Resistivity Relaxation Behavior of Carbon Black Filled High-Density Polyethylene Conductive Composites

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ABSTRACT: The variation of resistivity for high-density polyethylene (HDPE) conductive composites filled with carbon black (CB) with time was investigated under the excitation of different temperature field. The movement of CB particles in the HDPE matrix was not a momentary equilibrium process, but a relaxation process. The relaxation of resistivity of the composites was monotonic, and it could be described by an exponential form above melting temperature. However, the relaxation of resistivity was nonmonotonic below melting temperature, herein a parameter t_0 which was the beginning time of the resistivity attenuation could be introduced into the exponential equation. The attenuation of resistivity at constant temperature was limited for the composites with certain content of CB. The resistivity of the composites would incline to a constant value with the prolongation of time no matter what the heat treatment temperature was. Heating rate had influence on the relaxation of resistivity of the composites, and the lower heating velocity resulted in less time to approach to the equilibrium resistivity. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1104–1108, 2013

INTRODUCTION

It has been known that a composite consisting of conductive fillers and an insulating polymer becomes electrically conductive as the filler content exceeds a certain critical value. One of the most important characteristics of the filled polymer conductive composites is that their electrical conductivity increases nonlinearly with increase of the volume fraction of filler particles.[1–3] When the volume fraction of filler particles is up to a certain critical value, a drastic transition from an electrical insulator to a conductor will be exhibited, which results from the massive formation of conductive networks.[4–6] However, the conductive networks of polymeric conductive composites are thermodynamic unstable, it can be changed under the excitation of external fields, such as temperature,[7] pressure,[8] electric field,[9–11] and so on, and this change is macroscopically presented in the variation of resistivity. The change of conductive networks cannot keep up with the change of external field due to the lag of chain segment motions results from the chemical and physical structure of polymer matrix,[12,13] thus shows the dependence of resistivity on time, namely resistivity relaxation phenomenon.

Temperature is one of the most important influence factors on electric conductivity of the composites. The investigation of resistivity relaxation behavior at constant temperature is helpful to further reveal the micromechanism of positive temperature coefficient (PTC) and negative temperature coefficient (NTC) characteristics of the conductive composites.[14] In the past few years, although a lot of studies have been carried out to analyze the conductive behavior in the filled conductive polymer composite,[15–18] but a few of them has focused on the resistivity relaxation phenomenon of these composites. In this instance, it is necessary to investigate the resistivity relaxation behavior of these composites.

In the previous work, the authors[19] studied electrical properties and morphology of carbon black (CB)-filled high density polyethylene (HDPE)/ethylene vinyl acetate (EVA) composites. In the present article, the resistivity relaxation behavior of HDPE/CB composites at constant temperature is investigated, and the correlated mathematical expression is proposed to describe this behavior at different temperature field.

EXPERIMENTAL

Materials

The CB with trade mark of Vulcan XC-72, used as the conductive filler, was provided by Cabot Co. (Shanghai, China). Its average diameter, specific surface area (BET), and oil absorption
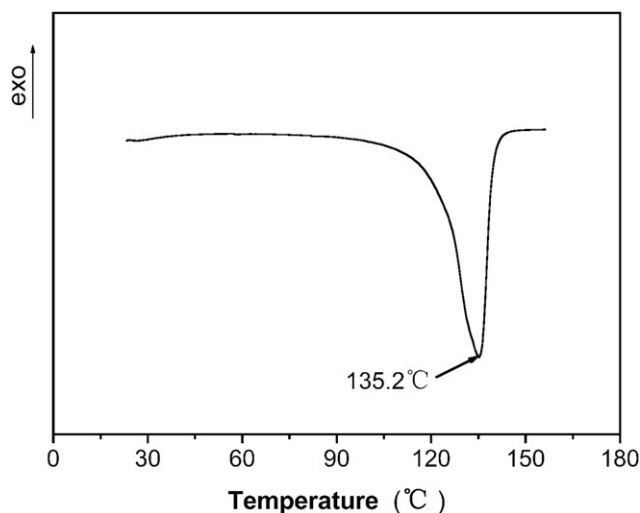
Figure 1. DSC curve of HDPE/CB composite with CB weight fraction of 16%.

Figure 2. DSC curve of HDPE/CB composites. (a) 0 wt. %, (b) 4 wt. %, (c) 12 wt. %, (d) 16 wt. %.

value (DBP) of CB were 30 nm, 254 m^2/g, and 178 mL/100 g, respectively. The HDPE with trade mark of 5000 S was supplied by Petro China Co. (Daqing city, China). The melting index of the resin was 0.9 g/10 min (190°C, 2.16 kg).

Preparation
The HDPE resin was melt mixed with the CB in a Brabender mixer with model of plasti-corder supplied by Brabender Co. (Duisburg, Germany) at 155°C and 40 rpm for 8 min, and the proportions between the HDPE and CB were desired. Then the blends were compressed into sheets with a thickness of 2 mm by compression modeling at 160°C under a pressure of 10 MPa for 10 min. The sheets were cut into 70 mm × 10 mm × 2 mm in size. The weight fractions of the CB were from 0% to 16%.
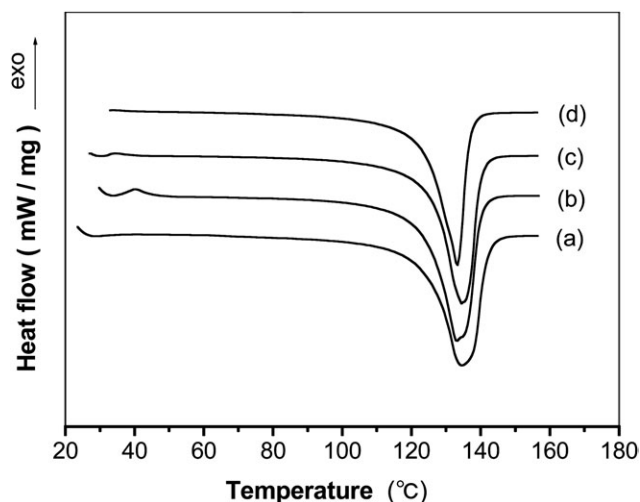
Measurement of Electrical Properties
The volume resistivity of the composites was measured by a four-probe method (ASTM D-991) using two multimeters and a voltage supply. The four-probe method could effectively avoid the contact resistance which affected the precision of the measurement. The relationship between the resistivity and the time of constant temperature heat treatment was investigated.

Measurement of Thermal Properties
The thermal properties of the composites were measured using a differential scanning calorimeter (DSC), the model was ZETZCH DSC204C supplied by NETZCH company (Selb, Bavaria, Germany), and the heating rate was 10 °C/min in nitrogen.

Fractography
The fracture surface of the specimen was examined by means of a scanning electron microscope (SEM, model S-550) supplied by Hitachi Co. Ltd. (Tokyo, Japan) to observe the dispersion or distribution of the CB particles in the HDPE matrix. The specimens were gold coated before SEM examination.

RESULTS AND DISCUSSION

DSC Curves
The DSC curves of HDPE/CB composite with the CB weight fraction of 16% is shown in Figure 1, from which we can get a melting peak temperature of 135.2°C. The HDPE/CB composites were heated with a heating rate of 1 °C/min to a certain temperature, and then isothermal heat treatment was carried out. Figure 2 shows the DSC curves of HDPE/CB composites with different CB weight fractions. It can also be seen that the variation of the location and the area of the melting peak of the composite systems are not obvious. In other words, the addition of CB does not change obviously the melting peak temperature. Table I lists the measured data of the temperature at melting peak and the crystalline degree of the HDPE/CB composites. The crystalline degree (χ_c) of polymeric materials is usually defined as follows:

$$\chi_c = (\Delta H_c / \Delta H^*) \times 100\% \tag{1}$$

where ΔH_c is the thermal enthalpy during crystallization of the composite, ΔH^* is the thermal enthalpy in crystallization for 100% crystalline HDPE homopolymers, $\Delta H^* = 270.028$ J/g.

It may be observed that the crystalline degree of the composites decreases slightly with increasing CB content. That is, the crystalline degree decreases from 61% to 49.9% when the weight fraction of the CB increases from 0% to 16%. Moreover, the melting peak temperatures are between 133°C and 135°C, which are close to the PTC peak temperatures. It means that the influences of the CB on the crystalline degree and the melting peak

Table I. DSC Data of HDPE/CB Composites

Weight fraction of CB (%)	0	4	12	16
Temperature at melting peak (°C)	134.5	133.1	134.4	133.1
Crystalline degree (%)	61.4	57.4	56.0	49.4
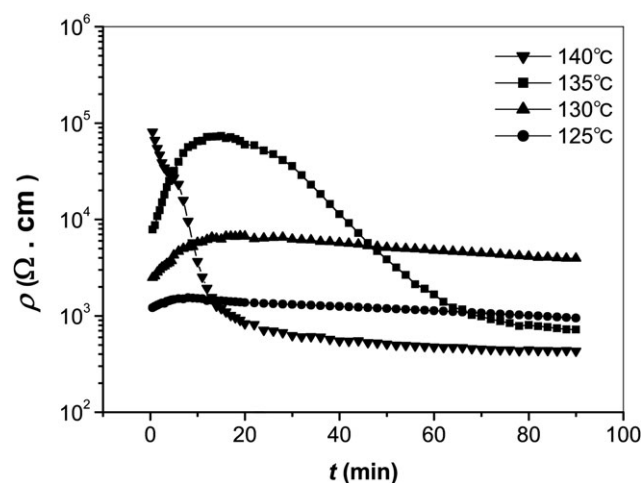
Figure 3. Relaxation curves of HDPE/CB composites during isothermal heat treatment.

temperature of the composites are insignificant. Namely, the CB particles in the HDPE matrix do not play the heterogeneous nucleation. This might be that the addition of the rigid CB particles should block, to certain extent, the movement of the HDPE macromolecular chains.

The above results indicate that the filling of the CB into the HDPE does not vary obviously the melting peak temperature of the HDPE, and does not affect the temperature of PTC shift in peak. However, there is certain influence of the CB on the crystalline property of the HDPE resin. When outside temperature is approaching gradually to the melting temperature of the HDPE, the thermal properties of the composite system will play significant variation, such as the rapid expansion of the HDPE matrix volume, the internal stress field rapidly disintegrating, etc. These variations provide enough driving force and space conditions for the relative motion of conducting particles. The variation of thermodynamic properties will affect significantly the CB conductive network, even will destruct massively the conductive network, leading to rapid increase of the resistivity of the composites.

Relaxation Curves

It may be found from Figures 1 and 2 that the effect of the CB content on the thermal behavior for the composites is significant. It is necessary, therefore, to investigate further the resistivity relaxation behavior for the composite system with higher filler content. Figure 3 shows the resistivity relaxation curves of the composites with CB weight fraction of 16% at different heat treatment temperatures. From Figure 3 we can find that the resistivity of the composites increases firstly when the heat treatment temperatures are less than melting temperature (the melting peak temperatures are between 133°C and 135°C), and then decreased with time. But when the heat treatment is above melting temperature, the resistivity decreases monotonously with the time. However, no matter what the heat treatment temperatures are, with prolongation of the time, the resistivity of the composites will incline to a constant value finally which is related to the heat treat temperatures. In other words, the

attenuation degree is limited at a constant temperature for the composites with a certain CB content, which shows that the movement of CB particles is a short range movement.[20]

When the isothermal heat treatment temperatures are less than the melting temperature of polymer matrix, the relative resistivity of the composites increases firstly and then decreases slightly with time. The cause of the change of the resistivity is that the expansion of the matrix cannot catch up with the change of temperature, which results from the relaxation of the macromolecular chain. The expansion of the matrix has basically completed after isothermal heating for some time, CB particles can only make short-range movement near the equilibrium position because of strong restriction of the matrix, the self-repair ability of the conductive networks is extremely limited, therefore the resistivity of the composites can only change with a tiny rate and inclines to a stable value. When the heat treatment temperature is 135°C, the resistivity increases significantly and then decreases rapidly. The temperature 135°C is just near to the melting temperature of the matrix, because the expansion and melting of the matrix cannot catch up with the change of temperature, therefore significant increase of the resistivity will go on. The expansion and melting of the matrix has basically completed after isothermal heating for some time, because of lower melt viscosity and reinforcement of the Brownian motion of CB particles, the CB particles can overcome restriction of the matrix and rearrange, therefore the conductive networks are perfected again and resulted in the rapid decrease of the resistivity.
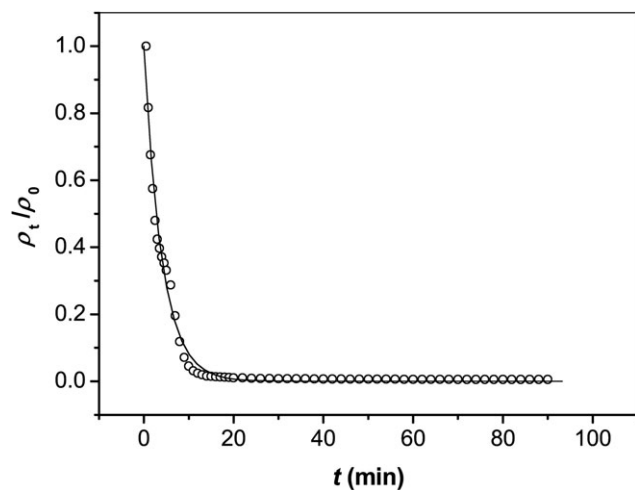
The resistivity–time curve of 140°C isothermal heat treatment is different with that of 125°C, 130°C, and 135°C. From Figure 2 we can find that there is no raising parts in the resistivity–time curve of 140°C isothermal heat treatment. That is because the matrix have melted completely and there is no factor which can effectively destroy the conductive networks, the Brownian motion which makes the conductive networks be repaired plays the dominant role. Because the Brownian motion of CB particles is short-range, the resistivity will incline to a constant value after isothermal heat treatment with a temperature of 135°C or 140°C. The resistivity equilibration time of 140°C isothermal heat treatment is shorter than that of 135°C, this is because the higher the temperature, the more drastic the Brownian motion, and the easier the aggregation of CB particles.

Relationship Between Relative Resistivity and Time

When the composite is isothermal, treated at the temperature higher than melting temperature of the matrix, the attenuation of its resistivity can be described as follows[21]

$$\frac{\rho_t}{\rho_0} = \frac{\rho_\infty}{\rho_0} + \frac{(\rho_0 - \rho_\infty)}{\rho_0} \cdot \exp(\frac{-t}{\tau}) \qquad (2)$$

where t is the time of isothermal heat treatment, τ is the time constant which represents attenuation rate of the resistivity, ρ_0 is the initial resistivity of the composites when $t = 0$, ρ_∞ is the equilibration resistivity when $t \to \infty$, ρ_t is the resistivity of the composites at time t. The relationship between resistivity and time is nonmonotonic below melting temperature, herein a parameter t_0 which is
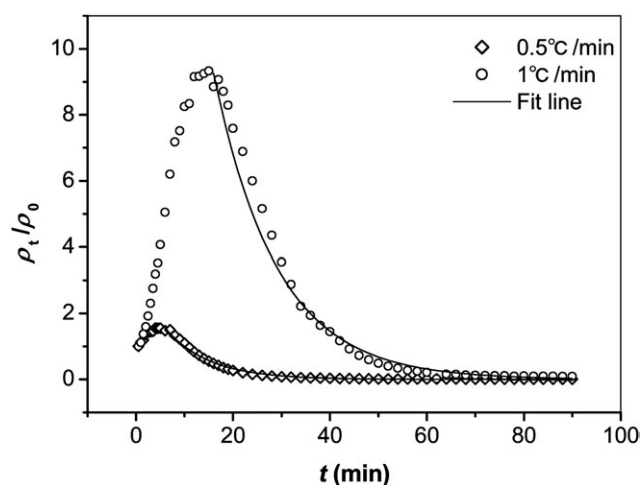
Figure 4. Relaxation curves of HDPE/CB composites during isothermal treatment at the temperature of 140°C.

the beginning time of the resistivity attenuation can be introduced into the exponential eq. (2). The expression is

$$\frac{\rho_t}{\rho_0} = \frac{\rho_\infty}{\rho_0} + \frac{(\rho_{t_0} - \rho_\infty)}{\rho_0} \cdot \exp\left[\frac{-(t - t_0)}{\tau}\right] \quad (3)$$

where ρ_{t_0} is the resistivity of the composites at the beginning of the resistivity attenuation.

Figure 4 shows the relationship between the relative resistivity of the composites with CB weight fraction of 16% and time. It can be seen that the resistivity–time curve of 140°C isothermal heat treatment fitted by eq. (2) is represented by solid line, and the fitting time constant $\tau = 4$. The resistivity–time curves of the composites fitted by eq. (3) are shown in Figure 5, the CB weight fraction is also 16%. The composites were heated to 135°C with different rate and then isothermally treated for 90 min. The beginning time of resistivity attenuation in the resistivity–time curves with the rate of 1 °C/min and 0.5 °C/min are

15 min and 6 min, respectively, and the fitting time constants τ are 13 and 9, respectively. From Figures 4 and 5, we can find that the reasonably good agreement of eq. (1) and eq. (2) with the experiment data suggests that eq. (1) and eq. (2) can preferably predict the resistivity attenuation of CB filled polymer conductive composites.

The time constant τ reflects the restructuring speed of the CB conductive networks and depends on temperature and structure of the composite, and meanwhile, it obeys Arrhenius equation
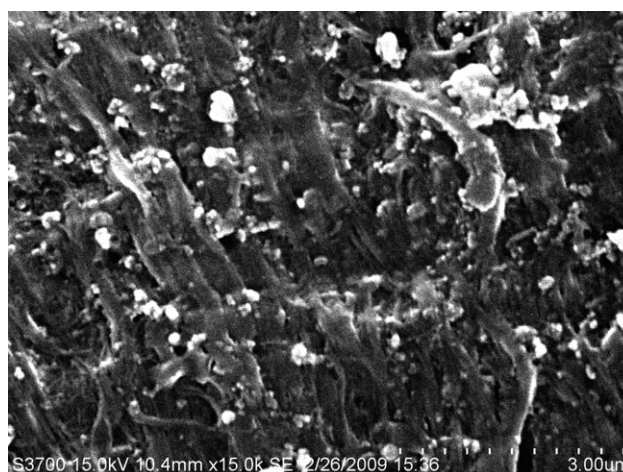
$$\tau = \tau_0 \exp\left(\frac{\Delta E}{RT}\right) \quad (4)$$

where R is the gas constant, ΔE is the activation energy. The eq. (4) indicates that rising temperature and extending time are equivalent. According to the character of resistivity relaxation behavior, the heating rate has inevitable influence to resistivity attenuation. From Figure 5, we can find that the smaller the heating rate, the faster the resistivity approaching equilibrium value. The reason may be that the polymer matrix and CB particles have enough time to adapt to the change of temperature when the heating rate is small.

It is generally believed that the mechanical or physical properties of polymer composites depend, to much extent, on the status of the dispersion of the filler in the matrix and the interfacial morphology between them. Figure 6 is the SEM photograph of fracture surface for the HDPE/CB composite when the filler weight fraction is 16%. It may be observed that the dispersion and distribution of the CB particles in the HDPE matrix are roughly uniform. In addition, the interface between the inclusions and the matrix is unclear. It means that the compatibility between the CB and HDPE is good.

CONCLUSIONS

The motion of CB particles in the HDPE matrix was not a momentary equilibrium process, but a relaxation process. The resistivity attenuation could be described by an equation with exponential form. The attenuation of resistivity at constant

Figure 5. Relaxation curves of HDPE/CB composites during isothermal treatment at temperature of 135°C with different heating rate.

Figure 6. SEM photograph of fracture surface for HDPE/CB composite with filler weight fraction of 16%.

temperature was limited for the composites with certain content of CB because the motion of CB particles was short-range. The resistivity of composites would incline to an equilibrium value with the prolongation of time no matter what the heat treatment temperature was. The equilibrium value depended on the heat treatment temperature. Heating velocity had influence to the relaxation of resistivity, the lower heating velocity resulted in less time to approach the equilibrium resistivity. These findings are beneficial to understand the mechanisms of the resistivity relaxation behavior for the HDPE/CB conductive composites.

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