterized in a Perkin-Elmer differential scanning calorimeter (DSC-2) parallel to the R-T tests. The heating rate for all DSC tests was also 2°C/min.

## RESULTS

### R-T Relationships and the Melting Processes of the CB/HDPE Composites

The R-T measurements were undertaken of six samples of  $20 \times 20 \times 2 \text{ mm}^3$ . The PTC effects were all found, and the R-T curves are basically the same in the six samples. The DSC tests were also done of other six samples of the same dimensions cut from the same plate as those for R-T measurements. The DSC curves indicating the heat flow of these samples are also basically the same. A representative R-T relation and a typical DSC curve obtained during linear heating (2°C/min) are drawn together in Figure 1.

The DSC curve in Figure 1 starts to deviate from the base line at 106°C to form a peak, and merge back to the base line at about 130.5°C, indicating a wide range of melting process of the HDPE matrix. The two temperatures have been defined as the beginning ( $T_{\text{begin}}$ ) and the ending temperatures ( $T_{\text{end}}$ ) of the melting curve, respectively. The onset and the peak temperatures ( $T_{\text{onset}}$  and  $T_{\text{peak}}$ ) on the DSC curve are also de-



**Figure 1** R-T relation and DSC curve of a CB/HDPE composite.

terminated to be 122.3 and 128.1°C, respectively, by tangent method shown in the figure.

On the R-T curve in Figure 1, two characteristic temperatures,  $T_{\text{switch}}$  and  $T_{\text{PTC/NTC}}$ , are the temperature from which the jump-like resistance increase starts and the temperature at which the PTC turns to be NTC. Also by tangent method,  $T_{\text{switch}} = 121.6^\circ\text{C}$  and  $T_{\text{PTC/NTC}} = 130.8^\circ\text{C}$  are obtained. All these characteristic temperatures of R-T and DSC curves are also summarized in Table I.

The temperature range from  $T_{\text{onset}}$  to  $T_{\text{end}}$  of DSC curve is almost the same as the range from  $T_{\text{switch}}$  to  $T_{\text{PTC/NTC}}$  of R-T curve, suggesting that the PTC effect took place during the melting of the polymer matrix, and NTC occurred right after the polymer matrix melted.

### R-t Relationships During Isothermal Courses

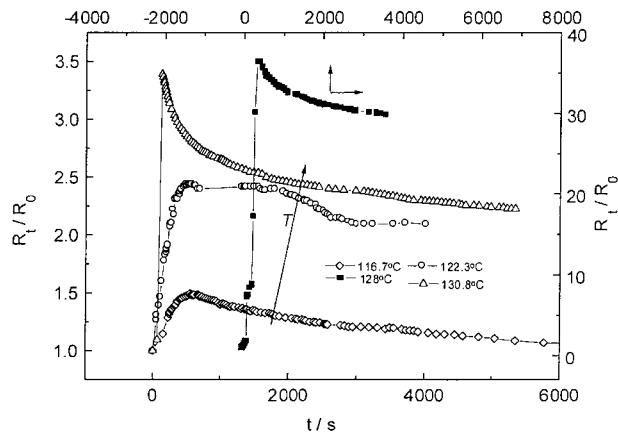
#### R-t Relationships at Isothermal Temperatures

$$T_{\text{iso}} \leq T_{\text{PTC/NTC}}$$

Figure 2 reports the isothermal resistance changes with time at constant temperatures of 116.7, 122.3, 128.0, and 130.8°C. Before reaching

**Table I** Characteristic Temperatures of DSC and R-T Curve in Figure 1

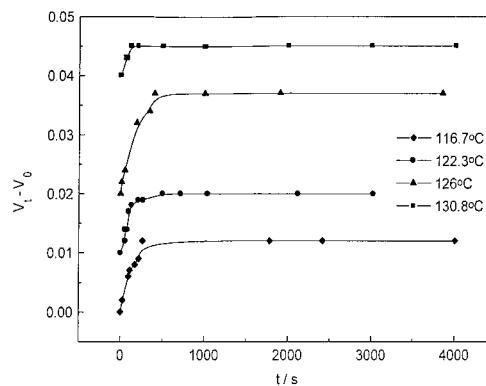
DSC Curve	$T_{\text{begin}}$	$T_{\text{onset}}$	$T_{\text{peak}}$	$T_{\text{end}}$
	106.0°C	121.1°C	128.1°C	130.5°C
R-T Curve	$T_{\text{switch}}$		$T_{\text{PTC/NTC}}$	
	121.6°C		130.8°C	



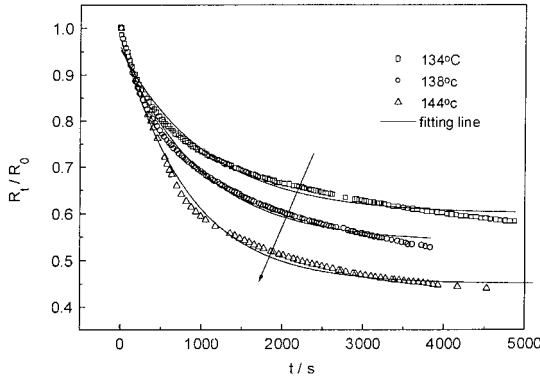
**Figure 2** Resistance-time curves of HDPE/CB composites during isothermal course ( $T_{\text{iso}} < T_{\text{PTC/NTC}}$ ).

these constant temperatures, the heating rates were controlled to be 0.5°C/min. These temperatures were all below or equal to  $T_{\text{PTC/NTC}}$  in the PTC curve and  $T_{\text{end}}$  in DSC curve in Figure 1. In Figure 2, instead of real resistance  $R$ , the ordinate stands for  $R_t/R_0$ , ratio of resistance at time  $t$  to that at time zero (initial resistance). Each curve displays a sudden increase followed by a mild decrease in  $R_t/R_0$  with time during the isothermal course. The sudden increase is steeper as the isothermal temperature is higher. The maximum value of  $R_t/R_0$  is higher as the isothermal temperature is higher. The resistance decreases with time after the sudden increases can be reluctantly thought as a relaxation behavior, particularly the curve for the temperature of 116.7°C.

The volume changes  $V_t - V_0$  in these isothermal courses with time are shown in Figure 3. Corresponding to the sudden resistance increases



**Figure 3** Volume change of sample during isothermal treatment ( $T_{\text{iso}} < T_{\text{PTC/NTC}}$ ).

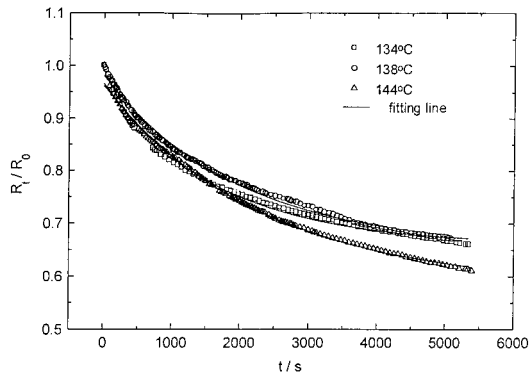


**Figure 4** Resistance-time curves of HDPE/CB composites during isothermal course ( $T_{\text{iso}} > T_{\text{PTC/NTC}}$ ).

at the beginning of isothermal courses in Figure 2, a quick volume expansion is found. However, the volume keeps unchanged after the quick volume expansion.

#### ***R-t Relationships at Isothermal Temperatures $T_{\text{iso}} > T_{\text{PTC/NTC}}$***

Figure 4 shows the isothermal resistance change with time as the temperatures are greater than  $T_{\text{PTC/NTC}}$ . Before reaching the isothermal temperatures the heating rate was carefully controlled to be  $0.46^\circ\text{C}/\text{min}$ . As seen in Figure 4, each curve only displays a monotonic attenuation of resistance with time. The higher the isothermal temperature is, the faster the attenuation is seen. Figure 5 shows the isothermal changes of the resistance with time of the same batch of samples, but heated at  $0.26^\circ\text{C}/\text{min}$  before reaching the isothermal temperatures. Being different from Fig-



**Figure 5** Resistance-time curves of HDPE/CB composites during isothermal course ( $T_{\text{iso}} > T_{\text{PTC/NTC}}$ ) at lower heating rate.

**Table II** The Computer Fitting Results of  $R_t/R_0$  vs  $t$  in Figures 4 and 5

$T$ ( $^\circ\text{C}$ )	$R_\infty/R_0$ (Fig. 4/Fig. 5)	$\tau$ (s) (Fig. 4/Fig. 5)	$(R_0 - R_\infty)/R_0$ (Fig. 4/Fig. 5)
134	0.6/0.66	1064/1927	0.4/0.34
138	0.54/0.66	969/1940	0.46/0.34
144	0.45/0.62	836/1968	0.55/0.38

ure 4, the three relaxation curves become closer, but maintain the same tendency.

The attenuation in Figures 4 and 5 can be described using a relaxation equation:

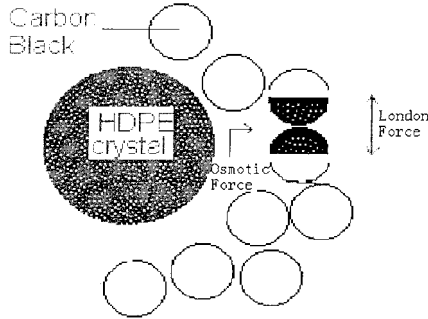
$$R_t/R_0 = R_\infty/R_0 + (1 - R_\infty/R_0)\exp(-t/\tau) \quad (1)$$

where  $R_\infty$  is the resistance after a long time isothermal aging, and  $\tau$  is the time constant.  $R_\infty/R_0$  and  $\tau$  for each curve in Figures 4 and 5 were obtained by fitting the data points into the equation. The least square method was held during the fitting. The errors for  $R_\infty/R_0$  and  $\tau$  were found negligible, indicating the isothermal change of resistance with time is a time relaxation process described by eq. (1). The fitting results are summarized in Table II.

According to the fitting data of Figure 4, the time constant  $\tau$  is shorter as the isothermal temperature is higher, suggesting an increase in thermal driving force for agglomeration. However, for Figure 5 the time constant  $\tau$  changes in a reverse way with isothermal temperature, but they are close to each other.

## DISCUSSION

As shown in Figure 1, when the sample is heated from room temperature to  $T_{\text{switch}}$ , the resistance increases only by a factor of  $10^{0.3}$ , which is far smaller than  $10^3$  for the jump-like resistance increase in the temperature range from  $T_{\text{switch}}$  to  $T_{\text{PTC/NTC}}$ . This suggests that a pure volume expansion leads to only a little increase in the resistance, and the higher order of magnitude increase of resistance may be attributed to something else besides the volume expansion. According to Allek,<sup>3</sup> CB agglomerates favorably stay in the amorphous region of the HDPE matrix, where the polymer chains are in viscoelastic state because  $T_g$  is far below the room temperature. The



**Figure 6** Schematic illustration of CB aggregates shielding a HDPE crystal.

CB agglomerates in the amorphous region are thought to act as a shielding layer of a crystalline region, as illustrated in Figure 6. The amorphous volume increase with temperature leads to a dilution of CB aggregates within whole amorphous region, and hence increases the material resistance. As approaching the melting region, a chain concentration gradient may be built up across the CB shielding layer from crystalline region (higher chain density) to amorphous region (lower chain density; Fig. 6). The size of a spherical crystal is estimated to be about 300 nm, and the CB aggregates measure about 60 nm. The CB agglomerates shielding a crystal may be regarded as semi-membrane, and the osmotic pressure can be estimated by

$$\Pi = cRT/M,^4 \quad c = \Phi(\rho_c - \rho_a) \quad (2)$$

where  $\Phi$  is the weight fraction of HDPE in the composite,  $\rho_c = 1 \text{ g cm}^{-3}$  the density of crystalline phase,  $\rho_a = 0.85 \text{ g cm}^{-3}$  the density of amorphous phase.  $R$  is the gas constant, and  $T$  is absolute temperature. For a molecular weight of  $M = 10^4$ , the osmotic pressure is calculated to be about 25 Pa for a temperature of 130°C. Two agglomerates of 60 nm in diameter join together with a gap of 0.4 nm through van der Waals force. They can be treated as the microscopic acceptor of the osmotic pressure. Using  $F = \Pi D^2$ , where  $D$  is the diameter of a CB aggregate, the osmotic force can be calculated to be about  $0.9 \times 10^{-12}$  Newton. On the other hand, the Van der Waals force binding two aggregates is mainly the London force with  $0.8 \sim 8 \text{ kJ/mol}$ . Through the general equation  $E = a/r^6$ ,<sup>5</sup> the attraction force between the two aggregates can be defined as

$$F = -dE/dr = 6E/r$$

where  $a$  is a property constant and  $r$  is the distance between the centers of two aggregates. The calculated attraction force ranges from 1.3 to  $13 \times 10^{-12}$  Newton, which is comparable to the osmotic force. It is thus reasonable to suggest the possibility for the polymer chain to diffuse from the crystalline phase to the amorphous phase by virtue of the osmotic pressure. The osmotic force acts as a wedge to separate two neighboring aggregates and to destroy the CB conductive network, hence to make the resistance sharply increase by orders of magnitudes.

When the temperature is above the melting point, the difference of the chain concentration in different regions levels off, and the chain diffusion is gradually diminished. The polymer chains in molten state exhibit the characteristics of Gaussian chains and the chain segments move frequently according to mean-field theory.<sup>6</sup> Although the volume of the composite continues to expand, the CB aggregates are actually compressed or compacted more closely because of the enhanced movements of the polymer chain segments. The weakening diffusion and thermal activating agglomeration work together to make the CB conductive network reconstructed or repaired, and a NTC phenomenon thus occurs.

By comparing PTC section with NTC section with the reference of the absolute value of  $dR/dT$  in Figure 1, it is found that the destroyed conductive network in the PTC region (large  $dR/dT$ ) was only partly repaired in NTC region (small  $dR/dT$ ). The destructive effect due to the temperature increase of the polymer matrix still remains important all the way from PTC to NTC.

When the sample is held at a constant temperature below  $T_{\text{PTC/NTC}}$  or  $T_{\text{end}}$ , the unvarying volume of the composite shown in Figure 3 suggests no further melting during the isothermal courses. The sudden increase followed by the mild decrease in resistance with time in Figure 2 suggests the existence of compacting effect on CB aggregates in the melting course. The CB network destruction due to the polymer chain diffusion and the CB network reconstruction due to the compressive effect may compete each other. The time for the resistance to reach the maximum is shorter as the isothermal temperature is higher (Figure 2). This indicates that the chain diffusion leading to CB agglomerate separation took place immediately, but the compression leading network reconstruction lagged behind, although the two competition processes accelerate at higher temperature. Additionally, the ratio of peak resis-

tance to initial resistance at time zero is largest at the isothermal temperature of 128.1°C, the same as  $T_{\text{peak}}$  on the DSC curve (Table I). This ratio embodies the damaging rate of the CB agglomerate network. At the temperature corresponding to the  $T_{\text{peak}}$  on the DSC curve, the heat flow  $dQ/dt$  reaches the maximum such that the melting rate and the diffusion of polymer chain become maximum, and the CB network is, correspondingly, seriously damaged. This could explain why the initial resistance ratio reaches the maximum for the isothermal temperature of  $T_{\text{peak}}$  (Fig. 2).

When temperature is kept constant above  $T_{\text{PTC/NTC}}$  or  $T_{\text{end}}$ , the resistance attenuation is more serious as the constant (isothermal) temperature is higher (Figs. 4 and 5). This can be explained by the stronger compressive effect due to the enhanced movement of polymer segments at higher temperature. As further illustrated by Figures 4 and 5, lower heating rate before reaching the constant temperatures diminishes the difference of attenuation rates at various isothermal temperatures. The reason may be that the polymer chain segments agitate more violently before complete melting and the difference of compression after melting diminishes, as the heating rate is lower.

## CONCLUSIONS

1. For CB/HDPE composites, The temperature scope of the PTC change coincides with the melting range of material from DSC curve. The noticeable resistance increase during melting may originate from the destruction of CB conductive network due to the diffusion of polymer chain and the dilution of the concentration of CB aggregates. The NTC phenomenon after the melting of the HDPE matrix results from the compression of CB aggregates due to the more strong agitations of polymer chain in molten state.
2. During isothermal courses of  $T_{\text{iso}} < T_{\text{PTC/NTC}}$ , the resistance of the composite dis-

played a sharp increase and thereafter a mild decrease with time. This indicates that the chain diffusion leading to CB agglomerate separation took place immediately, but the compression leading network reconstruction was lagging behind, although the two competition processes accelerate at higher temperature. The sharp relative resistance increase is maximum at the isothermal temperature  $T_{\text{peak}}$  of DSC curve. The CB particle agglomeration has been started after the beginning of melt of HDPE matrix and is earlier than PTC/NTC transition.

3. During isothermal courses of  $T_{\text{iso}} > T_{\text{PTC/NTC}}$ , the resistance attenuation with time fits to first order exponential decay equation. The relaxation time constant  $\tau$  decreases with the rise in temperature, suggesting an increase in thermal driving force for agglomeration.
4. The attenuation differences among various isothermal temperatures decreases with the decrease in the heating rate before isothermal temperature.

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