

# Improvement of Conductive Network Quality in Carbon Black-Filled Polymer Blends

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**ABSTRACT:** Heat treatment of polymer-based composites is critical for the enhancement of both stability and long-term service life, especially when the materials function under an inconstant temperature environment. The present article discusses the effect of heat-treatment conditions on the electrically conductive properties of carbon black (CB)-filled low-density polyethylene (LDPE) and ethylene–vinyl acetate copolymer (EVA) composites, which are candidates for positive temperature coefficient (PTC) materials. It was found that the dispersion mode of CB particles changes as a function of the matrix morphology. When the composites are irradiated to form crosslinked networks in the matrix for the elimination of negative temperature coefficient (NTC) behavior, some of the produced free radicals are also entrapped for quite a long time after the irradiation treatment. These residual radicals further enhance the interaction between CB and the matrix and further induce the crosslinking of the matrix so that the composites' conductivity changes with time as a result of the continuous variation in the contacts between the conductive fillers. To improve the quality of the conduction paths in the composites, appropriate post-heat treatment should be carried out, which speeds up the formation of the above-mentioned two kinds of crosslinked structures within a limited time. Annealing at 75°C for more than 10 h is believed to be an effective way. After the treatment, a balanced performance characterized by reduced room-temperature resistivity and improved PTC intensity was obtained. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2768–2775, 2002

**Key words:** conductive polymer composites; annealing; PTC; irradiation; stabilization

## INTRODUCTION

Resistivity of carbon black (CB)-filled semicrystalline polymer composites increases drastically when

the temperature approaches the melting points ( $T_m$ 's) of the matrices, an effect described as the positive temperature coefficient (PTC) phenomenon.<sup>1</sup> Voet suggested that this effect results from an increase of the average conductive particle or aggregate gaps.<sup>2</sup> Accordingly, the stronger PTC effect of a semicrystalline polymer-based composite, compared with amorphous matrices, was attributed to a larger thermal expansion upon melting of the crystalline phases. This idea has been well accepted.<sup>3</sup> In addition, electron tunneling and hopping across dispersed CB particles is believed to be the governing conduction mechanism involved.<sup>4</sup>

Owing to the commercial significance of the PTC switching effect, conductive polymer composites have found applications in self-regulating

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heaters, self-resetting overcurrent protectors, solvent sensors, etc., with the advantages of excellent processability, light weight, and flexibility over the conventional inorganic PTC materials. It should be noted, however, that a resistivity decrease above the  $T_m$  of the crystalline phase, namely, negative temperature coefficient (NTC) behavior, is detrimental.<sup>5</sup> Crosslinking of the matrix polymers can effectively eliminate the NTC effect by forming a network and reducing movement of the CB particles,<sup>6</sup> but the problem of performance stabilization becomes more complicated due to the introduction of the crosslinked structure. To improve the composites' electrical reproducibility, efforts have been made in two directions by our group: (1) The processing window was broadened by using immiscible polymer blends, instead of a single polymer, to realize a two-step percolation,<sup>7,8</sup> and (2) the conditions of post-heat treatment were optimized based on a careful investigation of morphological variations in the polyblends.<sup>9</sup>

In fact, heat treatment of a composite has an important influence on a series of factors related to the electrical properties,<sup>10-12</sup> such as crystallinity, crystalline size, and filler distribution. An analysis merely focusing on the crystalline microstructure could not provide sufficient information about the mechanism of performance stabilization.<sup>9</sup> Therefore, the present work focused on the effect of CB agglomeration and filler/matrix interaction on the conduction behavior of conductive polyblends as a function of annealing processes, aimed at obtaining a thorough understanding of the improvement of the conductive network quality. It can be imagined that the conduction paths of high quality will certainly make a positive contribution to the performance stabilization of the composites.

As one of our serial articles on CB-filled ethylene-vinyl acetate copolymer/low-density polyethylene (EVA/LDPE) composites, the present work employed both uncrosslinked and crosslinked versions of the system. In this way, the results will provide evident technical importance. In addition, the conclusions made in previous studies on the same materials (e.g., refs. 7-9, 13, and 14) will help in the discussion of the experimental data produced in this article.

## EXPERIMENTAL

LDPE and EVA, with identical melt-flow indexes of 2.0 g/10 min, were used as the matrix polymers.

An electrically conductive CB was employed as the filler.

The polymers and CB with the desired proportions (LDPE/EVA = 80/20 and the weight percentage of CB in EVA/LDPE is always 18%) were melt-mixed in a laboratory-size Brabender plastimeter Model XB20-80 under standard conditions of the experiments, in each case at 160°C, 20 rpm, and 15 min. After being removed and granulated, the composites with preembedded electrodes were compression-molded at 140°C and then cooled in air to room temperature. The sheet samples (65 × 45 × 3 mm<sup>3</sup>) were allowed to rest overnight before the subsequent measurements.

Room-temperature crosslinking was conducted by irradiation with a <sup>60</sup>Co  $\gamma$ -ray source in air to minimize the undesired NTC effect. The radiation dose was 25 Mrad. The gel fraction was characterized by the polymer fraction that could not dissolve in boiling xylene after being extracted by a Soxhlet apparatus for 72 h.

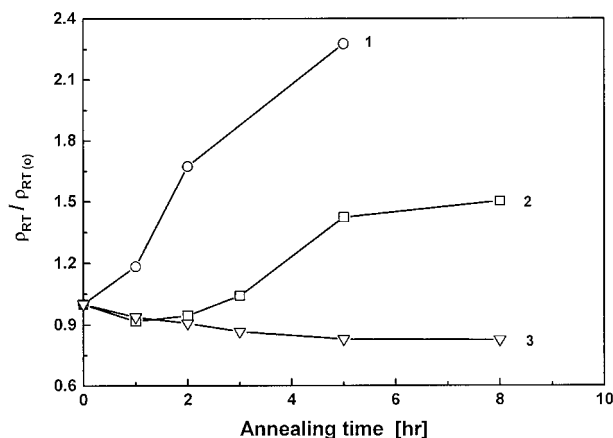
After irradiation, the materials were annealed in an oven with its temperature being kept at a preset value. Then, the samples were cooled inside the oven by simply switching off the electricity supply. The time needed to reach the room temperature was generally more than 2 h.

The volume resistivity of the composites was measured with a four-lead system. The two current electrodes made of brass net (45 × 5 mm<sup>2</sup>) were preembedded at the ends and through the breadth of the rectangular specimens. The two potential electrodes (a pair of brass rods 1 mm in diameter and 45 mm in length) were also preembedded through the breadth of the specimens. The center-to-center distance between a current electrode and its neighboring potential electrode was 8 mm and that between the two potential electrodes was 44 mm. The temperature dependence of resistivity was recorded by heating the specimens at a heating rate of 2°C/min. The electron spin resonance (ESR) spectra of the samples were obtained by a JES-FEIS ESR meter at room temperature in air.

## RESULTS AND DISCUSSION

### Effect of Heat Treatment on the Structure-Property Relationship of the Uncrosslinked Composites

As mentioned in the Introduction, conductive composites acting as PTC candidates should be crosslinked to a certain extent prior to service. This might be somewhat unfavorable for obtain-



**Figure 1** Effect of heat treatment on the room-temperature resistivity,  $\rho_{RT}$ , of uncrosslinked CB/EVA/LDPE composites. Annealing temperature: (1) 90°C; (2) 80°C; (3) 75°C [ $\rho_{RT(0)}$ : room-temperature resistivity of the as-manufactured composites].

ing a clear image of the microstructural variation induced by annealing. Therefore, the uncrosslinked composites are studied in this section first for the convenience of discussion.

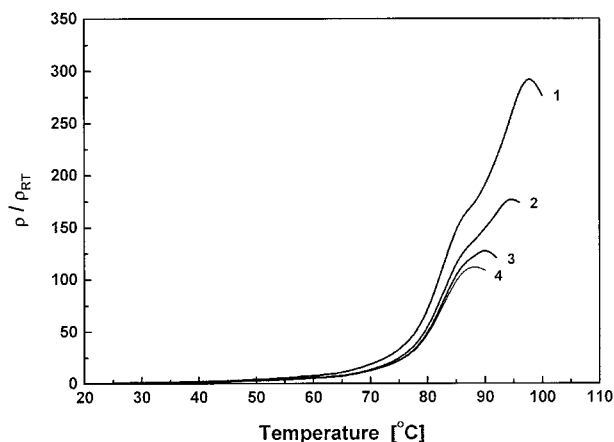
In considering the fact that both LDPE and EVA employed in the current work are crystalline polymers, the heat-treatment temperature must not exceed the melting point of LDPE ( $\sim 110^\circ\text{C}$ ). In addition, an annealing at  $100^\circ\text{C}$  is found to be not appropriate because substantial melting of LDPE and EVA occurs.<sup>9</sup> Accordingly, three annealing temperatures, 75, 80, and  $90^\circ\text{C}$ , were chosen. Two of them are factually lower than the melting point of EVA ( $\sim 87^\circ\text{C}$ ).

Figures 1 and 2 and Table I illustrate the results of heat treatment at the temperatures selected above. It should be stated at the very beginning that a lower room-temperature resistivity, ensuring sufficient electrothermal output and a higher PTC intensity (the ratio of the maximum resistivity to the room-temperature resistivity calculated from the temperature dependence of composite resistivity), which prevents the material from overheating, is always expected.<sup>15</sup> This can serve as an assessment criterion of heat treatment besides the consideration based on cost effectiveness.

As can be seen in Figure 1, with increase in the annealing time, room-temperature resistivity of the composites treated at  $75^\circ\text{C}$  becomes slightly lower than that of the original version, while the composites annealed at 80 and  $90^\circ\text{C}$  exhibit an opposite trend. On the other hand, the PTC in-

tensity of all the composites increases, particularly when the specimens had been treated at 80 and  $90^\circ\text{C}$  (Fig. 2 and Table I). Since the variation in the matrix morphology induced by heat treatment determines the dispersion mode of CB and hence, the conductivity,<sup>9,12,16</sup> the above phenomena should be analyzed in this direction.

In our earlier study, with the CB-filled EVA/LDPE composite, it was found that EVA and LDPE are incompatible. Driven by thermodynamic factors, CB particles are predominately located in the continuous LDPE phase first and then at the interface of EVA and LDPE with increasing CB content.<sup>7</sup> When the temperature approaches  $90^\circ\text{C}$ , 50 wt % of the crystalline portion of the blended matrix melts.<sup>13,14</sup> Although the melted fraction of each component is hard to determine due to overlap of the exothermic peaks on the DSC heating scans, it can be reasonably estimated that molten EVA is in the majority. Under this circumstance, the existing electrical networks (especially those at the interface of EVA/LDPE) are partially destroyed by the significant volume expansion of EVA, and the original agglomeration of the CB particles characterized by good dispersion is no longer available. A reagglomeration of the fillers in molten zones takes place, resulting in new conduction paths as evidenced in ref. 16. It is believed that these newly generated networks are quite heterogeneous in structure and less effective in conduction, that is, the amount of both (1) defects characterized by worse contacts easy to be damaged and (2) improved contacts is increased in the conductive networks. As a result, room-temperature resistivity of the annealed com-



**Figure 2** Temperature dependence of the resistivity,  $\rho$ , of uncrosslinked CB/EVA/LDPE composites annealed at different temperatures for 5 h in comparison to the (curve 4) as-manufactured sample. Annealing temperature: (1)  $90^\circ\text{C}$ ; (2)  $80^\circ\text{C}$ ; (3)  $75^\circ\text{C}$ .

**Table I PTC Behavior of Uncrosslinked CB/LDPE/EVA Composites as a Function of Annealing Temperature (Annealing Time: 5 h) in Comparison to the As-manufactured Composite**

Measurement	Annealing Temperature (°C)			As-manufactured Composite
	75	80	90	
PTC intensity	130	179	297	113
$T_S^a$ (°C)	69	67.5	64	70

The data listed in this table are estimated from Figure 2.

<sup>a</sup> Switching temperature,  $T_S$ , represents the temperature at which resistivity increases drastically and is defined as the peak position of the first derivative of resistivity with respect to temperature.<sup>15</sup>

posites increases (Fig. 1) and the switching temperature,  $T_S$ , decreases (Fig. 2 and Table I). Besides, the PTC intensity and the peak temperature corresponding to the maximum resistivity on the temperature dependence of resistivity are increased (Fig. 2 and Table I).

The negative influence of EVA melting can also be perceived when the composites are treated at 80°C. The data in Figures 1 and 2 and Table I show a trend of a change in the resistivity similar to the case of aging at 90°C. When only LDPE serves as the matrix, however, the treatment at 80°C leads to a result different from that at 90°C (Fig. 3). It gives more supporting evidence for the above analyses.

Returning to Figures 1 and 2, it is evident that the treatment at 75°C provides a milder environment. Improvement of crystallinity and crystalline perfection as well as uniformization of the crystal-

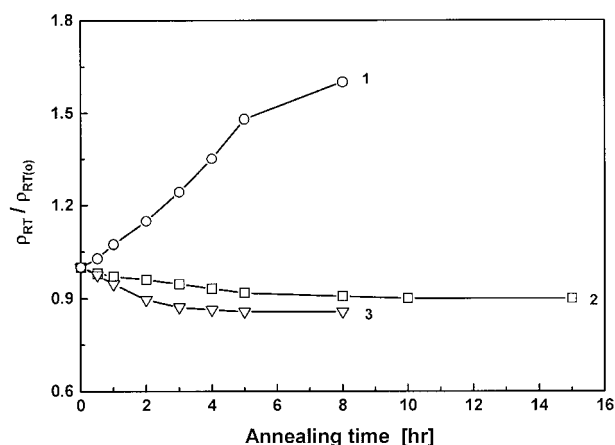
lite dimension should be the main morphological variations.<sup>9,11,13</sup> Better interfiller contacts can thus be established, as reflected by the reduced room-temperature resistivity (Fig. 1). On the other hand, volume expansion originated from the melting of the matrix of higher crystallinity can breakdown more conductive pathways and bring a higher PTC intensity (Fig. 2 and Table I).

In short, heat treatments at a temperature lower than the  $T_m$  of LDPE have different effects on the conduction behavior of the composites. Only when the composites are annealed at a temperature lower than the  $T_m$  of EVA (e.g., 75°C) could an improvement of conduction network quality be achieved.

### Effect of Heat Treatment on the Structure–Property Relationship of the Crosslinked Composites

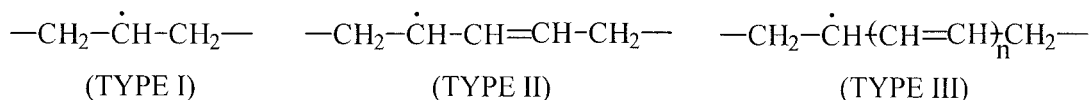
Crosslinking has been widely used to eliminate the NTC phenomenon of a CB-filled polymer composite, but there are few publications dealing with the effect of heat treatment on the properties of crosslinked composites to the authors' knowledge. Therefore, an investigation on the combined effects of irradiation treatment and annealing are made hereinafter so as to understand the microstructural details. Based on the above results, two annealing temperatures, 75 and 80°C, was employed. In addition, ESR, which records the transition of unpaired electrons between different energy levels in an external magnetic field and is able to measure species and the number of free radicals produced by physical or chemical processes, was employed to determine the decay of the radicals in the system studied.

It has been long known that three kinds of free radicals are generated by irradiation of polyethylene<sup>17</sup>:



**Figure 3** Effect of heat treatment on the room-temperature resistivity,  $\rho_{RT}$ , of uncrosslinked CB/LDPE composites. Annealing temperature: (1) 90°C; (2) 80°C; (3) 75°C.



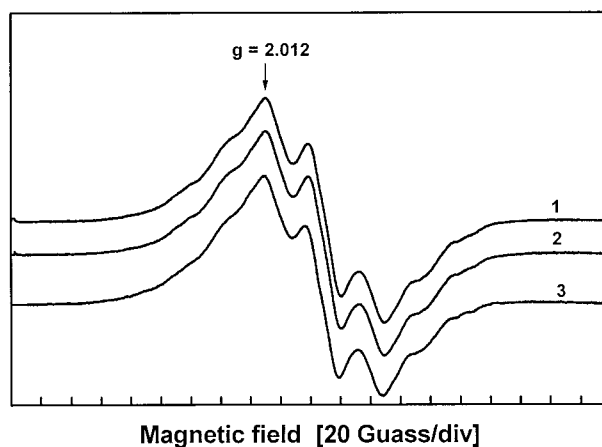


where type II is the predominant product when being irradiated with an intermediate dose, as in the present work. This is evidenced by comparing the profiles and peak positions of the ESR peaks in Figure 4 with those of the standard spectra in ref. 17. Besides, Figure 4 demonstrates that irradiation produced the same type of radicals in LDPE and the EVA/LDPE and CB/EVA/LDPE systems. Although CB had little effect on the type of free radicals induced in EVA/LDPE by irradiation, the activity of the radicals is greatly affected by the presence of CB (Fig. 5). For the EVA/LDPE system without CB, a treatment at 75°C for 10 h is needed to have a complete decay of the radicals. In CB/EVA/LDPE composites, however, free radicals can still be observed after being annealed at 75 or 80°C for more than 20 h. Tang et al. concluded that the free radicals induced in polyolefin might react with some groups at the surface of CB and form CB radicals which are difficult to terminate.<sup>18</sup> In this way, chemical interaction between CB and the matrix polymer takes place. Therefore, it can be expected that the radicals remaining in the composites after irradiation treatment could further induce crosslinking of the matrix polymer and enhance crosslinking between CB and the matrix. On the other hand, it can be known from Figure 5 that the higher the annealing temperature is the faster the radicals are terminated.

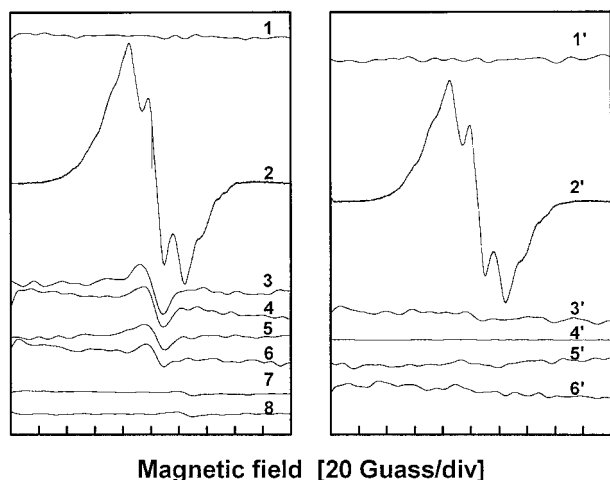
Figure 6 shows the room-temperature resistivity of crosslinked composites as a function of the annealing time. Clearly, the  $\rho_{RT}$  of the sample treated at 75°C remains nearly unchanged, while that treated at 80°C increases sharply. Figure 7 further indicates that the heat treatment at the two temperatures can also improve PTC intensity. Compared to the uncrosslinked samples discussed in the last section, it is known that the treatment at 80°C affects the crosslinked samples more remarkably. Because the crosslinking of polyolefin occurs mainly in the amorphous phase<sup>19-22</sup> and exerts little influence on the crystallization structure and melting behavior,<sup>9</sup> it can be deduced that crosslinking of the matrix itself and the CB/matrix in the course of annealing caused by the residual radicals must be responsible for the above results.

At the beginning of heat treatment, crosslinked networks of the matrix polymer have not yet been fully established. As shown by the time dependence of the gel fraction of the system (Fig. 6), at least 10 h should be taken to reach the equilibrium value for the annealing at 75 and 80°C. In addition, the free-radical reaction between CB and the matrix polymer gradually enhances the adhesion of the fillers to the surrounding polymers with an increase in the annealing time. Because the interparticle distance of the CB aggregates was increased when the temperature was increased from room temperature to the annealing temperature, the changed electrical paths are thus "frozen" by these two kinds of crosslinking structures and could not recover. This explains the difference between the plots of  $\rho_{RT}/\rho_{RT(0)}$  against the annealing time in Figures 1 and 6. Since a greater portion of crystalline melts when the composite is treated at 80°C, as compared with the treatment at 75°C, the irreversible change in the room-temperature resistivity is more severe. What is more, the restricting function offered by the crosslinked matrix and the strong CB/matrix interaction limits the possible movement of the CB particles and eventually improves the PTC intensity (Fig. 7).

Peroxide crosslinking of CB-filled polyethylene, which was conducted at 190–200°C, gives evidence



**Figure 4** ESR spectra of (1) LDPE, (2) EVA/LDPE, and (3) CB/EVA/LDPE. The samples were kept at room temperature for 6 h in air after irradiation.

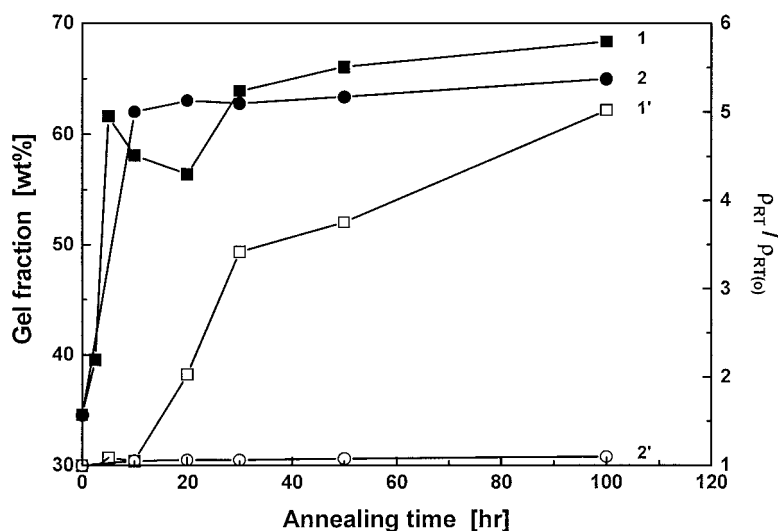


**Figure 5** ESR spectra of (curves 1–8) CB/EVA/LDPE and (curves 1'–6') EVA/LDPE. Details of the samples: (1, 1') uncrosslinked; (2, 2') kept at room temperature for 6 h in air after irradiation crosslinking; (3, 3') crosslinked samples annealed at 75°C for 10 h; (4, 4') crosslinked samples annealed at 75°C for 20 h; (5, 5') crosslinked samples annealed at 80°C for 10 h; (6, 6') crosslinked samples annealed at 80°C for 20 h; (7, 8) crosslinked samples annealed at 75 and 80°C for 30 h, respectively.

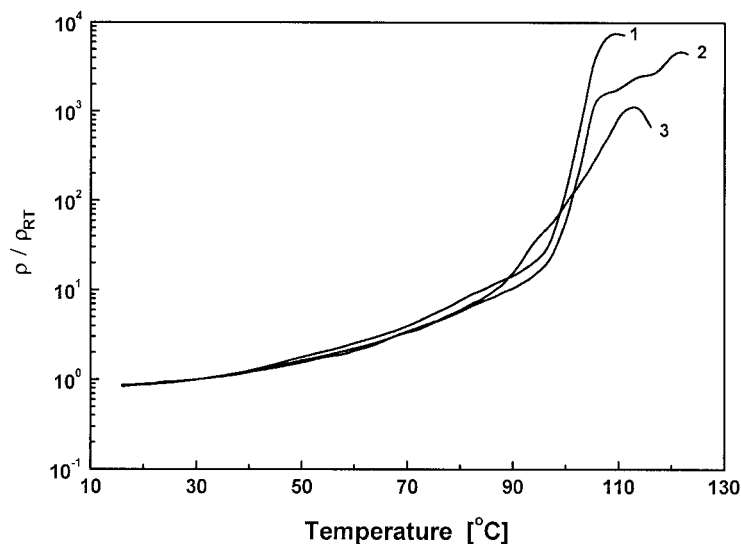
supporting the above discussion.<sup>23</sup> The room-temperature resistivity of the crosslinked composites can be greatly increased in comparison with that of the uncrosslinked composites as a result of the high-temperature crosslinking reaction.

It should be noted that, even though the number of crosslinked networks of the matrix polymer

is almost constant after a heat treatment for a time longer than 10 h (Fig. 6), there still are free radicals in the system (Fig. 5), that is, the chemical absorption of the matrix macromolecules on CB can extend for a quite long time. Consequently, the rate of the change in the room-temperature resistivity is much higher than that in the gel fraction (cf. curves 1 and 1' in Fig. 6). To examine this estimation, the annealed and unannealed samples were put into an oven that had already been set at 90°C and the time dependence of the resistivity was recorded simultaneously (Fig. 8). According to Figure 5, it is known that free radicals should still be active in the latter composites rather than in the former ones. It is seen from Figure 8 that the resistivity of the sample annealed at 75°C for 30 h after irradiation increases drastically to the maximum and then remains unchanged with an increase in time. This suggests that CB had already been effectively attached to the crosslinked networks of the matrix during the annealing at 75°C. The electrical paths could not even be damaged by the subsequent partial melting of the matrix polymers at 90°C. With respect to the sample that had not been annealed but kept at room temperature for 30 h, its resistivity increased to the maximum first and then decreased to an equilibrium. The result indicates that the conductive paths are of poor quality when the polymer networks and CB-polymer bonding have not yet completely formed. The filler particles still have a certain freedom to migrate and to aggregate, leading to



**Figure 6** (curves 1 and 2) Time dependence of gel fraction and (curves 1' and 2') room-temperature resistivity of crosslinked CB/EVA/LDPE composites annealed at different temperatures. Annealing temperature: (1, 1') 80°C; (2, 2') 75°C.

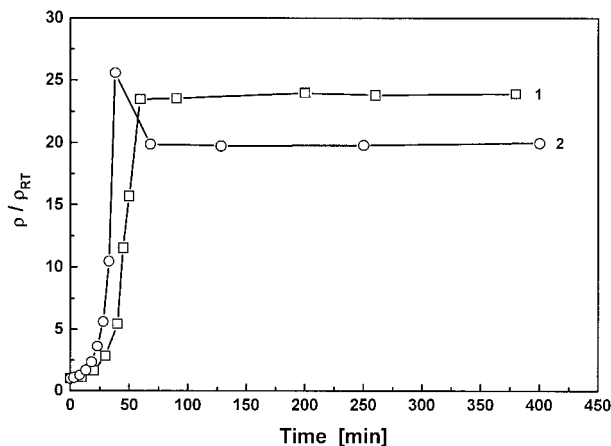


**Figure 7** Temperature dependence of resistivity,  $\rho$ , of crosslinked CB/EVA/LDPE composites annealed at different temperatures for 10 h after irradiation in comparison to (curve 3) the sample which was stored at room temperature for 24 h after irradiation. Annealing temperature: (1) 80°C; (2) 75°C.

the fluctuation of resistivity. Only when the above-mentioned two kinds of crosslinking structures are well established, especially under the accelerative effect of a high temperature (i.e., 90°C in the current case shown in Fig. 8), is the quality of the composites' conductive paths able to be improved, as shown by the flat part of curve 2 in Figure 8 at a time longer than 70 min.

## CONCLUSIONS

Based on the above discussion, the following statements can be made:



**Figure 8** Time dependence of resistivity,  $\rho$ , of CB/EVA/LDPE composites treated at 90°C. Sample histories: (1) annealed at 75°C for 30 h after irradiation crosslinking; (2) kept at room temperature for 30 h after irradiation crosslinking.

1. For the crosslinked CB/EVA/LDPE composites, which can function as a PTC material in practice, a post-heat treatment is necessary. The optimum annealing temperature and annealing time are found to be 75°C and 10 h, respectively. Under these conditions, electrical networks of improved quality coupled with low room-temperature resistivity and high PTC intensity can be obtained.
2. The radicals produced in the composites during the irradiation process possess long-term activity. After irradiation, some of them keep on inducing crosslinking of the matrix polymer and the free-radical reaction between CB and the matrix. As a result, the dispersion mode of CB agglomerates is continuously changing, leading to the fact that the composites' conductivity changes as a function of time.
3. Termination of the residual free radicals in the composites can be accelerated through annealing. In general, the higher temperature associated with a longer annealing time facilitates faster termination. By taking the advantage of this, the crosslinking structure of the matrix polymer and the bonding between CB and the matrix can be completely formed within a limited time in terms of an appropriate heat treatment. In other words, a faster improvement of the conductive network quality is thus available.

4. The uncrosslinked CB/EVA/LDPE composites are less sensitive to heat treatment due to the absence of the residual radicals. Depending upon annealing conditions, redistribution of CB in response to the variation in the matrix morphology is the predominant mechanism involved.

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