High-Density Polyethylene/Carbon Black Conductive Composites. II. Effect of Electron Beam Irradiation on Relationship Between Resistivity–Temperature Behavior and Volume Expansion

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ABSTRACT: A study on the contribution of thermal volume expansion to electrical properties is carried out for high-density polyethylene (HDPE)/carbon black (CB) composites irradiated by an electron beam. The results show that the volume expansion obviously generates the positive temperature coefficient (PTC) characteristic of resistivity for unirradiated HDPE/CB composites, but the contribution of volume expansion is decreased for crosslinked HDPE in the composites by electron beam irradiation. A higher degree of crosslinking produced by irradiation in the molten state limits the movability of HDPE chains and CB particles so effectively that it decreases the PTC intensity, which is compared with that irradiated at room temperature. It is suggested that the differences in the resistivity–temperature behavior are not explained satisfactorily on only the basis of the thermal volume expansion, and the decreased movability of HDPE chains and CB particles are believed to be the most fatal factors in lowering the PTC effect. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 3117–3122, 2002; DOI 10.1002/app.10050

Key words: resistivity–temperature characteristic; thermal volume expansion; high-density polyethylene/carbon black composite; crosslinking; electron beam irradiation

INTRODUCTION

The positive temperature coefficient (PTC) effect of resistivity in the melting region of high-density polyethylene (HDPE) for HDPE/carbon black (CB) composites has attracted a great deal of academic and industrial interest for many years.[1–4] The appearance of the phenomenon is attributed to the separation of conductive pathways by thermal volume expansion that is due to the difference in the expansion coefficient between the polymer matrix and conductive filler.[5] It is easy to achieve the result through a comparison of the resistivity–temperature behavior measured with DSC under the same heating and cooling conditions.[6] Most of the researchers have mainly fo-

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cused their attention on uncrosslinked crystalline polymers and relative free volume expansion because a sharp change in the volume expansion exists at the glass-transition temperature or in the melting region of the polymer matrix.[7–9] The present work reports a preliminary study of correlating the resitivity–temperature behavior and thermal volume expansion of HDPE/CB composites irradiated by electron beams at different irradiation temperatures.

EXPERIMENTAL

The composites were prepared by incorporating 20 vol % CB (acetylene black, Chun An Chemical Co.) into HDPE (HDPE2480, Qilu Petro. Co.) by using a Bandury type mixer at 170°C for 15 min. They were then mixed on a two-roll mixer with the same condition. Plate samples were compression molded at 170°C. Electron beam irradiation was conducted by an electron accelerator at 25 and 170°C, corresponding to their solid (RT) and molten states (MT). The resistivity, temperature, and volume were simultaneously measured at a rate of 1°C/min using equipment designed by our group.[10] All the results were obtained from the second run to avoid the different thermal histories.

RESULTS AND DISCUSSION

The relative volume expansion ($V_R = V_T/V_{20}$) of the composites is defined as the ratio of the absolute volume expansion (V_T) at an arbitrary temperature (T) to the absolute value at 20°C (V_{20}). To understand the correlation between the PTC behavior and volume expansion the resistivity and V_R versus the temperature were plotted in the same figures. Figure 1 reveals that for the unirradiated sample the resistivity increases abruptly in the melting region of the composites and the V_R markedly increases simultaneously. The relationships of the logarithmic resistivity and the temperature as plotted in Figure 2(A) show that after being irradiated with 20 kGy, the irradiated sample at MT shows a much more decreased PTC intensity than that of the one at RT. The reason was explained by US[11] in the view of crystallization being attacked by high energy irradiation. On the other hand, the irradiated sample exhibits a decrease of V_R that is lower than

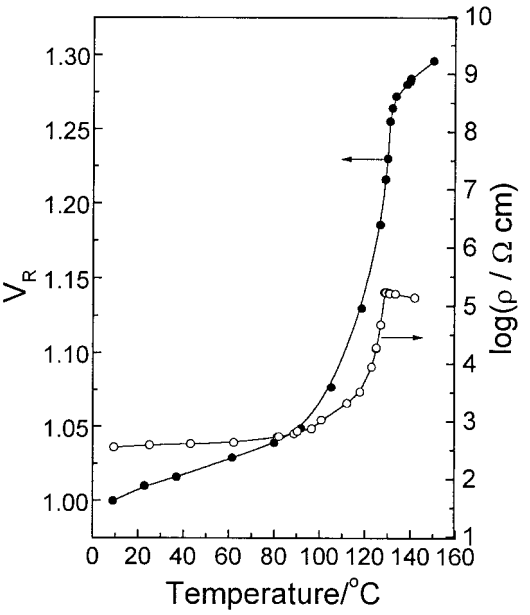

Figure 1 The (○) resistivity–temperature behavior and (●) volume expansion for unirradiated HDPE/CB composites.

that of the unirradiated one as shown in Figure 1. A noticeable difference exists in the volume expansion between MT and RT irradiated samples within the melt temperature region from 105 to 130°C. Here we point out that it is necessary to pay much more attention to those property changes, especially under conditions near the melt transition of HDPE. Thus, it is noted that in Figure 2(A) the lower V_R at MT than that at RT indicates decreased free volume because of its higher crosslinking. From Figure 2(B) it can be found that the resistivity of samples at both MT and RT increase with the V_R increase until V_R reaches 1.15 and 1.20, respectively, because of the breakdown of the conducting path in the composites. However, when the V_R is higher than those two values, the resistivity decrease of the samples is believed to be the result of the dominant effect of the easier movability of CB particles as compared with the dilution arising from the volume expansion under corresponding temperatures higher than about 130 and 135°C, respectively.

Figure 3 indicates the resistivity–temperature behavior and thermal volume expansion of the samples irradiated with 200 kGy. It is obvious that in Figure 3(A) that a remarked difference exists in V_R between MT and RT irradiated samples as compared with Figure 2(A). Additionally,

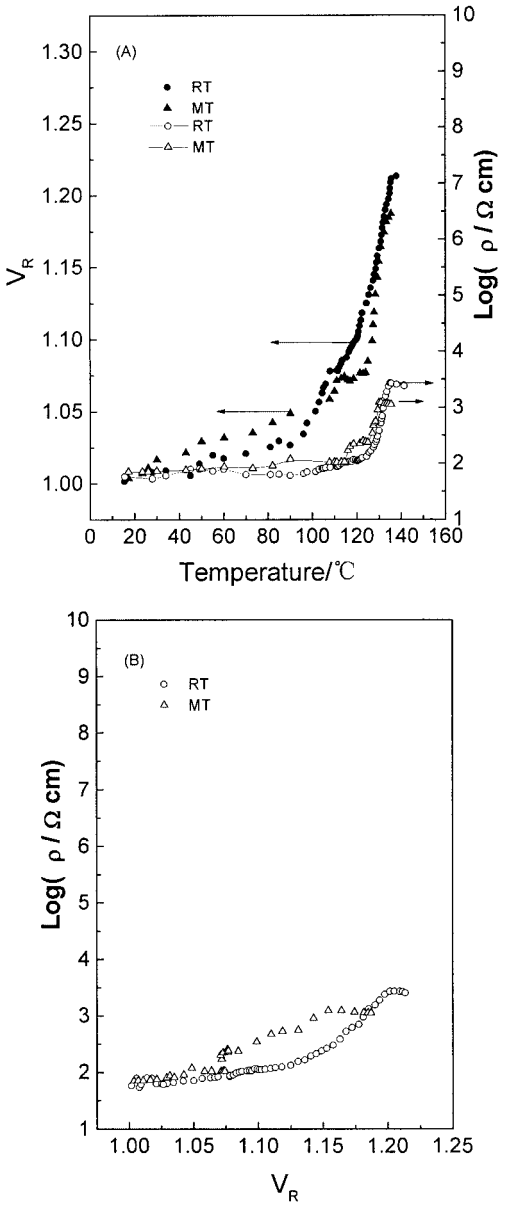

Figure 2 The (○, △) resistivity–temperature behavior and (●, ▲) volume expansion for HDPE/CB composites irradiated at RT and MT with 20 kGy: (A) the resistivity and volume expansion versus the temperature and (B) the resistivity versus the volume expansion.

it can be found that, different from those of the composites irradiated with 20 kGy, the resistivity–temperature behavior for MT and RT composites irradiated with 200 kGy shows an obvious difference: the RT irradiated sample possesses markedly higher PTC intensity. Correspondingly, the RT irradiated sample shows much more sensitivity of resistivity to a V_R increase than the MT one, as shown in Figure 3(B).

Figure 4 presents the relationship between the resistivity–temperature behavior and volume expansion for the composites irradiated with 400 kGy at MT and RT. It is noted that, as compared with the relationships between V_R and tempera-

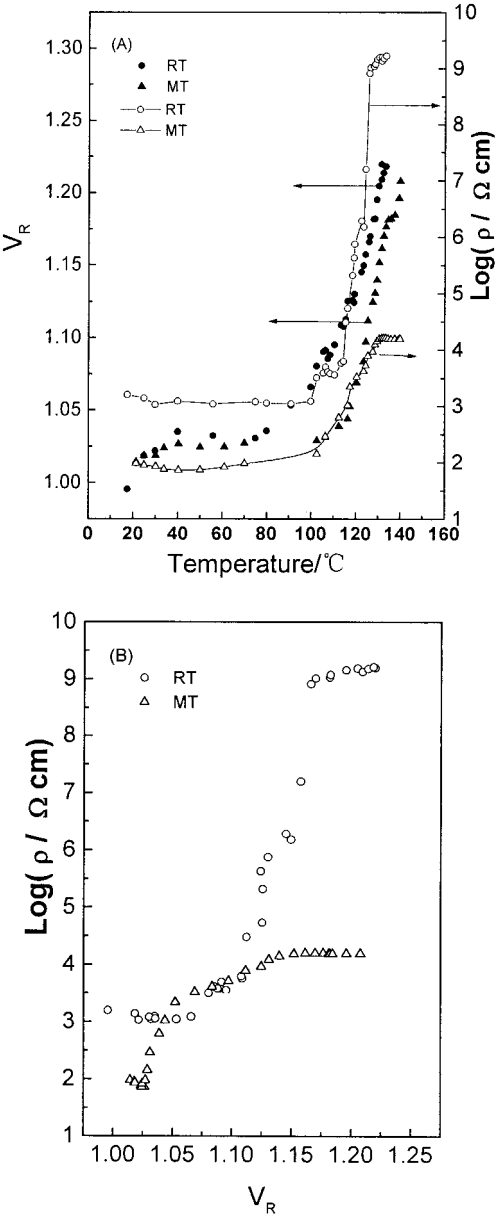

Figure 3 The (○, △) resistivity–temperature behavior and (●, ▲) volume expansion for HDPE/CB composites irradiated at RT and MT with 200 kGy: (A) the resistivity and volume expansion versus the temperature and (B) the resistivity versus the volume expansion.

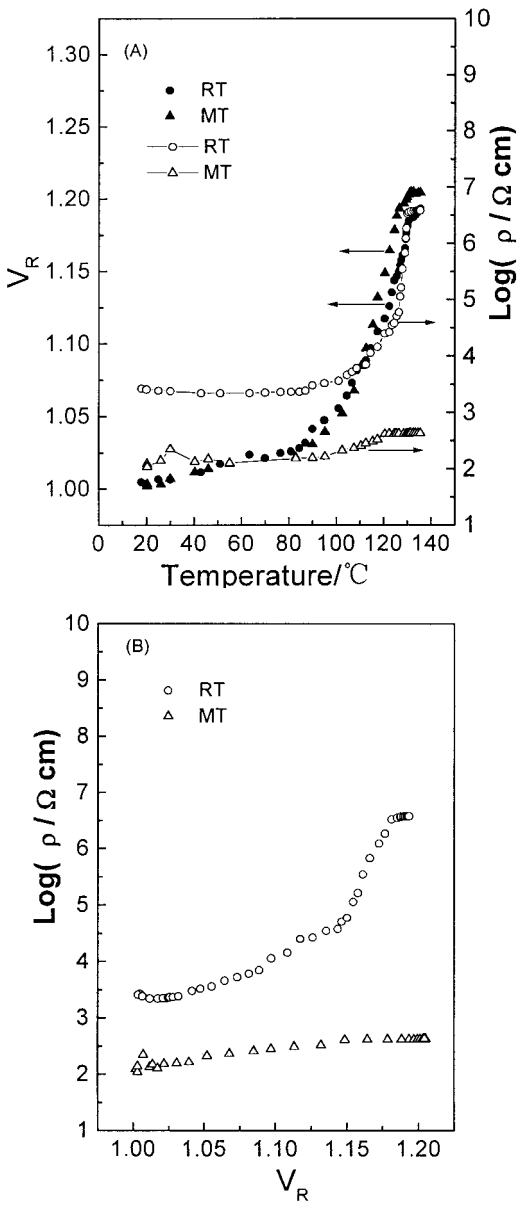

Figure 4 The (○, △) resistivity–temperature behavior and (●, ▲) volume expansion for HDPE/CB composites irradiated at RT and MT with 400 kGy: (A) the resistivity and volume expansion versus the temperature and (B) the resistivity versus the volume expansion.

ture for samples irradiated with a lower dose, the temperature dependence of V_R appears to be almost the same as far as irradiation at MT and RT is concerned. Moreover, the MT irradiated sample shows a rather low PTC intensity due to the lower volume expansion as shown in Figure 4(B), which is attributed to extensive crosslinking under this irradiation dose.

On the basis of Kolher[9] and our previous works,[8] the decrease of CB content induced by volume expansion could be determined as[5]

$$\phi(T) = \frac{\phi_0}{(1 - \phi_0) \cdot \dfrac{V_m(T)}{V_{m0}} + \phi_0}$$

where $\phi(T)$ represents the relative volume fraction of CB in the composites at T, ϕ_0 represents the volume fraction of CB at 20°C, $V_m(T)/V_{m0}$ is the relative volume expansion of the polymer, and V_{m0} represents the volume of the polymer at 20°C. Because the thermal expansion coefficient of CB is far below that of HDPE, it is assumed that the size of CB is unchanged with a temperature change in this study. Therefore, V_R approximates $V_m(T)/V_{m0}$.

Obviously, $\phi(T)$ decreases with the increase of $V_m(T)/V_{m0}$ (i.e., V_R), according to the aforementioned equation. It can be found from Figure 5 that $\phi(T)$ decreases sharply at the melting region of HDPE, which coincides with the results reported by Chiang and Flory.[7] On the basis of percolation theory, the reason for the resistivity increase for the composites is attributed to the CB fraction decrease.[12] The equation above takes the volume expansion as the only factor resulting in an increase of resistivity. However, Figure 4 indicates that, at a given temperature, even though the irradiated composites possess the same volume expansion, they exhibit different resistivities. Thus, the differences in the resistivity–temperature behavior are not explained satisfactorily on only the basis of thermal volume expansion.

There could be other factors affecting the change of resistivity, especially for samples irradiated at different temperatures. To investigate the variations of resistivity with time at different temperatures, Zhang et al.'s[13] isothermal treatment was performed. The calculated values of the activation energy for different irradiation doses are listed in Table I. It can be found that the activation energy obviously increases with the irradiation dose. It is suggested that the movability of CB particles and macromolecule chains are hindered due to the crosslinking. In other words, the high movability of CB or macromolecules is believed to result in high PTC intensity.

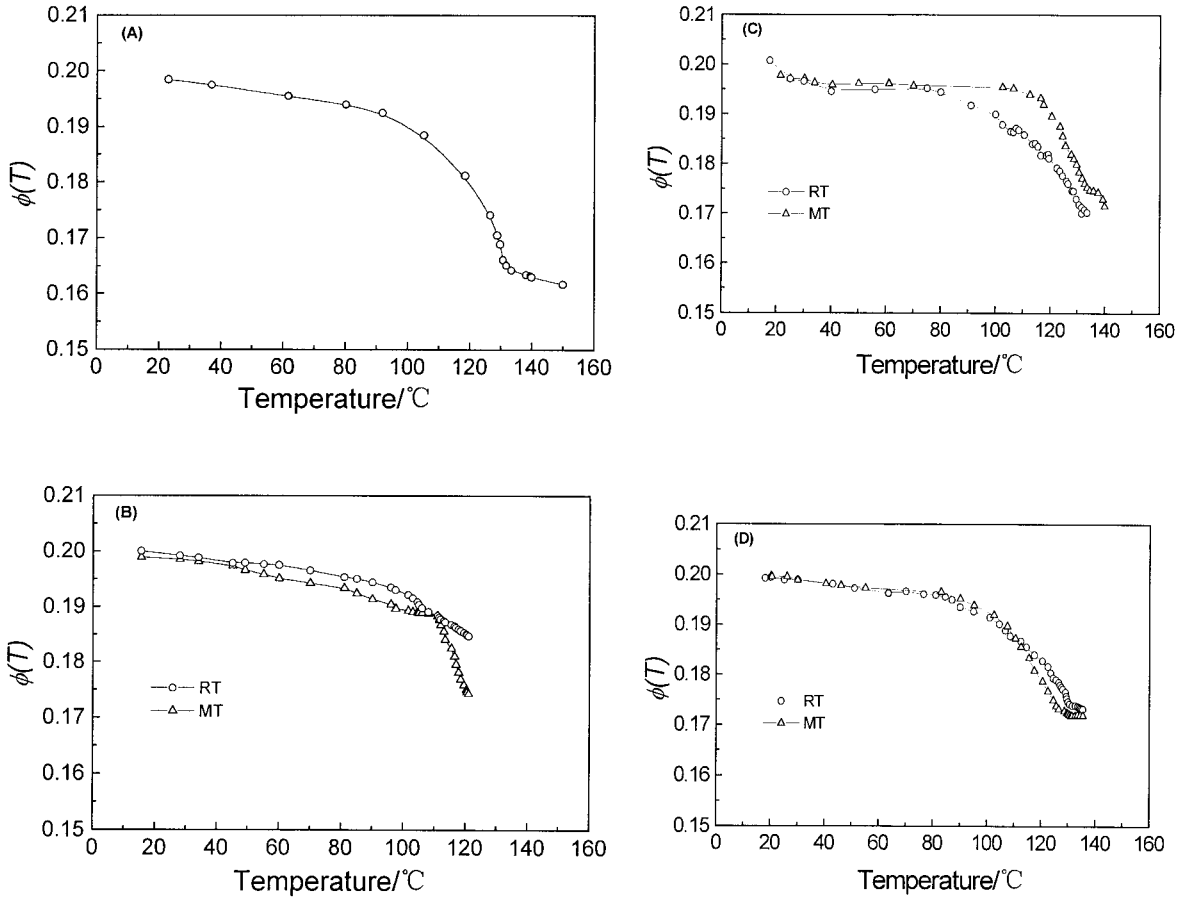

Figure 5 The relationships between the relative volume fraction of CB in HDPE/CB composites and the temperature under irradiation with (A) 0, (B) 20, (C) 200, and (D) 400 kGy.

CONCLUSIONS

The relationships between the resistivity–temperature behavior and volume expansion were studied. The volume expansion of the polymeric matrix could induce the decrease of the CB volume fraction, thus increasing the resistivity. However, when irradiated at different doses and temperatures, the samples showed distinctive differences in resistivity–temperature behavior, even if they contained the same CB volume fraction and possessed the same thermal volume expansion. We suggested that crosslinking of HDPE in the composites produced by electron beam irradiation limited the movability of CB and macromolecule chains. It should be emphasized that the volume expansion is the most important but not the only factor resulting in the PTC effect.

Table I Activation Energy of Irradiated HDPE/CB Composites at Different Irradiation Doses and Temperatures

Irradiation Doses (kGy)	Irradiation Temperature	Activation Energy (kJ)
0		39.6
20	RT	52.4
	MT	55.6
200	RT	74.5
	MT	80.1
400	RT	98.6
	MT	107.5

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