

# Time Dependences of Conduction and Self-Heating in Acetylene Carbon Black-Filled High-Density Polyethylene Composites

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**ABSTRACT:** The time dependences of electrical conduction and self-heating behaviors in high-density polyethylene filled with acetylene carbon black of 0.082 in volume fraction are studied in relation to voltage and ambient temperature. The characteristic decay current constant  $\tau_i$  and the exponential growth time constant for self-heating  $\tau_g$  are determined for the samples under voltages  $U$  above the critical value  $U_c$  for the onset of self-heating. The influences of voltage and ambient

temperature on  $\tau_i$  and  $\tau_g$  as well as the amplitude of the low-resistance to high-resistance switching are discussed on the basis of the random resistor network (RRN) model and the relationship between  $U_c$  and the intrinsic resistivity. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1124–1131, 2006

**Key words:** high-density polyethylene; carbon black; conduction; self-heating; time-dependence

## INTRODUCTION

Incorporation of conductive particles into a polymer matrix may result not only in conductivity but also in an anomalous increase in electric resistivity over a temperature range around the melting point of the matrix. The later behavior is termed as positive temperature coefficient (PTC) effect of resistivity in the literature.<sup>1–6</sup>

Characterization of polymer PTC composites has been made by measuring the temperature dependence of resistivity in such a way that the electric current passing through the specimen is small and the electric heating effect is negligible. Important industrial applications of the polymer PTC composites include over-current protection and self-regulating heater as two typical examples.<sup>7,8</sup> In both cases, application of a considerably high voltage to the PTC composites leads to a local Joule heating coupled with the intrinsic PTC effect, which modifies the electrical contact of conductive particles, and therefore, restricts the current passing through the composite. On the macroscopic scale, this leads to a global resistance increase (the resistance switching) and a current decay with time until a stationary “switched” state is reached.<sup>9,10</sup>

The dynamic processes of conduction in conductive polymer composites subjected to various actions, includ-

ing high-temperature treatment,<sup>11</sup> swelling,<sup>12</sup> pressure,<sup>13–16</sup> and electric field,<sup>10,13,17–21</sup> have attracted considerable attention in recent years. El-Tantawy and co-workers studied the current–voltage and the Joule heating characteristics of conducting composites based on butyl rubber<sup>19</sup> and epoxy resin<sup>17,18</sup> and proved that the Joule heating effect is a very effective way for enhancing the electrical and thermal stability of conducting composites. In the conducting composites based on high-density polyethylene (HDPE), the self-heating is involved in the initial resistance (the content of conductive filler), the electric field-induced PTC transition, the heat dissipation, as well as crosslinking of the matrix.<sup>10,20,21</sup> Because of the intrinsic PTC behavior in conducting composites with a semicrystalline polymer, the ambient temperature below the melting point should have a significant influence on the self-heating and the accompanied resistance switching. In this paper, we study the dynamics of the self-heating and the resistance switching of a HDPE/carbon black (CB) composite subjected to a wide range of electric field above room temperature, yet below the melting point of the matrix. Influences of voltage and ambient temperature on the amplitude and the rate of the self-heating and the resistance switching will be revealed.

## EXPERIMENTAL

### Materials

HDPE (density 0.942 g cm<sup>-3</sup>, melting point 130°C, melting index 0.14g/10 min) and acetylene CB (particle size 42 nm, Brunauer-Emmett-Teller special sur-

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face area  $63 \text{ m}^2 \text{ g}^{-1}$ , dibutyl phthalate absorption  $1.70 \text{ cm}^3 \text{ g}^{-1}$ ) were obtained from Yangzi Ethylene Co. (China) and Shanghai Jishan Chemical Co. (China), respectively. HDPE and CB were mixed on a two-roll mill at  $160^\circ\text{C} \pm 5^\circ\text{C}$  for 20 min followed by a compression molding at  $165^\circ\text{C} \pm 5^\circ\text{C}$  under 14.7 MPa for 10 min to form sheet samples with a size of  $20 \text{ mm} \times 20 \text{ mm} \times 3 \text{ mm}$ . The volume fraction of CB was 0.082, which is very slightly above the percolation threshold 0.080.

Two pieces of copper nets were mounted on the opposite wide surfaces of the sheet to ensure a good electrical contact with the attached copper electrodes. Two-probe resistance measurement was carried out using a M890B+ digital multimeter (Shenzhen Huayi Mastech Co., China) in a pulse mode for measuring the intrinsic resistivity  $\Sigma_0$  of the composite by applying a direct current (DC) voltage of 10 V.

## Method

The sheet samples were suspended in an oven without contact with the wall. The ambient temperature,  $T_a$ , was controlled using the oven, with an accuracy of  $\pm 0.5^\circ\text{C}$ . Resistance showed time-dependency at elevated temperatures even below the melting point of HDPE. The samples were therefore held at a desired ambient temperature  $T_a$  for 24 h to facilitate resistance to attain a relatively steady value. The intrinsic resistance was firstly measured. An alternating current (AC, 50 Hz) voltage adjusted by a transformer was then applied on the samples for at least 10 min to ensure that the current passing through the sample reached its steady value. The current  $I$  was measured using a digital multimeter. From technical point of view, the bulk temperature could accurately reflect the self-heating of the samples. However, the self-heating and the thermal dissipation resulted in a temperature distribution field inside the sample, *i.e.*, the temperature was the highest in the center and decreased towards to the surface. Because of the experimental difficulties in evaluating the temperature distribution, the surface temperature  $T_s$  of the sample was monitored using a copper-constantan thermocouple attached onto the wide surface of the sample.  $T_s$  was recorded using a TM902C digital thermometer (Hongyan Electron Co., China). After the current and  $T_s$  reached their steady values, the AC voltage was switched off. After the sample was naturally cooled down to the ambient temperature, the intrinsic resistance was measured again, after which a higher AC voltage was applied to the sample and another measurement of  $T_s$  and  $I$  was performed according to the same procedure described.

## RESULTS AND DISCUSSION

### Time dependences of $I$ and $T_s$

When an AC voltage  $U$  applied is sufficiently low, current  $I$  flowing through the sample is independent of time  $t$  and the sample does not show any self-heating behavior. Under a considerably high voltage,  $I$  decays from a value  $I_0$  corresponding to the intrinsic conduction until a steady value  $I_e$ . Simultaneously, the surface temperature  $T_s$  of the sample increases from  $T_a$  to a steady value  $T_{se}$ . At the electric-heating equilibrium, both  $I_e$  and  $T_{se}$  are independent of time but their values are related to the applied voltage. Figure 1 shows an example illustrating the time dependences of current  $I$  and surface temperature  $T_s$  for the composite subjected to a voltage  $U = 30 \text{ V}$  at  $T_a = 19^\circ\text{C}$ . During the process of self-heating,  $I$  and  $T_s$  could be described as<sup>13,22,23</sup>

$$I(t) - I_e = (I_0 - I_e) \exp\{-t/\tau_i\} \quad (1)$$

and

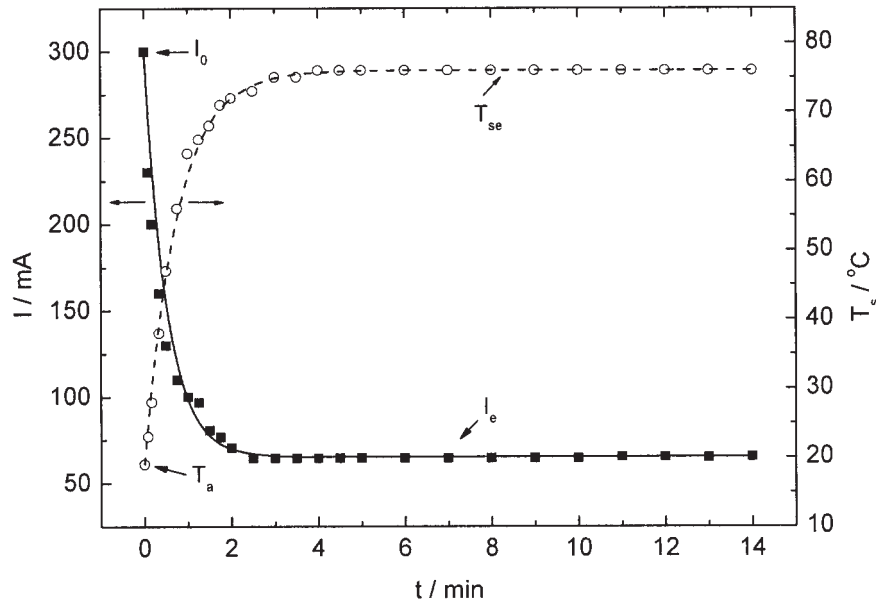
$$T_s(t) - T_a = (T_{se} - T_a)[1 - \exp\{-t/\tau_g\}] \quad (2)$$

respectively, as shown by the solid curves in Figure 1. In eqs. (1) and (2),  $\tau_i$  is a characteristic decay current constant and  $\tau_g$  is an exponential growth time constant for self-heating, respectively. These two parameters should be strongly dependent on the filler content, the dispersion of the filler in the matrix, the interface adhesion between the filler, and the matrix as well as the ambient temperature.

### Influence of voltage on resistance switching

$I_0$  and  $I_e$  determined experimentally are plotted against voltage  $U$  in Figure 2(a). It was seen that  $I_0$  and  $I_e$  are identical with each other when  $U$  is lower than the critical value  $U_c$ , the onset voltage for the occurrence of self-heating. It was found that  $U_c$  increases significantly with increasing  $T_a$ . At  $U > U_c$ ,  $I_e$  becomes lower than  $I_0$  due to self-heating and the resultant resistance rise. There exists a maximum in  $I_e$  after which  $I_e$  decreases, as increasing  $U$ . The difference in  $I_0$  and  $I_e$  can be characterized using the ratio  $I_0/I_e$  equal to  $\rho_e/\rho_0$ , where  $\rho_0$  and  $\rho_e$  are resistivities at times zero and infinite, after an AC voltage is applied on the sample. Because the self-heating behavior occurs only when  $U$  exceeds  $U_c$ ,  $U_c$  might be defined as a scale of  $U$  for studying the nonlinear conduction under electric fields. The critical voltage  $U_c$  can be conveniently determined at the position where  $I_e$  starts to deviate from  $I_0$ , as indicated in Figure 2(a).

The random resistor network (RRN) model assumes that each resistor in the percolating network has a breaking current  $i_a$ . When the local current is higher



**Figure 1** Current  $I$  and self-heating temperature  $T_s$  as a function of time  $t$  for the HDPE/CB composite at ambient temperature  $T_a = 19^\circ\text{C}$  and under voltage  $U = 30\text{ V}$ . The solid curves are calculated according to eqs. (1) and (2), respectively.

than  $i_{cr}$ , the resistor becomes an insulator. If an externally applied voltage is sufficiently high, some of the resistors will break, which leads to a redistribution of current on the remaining resistors and thus causes them to break in succession.<sup>24,25</sup> By applying Monte Carlo simulation, Pennetta et al.<sup>26</sup> studied the resistance fluctuation in an RRN consisting two competing processes of the breaking and the recovering of elementary resistors. According to their results, variation of average resistivity,  $(\rho_e/\rho_0 - 1)$ , scales with the voltage ratio  $(U/U_c)$

$$\frac{\rho_e}{\rho_0} - 1 = \lambda \left( \frac{U}{U_c} \right)^\theta \quad (3)$$

where  $\lambda$  is a dimensionless coefficient and  $\theta$  is an exponent. Figure 2(b) shows  $I_0/I_e$  as a function of the reduced voltage  $(U/U_c)$ . The data at  $T_a \leq 100^\circ\text{C}$  collapse onto a master curve, which could be described by eq. (3) with  $\lambda \approx 0.09$  and  $\theta \approx 2$ . On the other hand,  $I_0/I_e$  at  $T_a = 120^\circ\text{C}$  increases much faster than those at lower temperatures. Well fitting of eq. (3) to the data at  $T_a = 120^\circ\text{C}$  yields  $\lambda \approx 0.09$  and  $\theta \approx 3$ . The higher  $\theta$  value might be ascribed to the partial melting of the matrix with a melting point of  $130^\circ\text{C}$ .

The percolating network becomes loose in the partial melted matrix, which enhances the conduction nonlinearity of the composite at the stationary state. In fact, eq. (3) describes the variation of percolating structure at the stationary state of electric-heating equilibrium with respect to the percolating structure corresponding to the intrinsic conduction in absence of self-heating. According to the RRN model, insulating

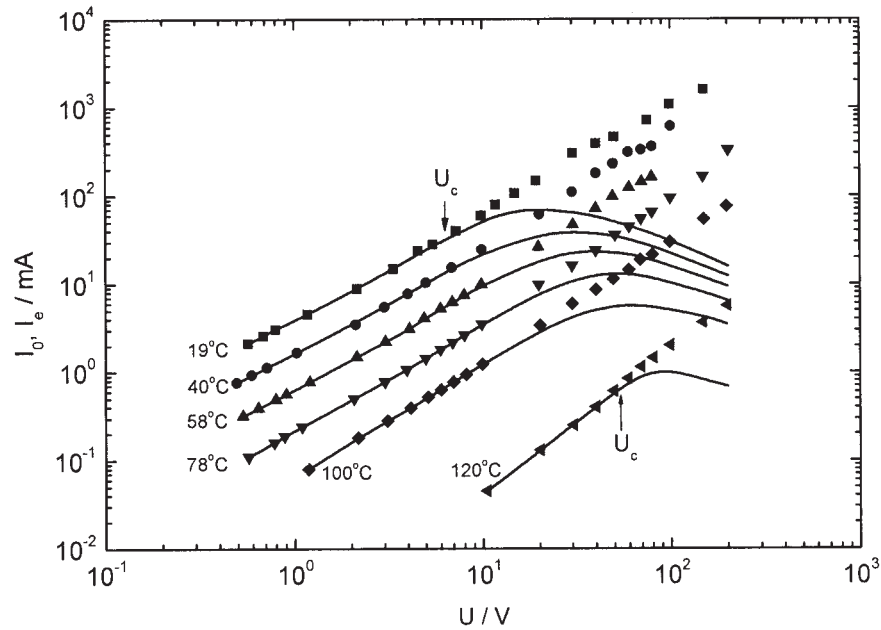
defect and additional conducting pathway generate randomly under electric fields. These two competing processes are comparable with each other at  $U < U_c$  so that the topology of the percolating network does not vary markedly. At higher voltages, however, the local breakdown of percolating backbone becomes dominant, which restricts the current flowing through the sample and makes the percolating network to reach a final stationary state whenever the field strength is below the electrical breakdown strength. The variation of the percolating network from the original to the stationary states is accompanied by the current decay and the temperature growth as a function of time.

#### Influence of voltage on $\tau_i$ and $\tau_g$

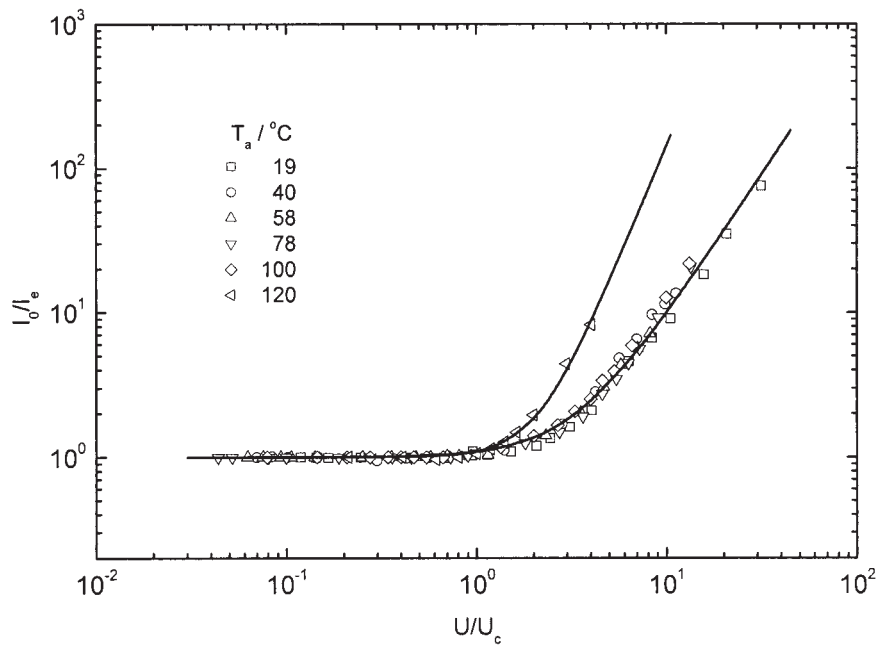
Equations (1) and (2) are used to fit the data of  $I$  and  $T_s$  as a function of time measured at different voltages and at different ambient temperatures. The characteristic time constants  $\tau_i$  and  $\tau_g$  decrease as increasing voltage  $U$ , as shown in Figure 3. When  $\tau_i$  and  $\tau_g$  are plotted against the reduced voltage  $(U/U_c)$ , the two sets of data are superposed to form respective master curves, as shown in Figure 4. The master curves could

be written in  $\tau_i = f_i\left(\frac{U}{U_c}\right)$  and  $\tau_g = f_g\left(\frac{U}{U_c}\right)$ , respectively.

Here  $f_i$  and  $f_g$  are scaling functions, which should predict that  $\tau_i$  and  $\tau_g$  approach to constant values of 233 and 200 s, respectively, as  $U$  approaches to  $U_c$  from above. At  $U < U_c$ , the self-heating behavior does not occur and current does not vary with time so that  $\tau_i = \tau_g = 0$  s is expected. At  $2U_c < U < 15U_c$ , both  $\tau_i$  and  $\tau_g$  scales with  $(U/U_c)$  as



(a)



(b)

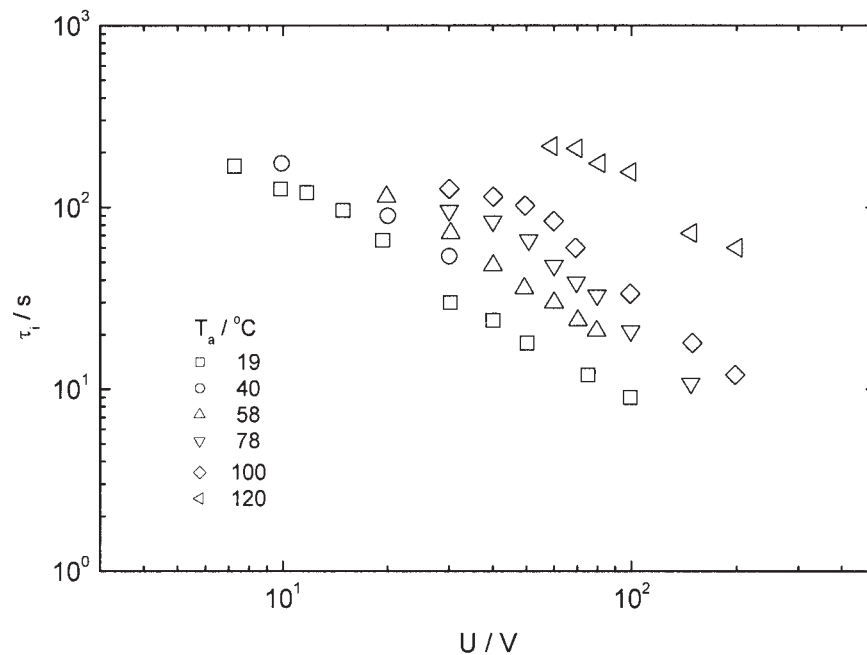
**Figure 2** (a) Currents  $I_0$  (solid symbols) and  $I_e$  (curves) and (b)  $I_0/I_e$  as a function of voltage  $U$  for the HDPE/CB composite at various ambient temperatures  $T_a$ . The solid curves are calculated according to eq. (3).

$$\tau_i \sim \left(\frac{U}{U_c}\right)^{-x} \quad (4)$$

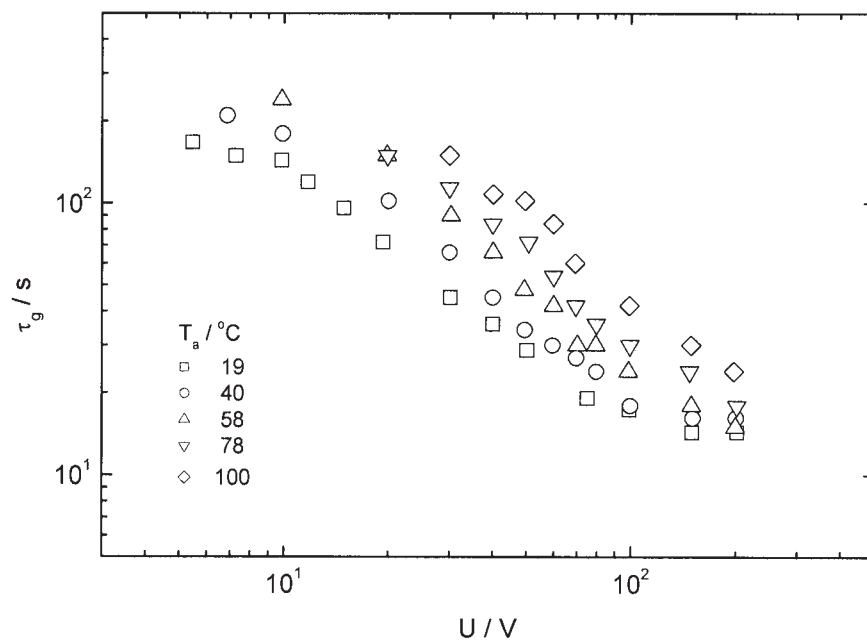
and

$$\tau_g \sim \left(\frac{U}{U_c}\right)^{-y} \quad (5)$$

The exponents  $x$  and  $y$  are estimated as  $1.25 \pm 0.03$  and  $1.05 \pm 0.02$ , respectively. At  $U > 20U_c$ , the data in Figure 4(b) suggest that  $\tau_g$  approaches a constant value of  $\sim 15$  s independent of voltage. This tendency is not yet clear for  $\tau_i$  in Figure 4(a) because of the limited voltage range measured. The results re-



(a)



(b)

**Figure 3** Rate constants  $\tau_i$  (a) and  $\tau_g$  (b) as a function of voltage  $U$  for the HDPE/CB composite at various ambient temperatures  $T_a$ .

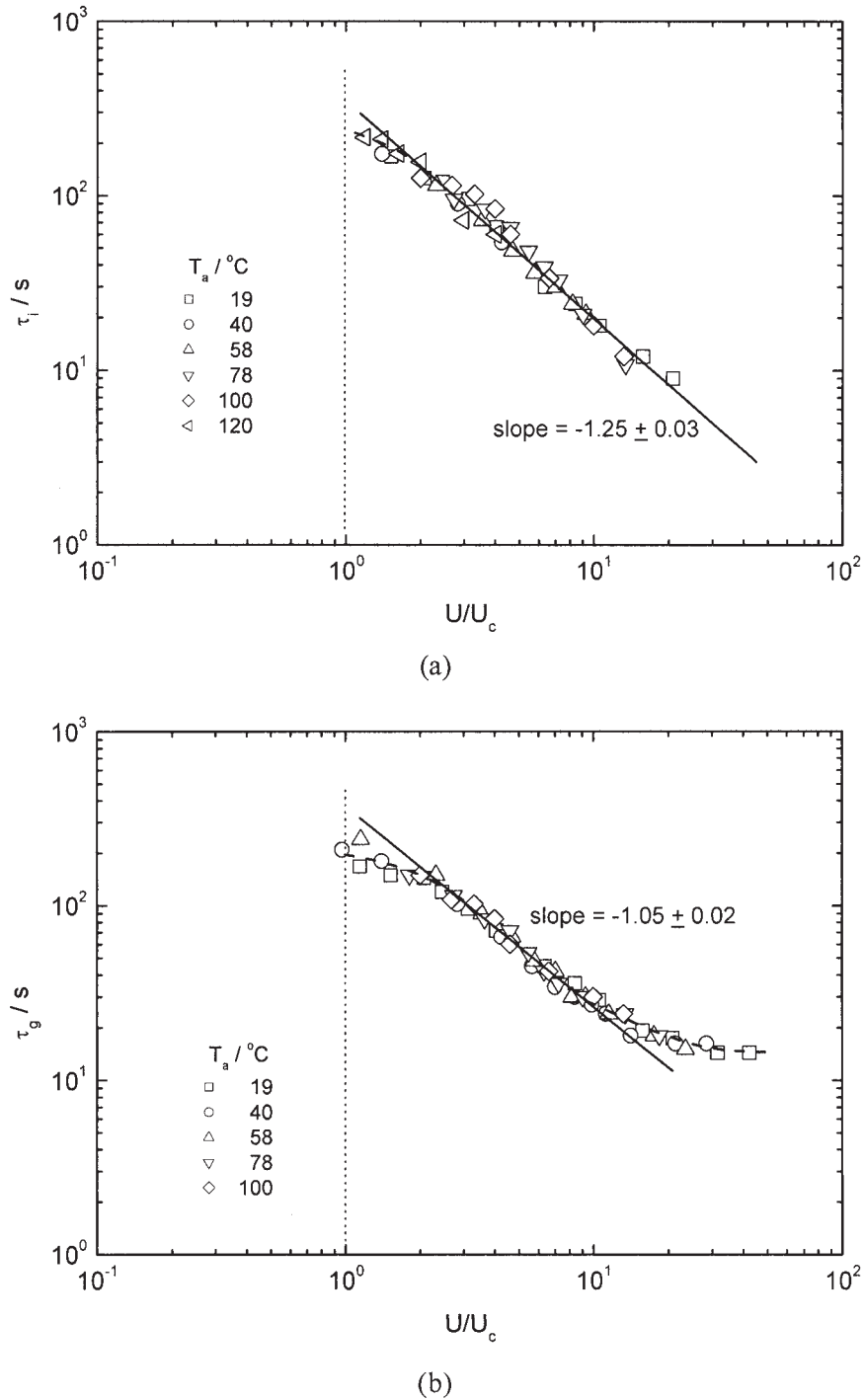
veal that the switching from the low-resistance to the high-resistance states is accelerated, as voltage is increased.

#### Influence of ambient temperature

The ambient temperature also has an importance influence on the amplitude and the rate of the resistance

switching under applied AC voltage. With increasing  $T_a$ ,  $\tau_i$  and  $\tau_g$  increase at the same level of voltage, i.e., the resistance switching becomes slow. This can be ascribed to the resistivity rise with increasing  $T_a$ , i.e., the intrinsic PTC behavior, as shown in Figure 5.

Because the critical voltage  $U_c$  are scales for both rate constants  $\tau_i$  and  $\tau_g$  as well as the resistance fluctuation  $(\rho_e/\rho_0 - 1)$ , influence of  $T_a$  on  $U_c$  is



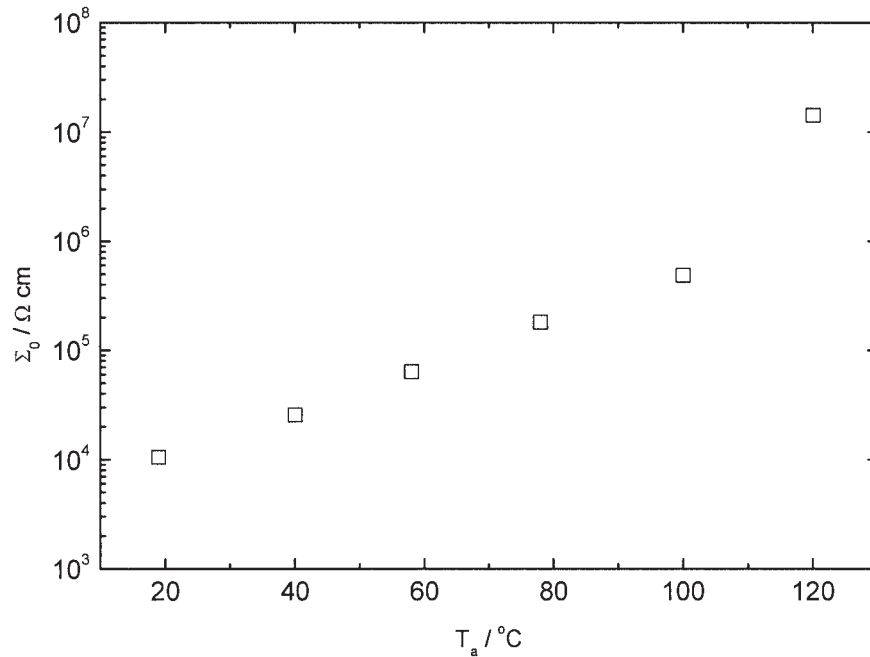
**Figure 4** Rate constants  $\tau_i$  (a) and  $\tau_g$  (b) as a function of reduced voltage  $U/U_c$  for the HDPE/CB composite at various ambient temperatures  $T_a$ .

essential for the onsets of the self-heating and also the current decay.  $U_c$  is plotted in Figure 6 against the intrinsic resistivity  $\Sigma_0$  measured using a pulsed DC voltage of 10 V before application of AC voltages. The result reveals that  $U_c$  scales with  $\Sigma_0$  as

$$U_c \sim \Sigma_0^m \tag{6}$$

and  $m = 0.32 \pm 0.01$  is a scaling exponent. Combining eqs. (3) and (6) yields a universal expression for the resistance variation from the initial to the stationary state of the percolating network as a function of voltage and ambient temperature as

$$\frac{\rho_e}{\rho_0} - 1 \sim U^\theta \Sigma_0^{-m\theta} \tag{7}$$



**Figure 5** Initial resistivity  $\Sigma_0$  measured using a pulsed DC voltage of 10 V before application of AC voltages as a function of ambient temperature  $T_a$  for the HDPE/CB composite.

Similarly, the characteristic times of current decay and self-heating temperature can be expressed as

$$\tau_i \sim U^{-x} \Sigma_0^{xm} \tag{8}$$

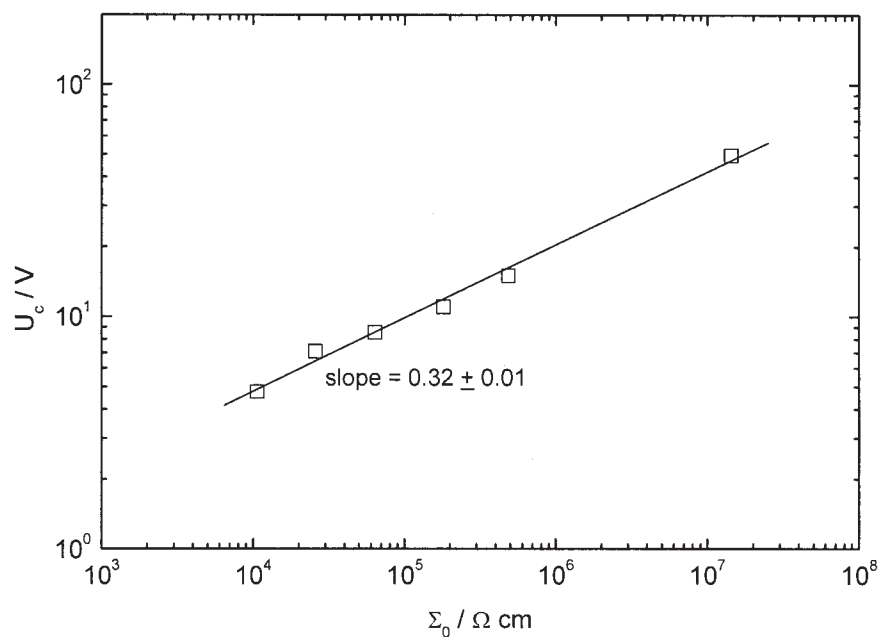
and

$$\tau_s \sim U^{-y} \Sigma_0^{ym} \tag{9}$$

respectively, at  $2U_c < U < 15U_c$ .

### CONCLUSIONS

The HDPE/CB composite with a CB volume fraction 0.082 slightly above the percolation threshold 0.080 shows self-heating and low-resistance to high-resis-



**Figure 6** Critical voltage  $U_c$  as a function of initial resistivity  $\Sigma_0$  measured using a pulsed DC voltage of 10 V for the HDPE/CB composite at various ambient temperatures  $T_a$ .

tance switching behaviors at voltages above a critical voltage, depending on the ambient temperature or the intrinsic resistivity. The critical voltage  $U_c$  for the onset of self-heating is found to be scaled with the intrinsic resistivity. On the basis of the scaling expression in the RRN model, the dynamic processes of self-heating and resistance switching characterized by the switching amplitude  $(\rho_e/\rho_0 - 1)$ , the characteristic decay current constant  $\tau_i$  and the exponential growth time constant for self-heating  $\tau_g$  are formulated as a function of voltage and intrinsic resistivity for a composite with a certain composition. This should be a supplementary to the previous studies showing that the dynamic processes are involved in the content of conductive filler and crosslinking degree of the matrix at a given ambient temperature.<sup>10,20,21</sup>

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