LDPE/Carbon Black Conductive Composites: Influence of Radiation Crosslinking on PTC and NTC Properties

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ABSTRACT: The electrical resistivity of low-density polyethylene/carbon black composites irradiated by ^{60}Co γ-rays was investigated as a function of temperature. The experimental results obtained by scanning electron microscopy, solvent extraction techniques, and pressure-specific volume–temperature analysis techniques showed that the positive temperature coefficient (PTC) and negative temperature coefficient (NTC) effects of the composites were influenced by the irradiation dose, network forming (gel), and soluble fractions (sol). The NTC effect was effectively eliminated when the radiation dose reached 400 kGy. The results showed that the elimination of the NTC effect was related to the difference in the thermal expansion of the gel and sol regions. The thermal expansion of the sol played an important role in both increasing the PTC intensity and decreasing the NTC intensity at 400 kGy. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2742–2749, 2002

Key words: carbon black; conductive composite; radiation crosslinking; positive temperature coefficient (PTC)

INTRODUCTION

The dispersion of a conductive filler, such as carbon black (CB; $\rho \sim 10^{-2}$ Ω cm), into an insulative polymer matrix ($\rho \sim 10^{18}$ Ω cm) can yield a conductive polymer composite.[1–3] These composites can exhibit a positive temperature coefficient (PTC) effect, often followed by a negative temperature coefficient (NTC) effect when the filler concentration is sufficiently high.[4–8] The resistivity of a composite increases with increasing temperature for a PTC, although it is also true that a NTC can appear after the melting temperature (T_m) of the polymer matrix. CB-filled polymer composites (PTC materials) have widespread commercial applications, including self-regulating heaters and circuit protection devices.[9,10]

The presence of a NTC effect has an adverse influence on the application of the PTC composites because of the instability of conductivity. Therefore, it is important that a strategy is found to eliminate the NTC effect. It is well known that chemical crosslinking and radiation crosslinking can result in more stable conductive behavior in those materials.[11–14] However, chemical crosslinking is limited in application because it always takes place above the melting temperature of the composites. On the other hand, radiation crosslinking is not dependent on temperature, and hence, it can be carried out below the T_m, usually at room temperature. In addition, radiation crosslinking of CB-filled composites can also provide good reproducibility of resistance if the temperature is cycled up to or above the T_m of the polymer.

Although radiation crosslinking is the most useful way to improve the PTC effect and eliminate the NTC effect, the influence of radiation

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crosslinking on the composite structure and the electrical conductivity is still not very well understood.[15,16] The purpose of this article is to report on the influence of radiation crosslinking on the PTC and NTC properties of CB-filled low-density polyethylene (LDPE) composites with scanning electron microscopy (SEM), solvent extraction techniques, and the thermal expansion techniques.

EXPERIMENTAL

Materials and Preparation

Materials

LDPE was a commercial resin (1I2A; Yanshan Petrochemical Co., China) with a melt index of 2 g/10 min and a density of 0.921 g/cm^3. The CB was Acetylene Black (Chun'an Chemical Co., China) with an average particle size of 40–50 nm, a surface area of 60–70 cm^3/g, a DBP value of 300–320 mL/100 g, and a pH value of 5.0–7.0.

Blending of Composites

The composite of LDPE and CB was made in a Brabender at 160°C for 5 min and was then mixed again on a two-roll mill at 160°C for 5 min. After removal and granulation, the composites with preembedded electrodes were compression molded at 150°C and then cooled down in air to room temperature, which made sheets about 100 × 10 × 3 mm^3 in size. The sheet samples were rested overnight to release residual thermal stress before the subsequent measurement.

Irradiation

The samples were sealed in glass tubes under vacuum and irradiated by ^{60}Co γ-rays at room temperature at different radiation doses. All of the samples were held for 1 day after radiation crosslinking to eliminate postradiation effect.

Testing Method

Resistivity

Electrical resistivity was measured with a digital multimeter when it was lower than 2×10^7 Ω, and a high-resistance meter was used when the resistivity exceeded 2×10^7 Ω. Electrical resistivity can be converted into volume resistivity (Ω cm) via simple geometric calculation. All values of resistivity reported in this work were values of direct current resistivity.

Gel Extraction

The percentage of insoluble material (gel) after irradiation was measured with a Soxhlet apparatus. Approximately 200 mg of sample wrapped in nickel mesh was exposed to refluxing xylene until the sample attained constant weight, which usually took 48 h. After that, the sample was dried in a vacuum oven at 100°C overnight, and the weight (corresponding to the weight of the network structure polymer) was measured. The degree of crosslinking (DOC) was calculated by eq. (1):

$$g\% = \frac{w_1 - w_c}{w - w_c} \quad (1)$$

where $g\%$ is the gel fraction, w_1 is the weight of the sample after refluxing, w is the weight of the sample before refluxing, and w_c is the weight of CB.

Morphology

Morphology observation was performed with a JEOL JXA-840 scanning electron microscope, prior to which 2-cm sheet composites were etched with refluxing xylene to remove the sol in the composites. Samples were fractured under liquid nitrogen, and then, the etched surfaces were vacuum-coated with a thin gold layer.

Pressure-Specific Volume–Temperature (PVT) Analyzer

PVT behavior was studied with PVT-100 equipment (SWO Polymertechnik GmbH, Germany). The heating rate was 1 K/min.

RESULTS AND DISCUSSION

Influence of Radiation Crosslinking on the PTC Effect and NTC Effect

Figure 1 shows the relationship between the room temperature resistivity (ρ_{RT}) of the unirradiated composites and different CB contents. We can see that the electrical resistivity of the composites decreased sharply with increasing CB content; this indicates that the composites transferred from insulating to conductive. It was reported

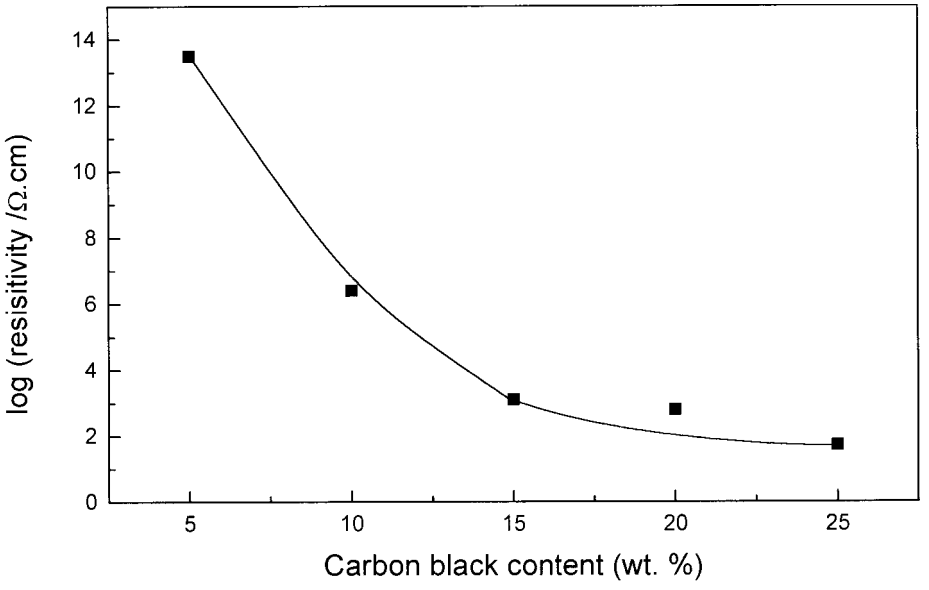


Figure 1 Dependence of ρ_{RT} on CB content.

that the composites showed a good PTC effect when the CB content was more than the critical content.[6] Thus, in this study, a 16.7% CB (wt %) composite was used.

In the case of semicrystalline polyethylene (PE), at a given dose of the gel point (critical dose for gelation), the molecular structure of the polymer is partitioned into two fractions, an insolvable three-dimensional network or gel and a soluble part, or sol, composed of isolated molecules.[14] It was reported that the gel point of LDPE is about 10 kGy.[18] Above the gel point, the amount of gel increases with increasing radiation dose.[19] LDPE/CB composites can also be crosslinked by radiation. Figure 2 shows that the DOC of the composites increased with increasing radiation dose.

In Figure 3, the unirradiated LDPE/CB composite clearly shows both PTC and NTC effects. After radiation crosslinking, ρ_{RT} and PTC intensity [I_p; logarithm of the ratio of maximal resistivity (ρ_m) near T_m and ρ_{RT}] increased as com-

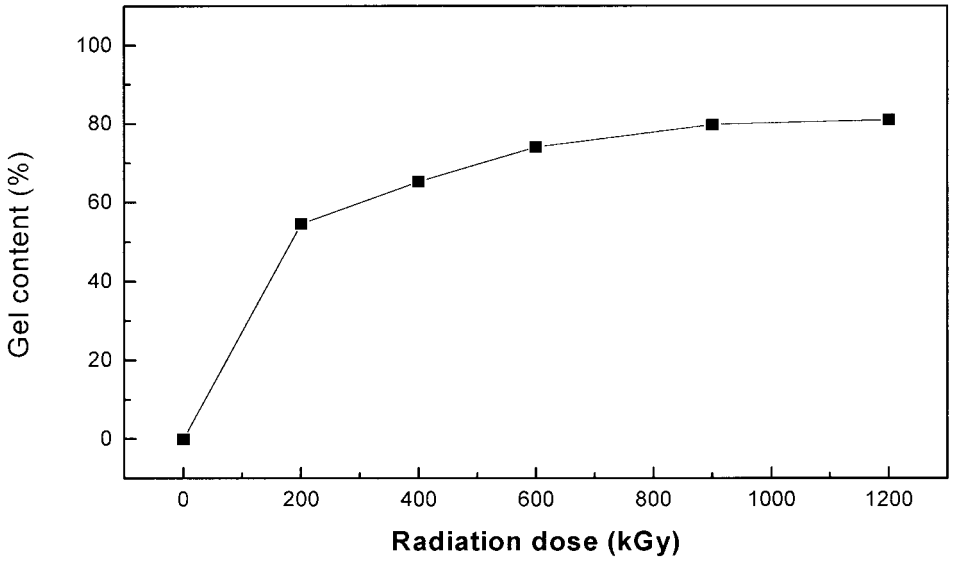


Figure 2 Influence of radiation doses on the DOC of LDPE/CB composites.

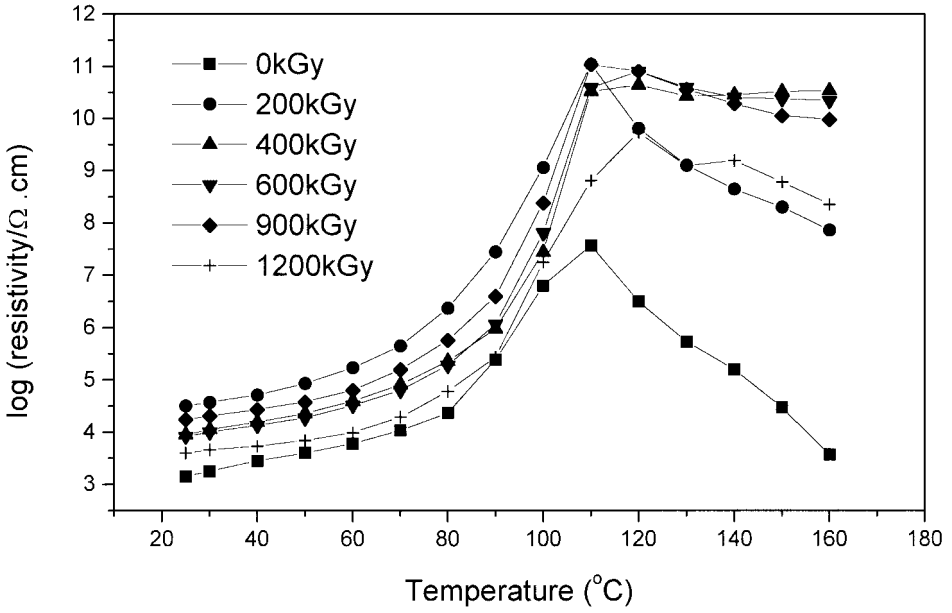


Figure 3 Resistivity–temperature behaviors of LDPE/CB composites irradiated with different radiation doses.

pared to unirradiated composites. Figure 4 shows the relationship of I_p and radiation dose and suggests that the I_p of irradiated composites was much larger than that of unirradiated samples. When the radiation dose rose from 0 to 400 kGy, the I_p increased with the radiation dose. Furthermore, with the increasing dose, the I_p remained unchanged up to 900 kGy and then decreased. However, the NTC intensity (I_n; logarithm of the ratio of ρ_m to the resistivity at 160°C) was different with I_p, in that it decreased monotonically with the rise of radiation dose from 0 to 400 kGy and increased monotonically above 400 kGy, as shown in Figure 5. These results show that both the behaviors of I_p and I_n depend on the radiation crosslinking behavior because the radiation crosslinking will restrict the movement of CB particles. Therefore, the electrical properties will be influenced.

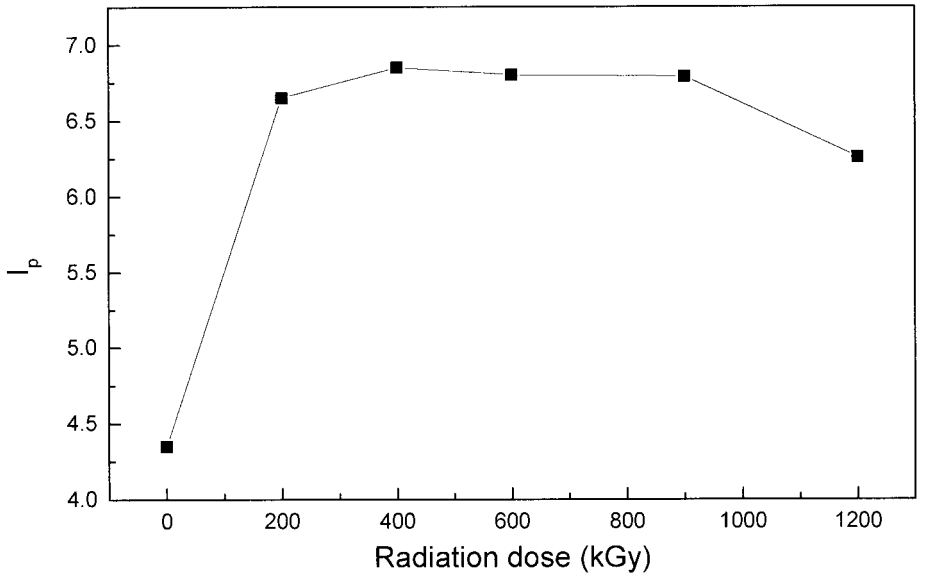


Figure 4 Influence of γ-radiation on the I_p of LDPE/CB composites.

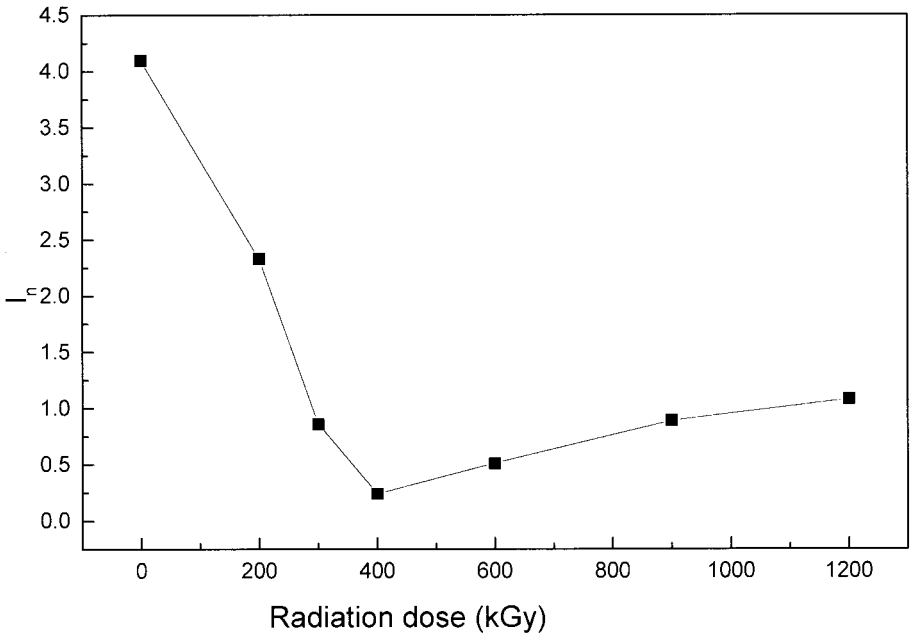
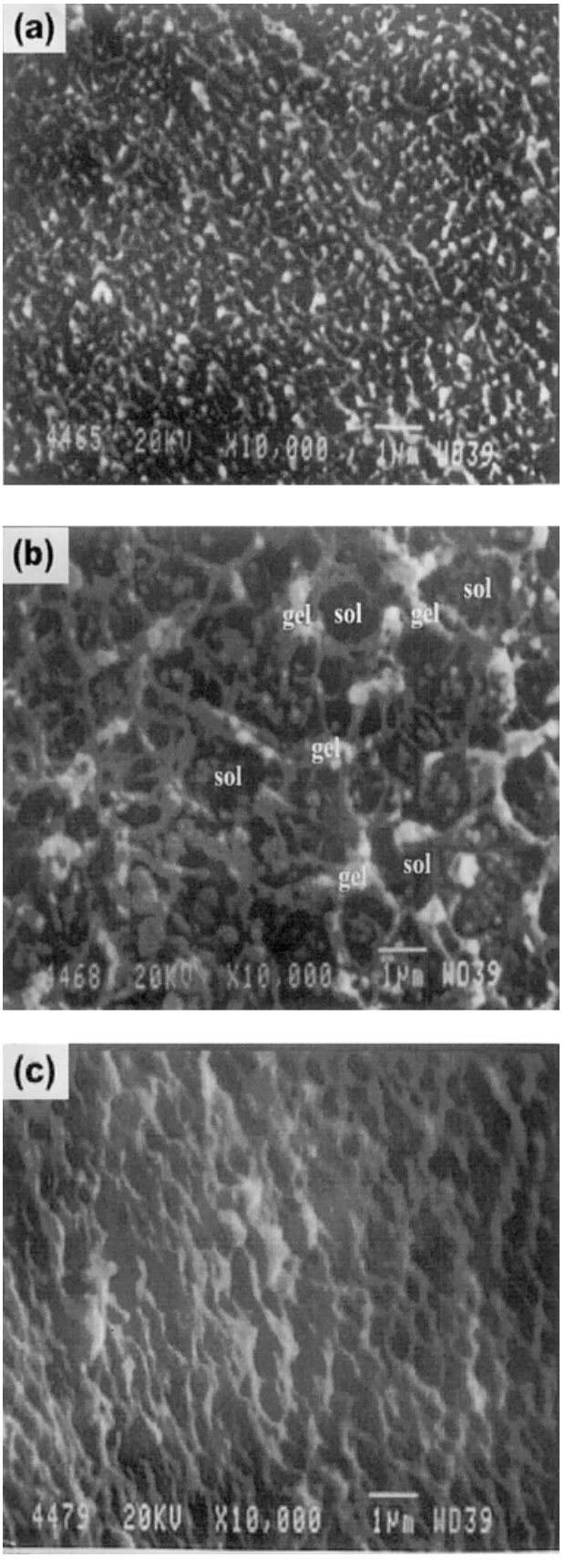


Figure 5 Influence of radiation doses on the I_n of LDPE/CB composites.

So the morphology of CB is very important for the electrical properties of conductive composites, especially morphology at an elevated temperature. It is well known that CB aggregates or agglomerates mainly disperse in the amorphous phase of the semicrystalline polymer excluding from the crystalline region after melting processes.[5] When CB-filled polymer composites are irradiated at room temperature, the network takes place mainly in the amorphous phase at the radiation dose above the gel point.[20] Consequently, the CB aggregates or agglomerates are bound to the three-dimensional networks of the irradiated composites. With solvent extraction techniques, the irradiated composites can be separated into insoluble network (gel) fraction and soluble (sol) fraction.[21] It is known that the sol contains the uncrosslinked part in the amorphous region and mostly in the crystalline region.[22] If the CB disperses in either region of the sol, it can be extracted out in the extraction experiments; but we did not observed the discoloration of the transparent solvent by the CB particles diffusing from the matrix of the composites as Narkis and Tobolsky reported.[23] On the other hand, because the LDPE was a saturation polymer and the CB particles were not pretreated by the chemical method used before, the interaction between the CB and matrix was physical absorption so that we could observe that the CB was easily extracted by boiling solvent in the unirradiated and nonnetwork composites. These phenomena can prove that CB aggregates attach on the crosslinking networks. It is not yet clear until how the CB particles are bounded to the crosslinking networks, but the confined CB was useful for improvement of the PTC effect and elimination of the NTC effect.

Figure 6 shows the SEM photographs of the fractured morphology of the irradiated CB-filled LDPE composites, which were etched with refluxing xylene and fractured in liquid nitrogen. In this case, the sol was extracted by the solvent, and the networks were left. In the photographs, the cavities are the sol, surrounded by the networks (gel). The CB particles dispersed in the networks cannot be observed because their size is too small.

In Figure 6, the size of the cavities of the irradiated composite at 200 kGy is smaller than that of those irradiated at 400 kGy, as shown in Figure 6(a,b). This suggests that not all the CB aggregates were bound to the crosslinking networks when the radiation dose was lower than 400 kGy. Above the T_m of polymer, the compressed CB particles in the original amorphous region started to migrate to the new amorphous area with the result that the NTC effect was observed.[4,24] However, with increasing radiation dose, many more CB particles were bound to the crosslinking networks, preventing the migration of the CB parti-



cles. Consequently, the I_n became smaller, whereas the I_p became larger (see Fig. 5). At 400 kGy, the I_n was close to zero. This means that the NTC effect was completely eliminated. With a further increase in radiation dose, the molecular weight between two crosslinking points of the networks became smaller, causing a decrease in sol content. In this case, the size of the cavities of the composites irradiated at 900 kGy was smaller than that of those irradiated at 400 kGy, as shown in Figure 6(c). It is very easy for electrons to tunnel through the intergrain gaps between CB particles when temperature is above the T_m of polymer.[24] Therefore, the NTC effect reappeared.

Influence of Thermal Expansion on the PTC Effect and NTC Effect

The specific volume of the pure LDPE [Fig. 7(a)] was more than that of the CB-filled LDPE composite [Fig. 7(c)] because the physical networks, which were formed by the interaction between CB and LDPE, restricted the thermal expansion of the matrix.[25] Moreover, the specific volume of the irradiated composite [Fig. 7(d)] was lower than that of the nonirradiated composite [Fig. 7(c)] due to the formation of three-dimensional networks that reduced the thermal expansion of the composite. In addition, the specific volume of the sol was smaller than that of the original PE, for the sol was composed of low-molecular-weight PE.

To measure the electrical resistivity of the gel of the irradiated LDPE/CB composites, a 4-cm sheet sample with electrodes was exposed to refluxing xylene for 72 h, with a change of solvent every 24 h. The sample was dried in a vacuum oven at 80°C overnight, after which the electrical resistivity of the gel of the composites was measured. Figure 8 shows the electric resistivity–temperature behaviors of the irradiated CB-filled LDPE composites and the pure gel of the composite irradiated at 400 kGy. Without the sol, the ρ_{RT} became smaller. The I_p became smaller, but the I_n was constant. As shown in Table I, the I_p was so small in the gel of the irradiated composites at 400 kGy, compared to the irradiated composites at the same radiation dose, that the pure gel has no practical means for use as a PTC material.

Figure 6 SEM photographs of LDPE/CB composites irradiated with different doses: (a) 200 kGy, (b) 400 kGy, and (c) 900 kGy.

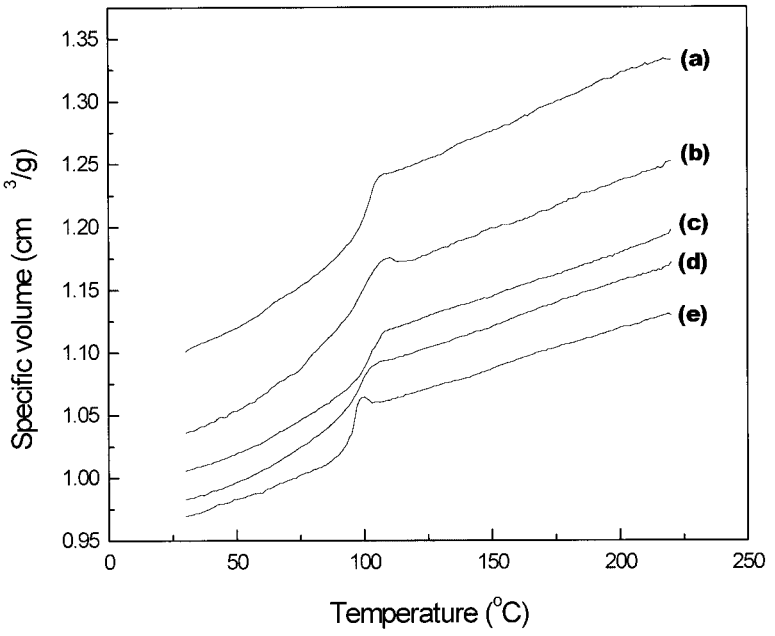


Figure 7 Thermal expansion behaviors of different materials: (a) pure LDPE, (b) sol of the irradiated LDPE/CB composite at 400 kGy, (c) unirradiated LDPE/CB composite, (d) irradiated LDPE/CB composite at 400 kGy, and (e) gel of the irradiated LDPE/CB composite at 400 kGy.

These results show that the electron tunneling through the intergrain gaps became easier without the sol. Consequently, the ρ_{RT} became smaller. The thermal expansion of the sol also played an important role in the elimination of the NTC effect for the irradiated CB-filled composites. The thermal expansion of the sol surrounded by the crosslinking networks was greater than that of the gel of the irradiated composites, as shown in Figure 7(b,c). The sizes of the cavities

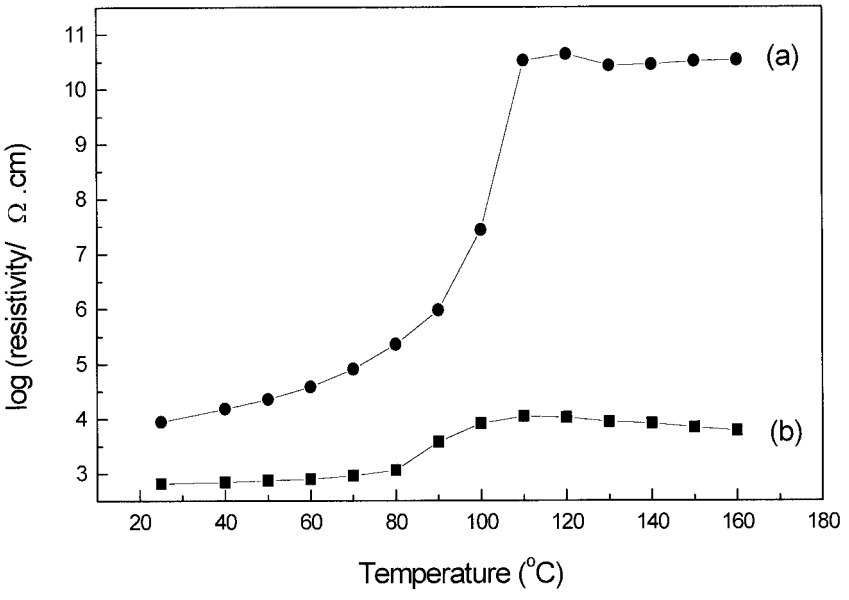


Figure 8 Resistivity–temperature behaviors of (a) the irradiated LDPE/CB composite and (b) the gel of the irradiated composites at 400 kGy.

Table I I_p and I_n for Irradiated LDPE/CB Composites and the Gels

Sample[a]	ρ_{RT} (Ω cm)	I_P	I_n
Irradiated LDPE/CB composites	8913	6.85	0.24
Gel of irradiated LDPE/CB composites	831	1.23	0.26

[a] Both samples were irradiated at 400 kGy.

(sol) became larger, causing difficulty for the electrons passing through at the vicinity of the T_m. In consequence, the electrical resistivity increased precipitously, and I_p reached the maximum. With the increasing temperature, the thermal expansions of the sol and the gel came to equilibrium. As a result, the I_p and I_n became constant. The NTC effect was eliminated.

CONCLUSIONS

We have shown that radiation crosslinking is an effective way to eliminate the NTC effect of CB-filled polymer composites. In CB/LDPE composites, with increasing radiation dose, the DOC increases. The CB particles are restricted by the crosslinking networks. Although with the increasing dose the PTC effect is improved, the NTC effect cannot be eliminated completely except for at a dose of 400 kGy. These results show that the PTC and NTC behaviors originated from the difference in thermal expansions of the sol and gel in the irradiated composites. The thermal expansion of the sol plays an important role in the elimination of the NTC effect.

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