Influence of Irradiation Crosslinking on 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 in high-density polyethylene/acetylene carbon black composites crosslinked with electron beam irradiation at three different dosages are studied in relation to voltage and ambient temperature. The characteristic decay current constant (τ_i) and the exponential growth time constant for self-heating (τ_g) are determined for the samples under voltages (U) above the onset voltage (U_c) of self-heating. The influence of crosslinking on the current decay dynamics, self-heating process, and amplitude of the resistance switching under field action are discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4418–4422, 2006

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

INTRODUCTION

Conductive particle filled semicrystalline polymer composites exhibit a positive temperature coefficient (PTC) effect of resistivity upon heating.[1–6] In important industrial applications such as excess current protection and self-regulating heaters,[7,8] a considerably high voltage usually leads to local Joule heating as well as global resistance switching and a current decay until a stationary "switched" state is reached.[9,10]

The dynamic processes of conduction in conductive polymer composites[10–21] have attracted considerable attention. In composites based on high-density polyethylene (HDPE), self-heating is involved in the initial resistance, electric field induced PTC transition, and heat dissipation, as well as crosslinking of the matrix.[10,20,21] In a recent article we studied the dynamic processes in a HDPE/acetylene carbon black (CB) composite in relation to ac voltage (U).[22] We found that the critical voltage (U_c) for the onset of self-heating scales with the intrinsic resistivity, the variation of the average resistivity ($\rho_e/\rho_0 - 1$) under voltages can be well explained using the random resistor network (RRN) model,[23–25] and the characteristic decay constant (τ_i) of current and the exponential growth time constant (τ_g) of self-heating scale with the reduced voltage (U/U_c).

Conductive composites based on semicrystalline polymers display a negative temperature coefficient (NTC) effect of resistivity above the melting point (T_m), which has an adverse influence on the application, but it could be reduced or eliminated by crosslinking the matrix.[7,26,27] In this article we investigate the dynamics of self-heating and resistance switching in HDPE/CB composites with different degrees of crosslinking. The influence of the degree of crosslinking on the rates of current decay and self-heating as well as the amplitude of resistance switching are discussed.

EXPERIMENTAL

Materials

HDPE (density = 0.942 g cm^{-3}, melting point = 130°C, melting index = 0.14 g/10 min) and CB (particle size = 42 nm, Brunauer–Emmett–Teller special surface a0rea = 63 m^2 g^{-1}, dibutyl phthalate absorption = 1.70 cm^3 g^{-1}) were obtained from Yangzi Ethylene Co. and Shanghai Jishan Chemical Co., respectively. HDPE and CB were mixed on a two-roll mill at 160 ± 5°C for 20 min followed by a compression molding at 165 ± 5°C under 14.7 MPa for 10 min to form 30 × 30 × 2 mm sheet samples. The volume fraction of CB was 0.082, which is slightly above the percolation

threshold (0.080). Electron beam irradiation of the composites was carried out using a BF-5 linear electron accelerator (Institute of Low Energy Nuclear Physics, Beijing Normal University, Beijing) at a dosage rate of 100 Gy s^{-1} in air at 25°C. The electron energy and the beam current were 3 MeV and 200 μA, respectively. On the basis of DSC measurements using a PerkinElmer Series 7 differential scanning calorimeter with a heating rate of 10°C/min, the melting points were determined as 127.2, 122.4, and 118.5°C and the crystallinities of HDPE were 0.42, 0.32, and 0.30 for composites after crosslinking with irradiation dosages of 8, 40, and 200 kGy, respectively.

Method

Two copper net pieces were mounted on the opposite wide surfaces of the sheet to ensure a good electrical contact with the attached copper electrodes. The two-probe resistance measurement was carried out using a M890B^{+} digital multimeter (Shenzhen Huayi Mastech Co.) in pulse mode for measuring the intrinsic resistivity (Σ_0) of the composite while applying a dc voltage of 10 V.

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 ±0.5°C. The resistance showed time-dependent behavior at elevated temperatures, even below the melting point of HDPE. The samples were therefore held at a desired T_a for 24 h to facilitate resistance to attain a relatively steady value. The intrinsic resistance was measured first. An 50-Hz ac voltage adjusted by a transformer was then applied on the samples for at least 10 min in order to ensure that the current passing through the sample reached its steady value. The current (I) was measured using a digital multimeter. From a technical point of view, the bulk temperature could accurately reflect the self-heating of the samples. However, the self-heating and thermal dissipation resulted in a temperature distribution field inside the sample; that is, the temperature was the highest in the center and decreased toward to the surface. Because of experimental difficulties in evaluating the temperature distribution, the surface temperature (T_s) of the sample was monitored using a copper-constantan thermocouple attached on the wide surface of the sample. The T_s was recorded using a TM902C digital thermometer (Hongyan Electron Co.). After the current and T_s reached their steady values, the ac voltage was switched off. When the sample had naturally cooled down to T_a, 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. The measurements were performed at six arbitrarily selected T_a values below the T_m for each sample.
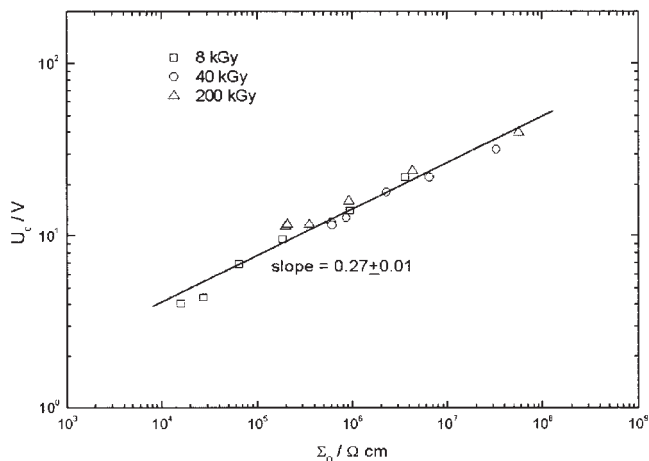
Figure 1 The critical voltage (U_c) as a function of the initial resistivity (Σ_0) measured using a pulsed dc voltage of 10 V for the HDPE/CB composites at various ambient temperatures (T_a).

RESULTS AND DISCUSSION

When an applied ac voltage (U) is sufficiently low, I flowing through the sample is independent of time (t) and the sample does not show any self-heating behavior. Under voltages higher than a critical value (U_c), I decays from an initial value (I_0) corresponding to the intrinsic conduction until a steady value (I_e), which is accompanied with an increment of the T_s from T_a to a corresponding 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. The onset voltage of self-heating (U_c) scales with the initial resistivity (Σ_0)

$$U_c \approx \Sigma_0{}^m \qquad (1)$$

as shown in Figure 1. Variation of the irradiation dosage from 8 to 200 kGy does not influence the relationship between U_c and Σ_0 and the scaling factor (m) is determined as 0.27 ± 0.01 using least-squares fitting. This value is slightly smaller than the $m = 0.32$ ± 0.01 found in the noncrosslinked composite with the same CB content,[22] which reflects the effect of crosslinking on either the percolating structure or the onset behavior of self-heating. Electron beam irradiation introduces interchain crosslinks in the matrix and improves the thermomechanical properties of the composites. It is well known that crosslinking can result in more stable conductive behaviors and the NTC effects have been marginalized compared to the noncrosslinked composites.[7,26,27] The resistance hysteresis and electrical set during heating–cooling cycles are also reduced because of crosslinking,[26] which is ascribed to the reduced mobility of polymer chains. Nevertheless, Figure 1 reveals that the U_c for self-

heating is exclusively related to the initial resistivity or the percolating network of the composites. Crosslinking of the matrix does not influence the underlying mechanism that causes the self-heating and the associated current decay.

During the process of self-heating, the decay in $I(t)$ and the increase in $T_s(t)$ could be described as[13,28,29]

$$I(t) - I_e = (I_0 - I_e)\exp\{-t/\tau_i\} \qquad (2)$$

and

$$T_s(t) - T_a = (T_{se} - T_a)[1 - \exp\{-t/\tau_g\}] \qquad (3)$$

respectively. In eqs. (2) and (3) the τ_i and τ_g should be dependent on various factors such as the filler content, the dispersion of the filler in the matrix, the interface adhesion between the filler and the matrix, the crosskinking of the matrix, the applied voltage, as well as the T_a. Equations (2) and (3) are used to fit the experimental data of $I(t)$ and $T_s(t)$ measured at different voltages and at different T_a values. The results are shown in Figure 2 as a function of the U/U_c. At moderately high voltages of $2U_c < U < 15U_c$, both τ_i and τ_g scale with U/U_c as

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

and

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

where x and y are scaling exponents.

The relative resistivity (ρ_e/ρ_0) under voltage action could be characterized using I_0/I_e. Here, ρ_0 and ρ_e are the respective resistivities at time zero and infinity after application of ac voltage on the sample. As shown in Figure 3, I_0/I_e as a function of U/U_c collapses onto respective master curves for the composites crosslinked with irradiation dosages of 8, 40, and 200 kGy. The collapsed data can be described using the scaling expression from the RRN model[23–25]

$$\frac{\rho_e}{\rho_0} - 1 = \lambda\left(\frac{U}{U_c}\right)^\theta \qquad (6)$$

where λ is a dimensionless coefficient and θ is an exponent. The θ value is determined as ~2.0 for the three crosslinked composites, which is the same as the noncrosslinked composite at $T_a \leq 120°C$.[22] Note that this value is consistent with the value of 2.1 ± 0.1 obtained by Pennetta et al.[25] for the two-dimensional RRN at 300 K.
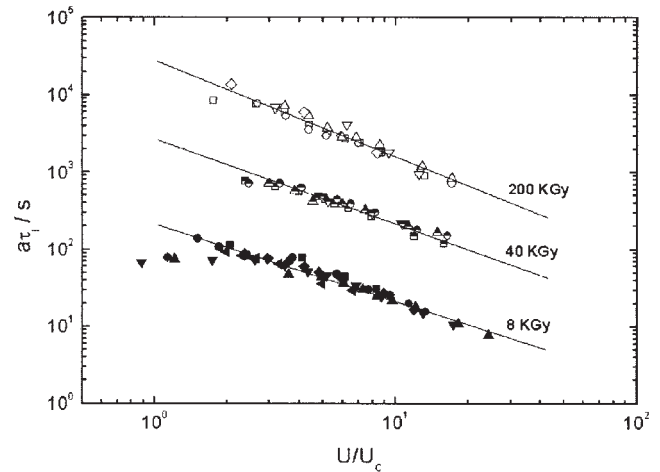
(a)
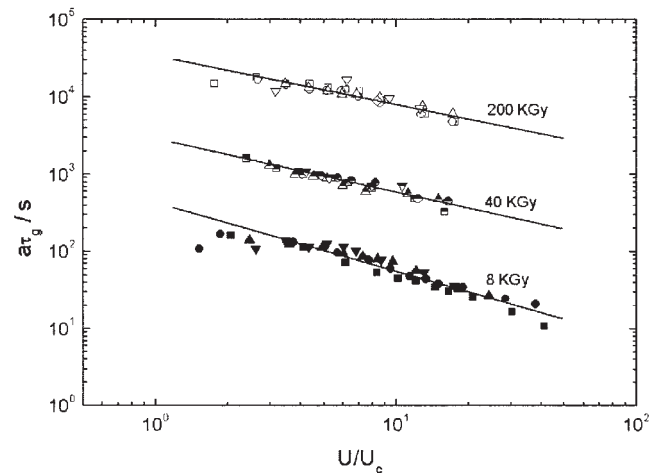
(b)

Figure 2 Characteristic time constants (a) τ_i and (b) τ_g as a function of reduced voltage (U/U_c) for the HDPE/CB composites at various ambient temperatures (T_a). The data of the 40- and 200-kGy samples are shifted along the vertical axis by a factor of $a = 10$ and 100, respectively.

The RRN model assumes that the resistors in the percolating network may become insulating when the local current is higher than the breaking current of the resistor. 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.[23,24] The application of eq. (6) to the collapsed data reveals that the microscopic processes that cause the global breakdown of the percolating network under field action are essentially independent of the crosslinking of the matrix. According to the RRN model, the insulating defect and additional conducting pathway are generated randomly under electric fields. These two competing processes are comparable with each other at $U < U_c$, so the topology of the percolating network does not vary markedly. At higher voltages, however, the

self-heating causes the volume expansion of the composite and the resultant local breakdown of the percolating backbone.

The influence of crosslinking on the rates of current decay and self-heating as well as the amplitude of resistance switching can be characterized using the values of x, y, and λ, respectively. Figure 4 shows x, y, and λ as a function of the irradiation dosage. It reveals that x and λ are at a minimum at irradiation dosages of 8 and 40 kGy, respectively, whereas y decreases continuously with increasing irradiation dosage. Application of a voltage above U_c on the sample leads to local melting of thin polymer layers between particle pairs. The y parameter in the composites with the same CB content is thus related to the crystallinity of the matrix that decreases with increasing irradiation dosage. For the current decay, the x parameter is involved in two competing factors. The decrease of the crystallinity accelerates the structural alternation to reach the switched state, whereas the presence of interchain crosslinks constrains the local rearrangement of the particle and hinders resistance switching. Therefore, x shows a minimum at a somewhat low irradiation dosage. The λ parameter reflects the variation of the average resistivity at $U = U_c$, which might be considered as a measure of the structural stability of the percolating network under voltage action. Figure 4 reveals that a suitable crosslinking of the matrix could reduce the amplitude of the resistance switching and improve the topology of the percolating network under field action.

CONCLUSION

The HDPE/CB composites crosslinked through electron beam irradiation at three different dosages show
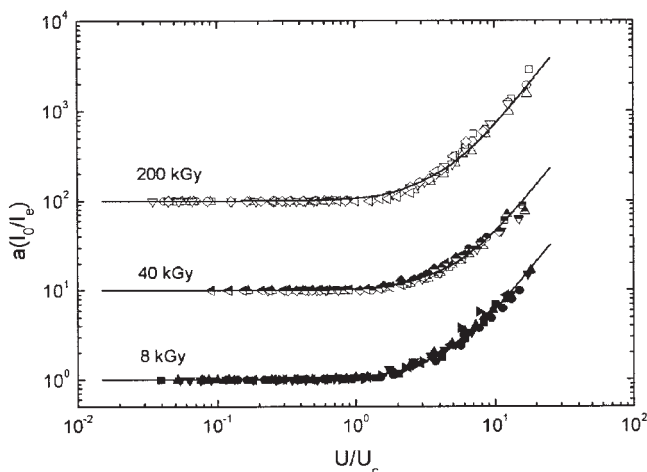
Figure 3 The initial current value/steady current value (I_0/I_e) as a function of reduced voltage (U/U_c) for the HDPE/CB composites at various ambient temperatures (T_a). The solid curves were calculated according to eq. (6). The data of the 40- and 200-kGy samples are shifted along the vertical axis by a factor of $a = 10$ and 100, respectively.
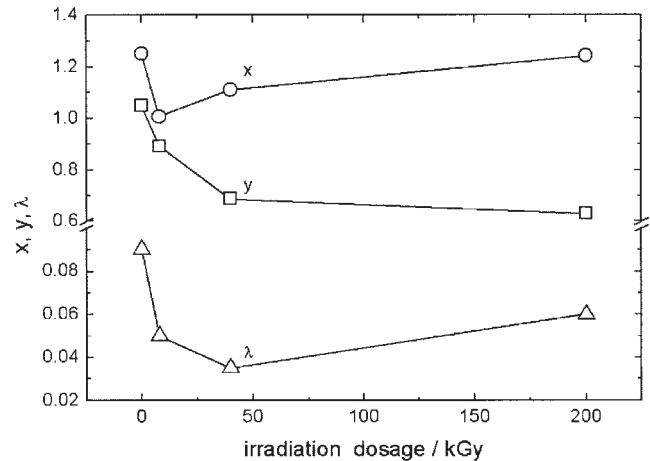
Figure 4 The influence of the irradiation dosage on the scaling exponents x and y as well as the dimensionless coefficient (λ).

self-heating and low-resistance to high-resistance switching behaviors at voltages above a critical voltage, depending on the ambient temperature or the intrinsic resistivity. The critical voltage for the onset of self-heating scales with the intrinsic resistivity and this scaling expression is independent of the irradiation dosage. Crosslinking does not influence the decay dynamics of current significantly, but it makes the self-heating dynamics become slow. In contrast, suitable crosslinking of the matrix can reduce the amplitude of the resistance switching under field action.

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