Property Balancing for Polyethylene-Based Carbon Black-Filled Conductive Compositesa

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ABSTRACT: Carbon black (CB) filled polyethylene (PE) and/or ethylene vinyl acetate (EVA) composites were prepared by conventional blending. Their electrical properties, including resistance–temperature relation, resistivity–CB content relation, and positive or negative temperature coefficient (PTC, NTC) intensity; mechanical properties such as break strength and the elongation at break; and processing conditions involving mixing torque and equilibrium temperature were studied to balance them from the fabrication and application points of view. A balanced property profile was achieved by mixing EVA with the primary CB–PE system to form a trinary blend. To enhance the thermal stability, the prepared samples were then filled with ZnO and talc and subsequently undertook either chemical or radiation crosslinking. This treatment mostly eliminated the NTC effect, the PTC transition was significantly intensified, and the room temperature resistance was slightly increased. J Appl Polym Sci **67:** 131–138, 1998

Key words: carbon black; polyethylene; property balancing; conductive composites

INTRODUCTION

Traditionally, materials with a positive temperature coefficient (PTC) resistance effect have been made of doped $BaTiO_3$ ceramics, in which the transition from the ferroelectric to the paraelectric state at the Curie temperature is utilized. Thermistors made of these materials exhibit a fairly large PTC resistance effect at the Curie temperature. They have been widely used for a long time, although they are limited to certain applications by relatively high room temperature resistivity and high manufacturing costs.

In a move toward lower room temperature resistivities, as well as away from relatively expensive ceramic processing, polymer-based materials have been developed.[1] The most common of these is one composed of conducting carbon black (CB) particles dispersed in an insulating matrix of semicrystalline polyethylene (PE). With this development, especially due to the great flexibility of forming (shaping), applications have been extended. A successful example is self-regulating heaters.[2]

The CB filled conductive PE composite has a low room temperature resistivity with a substantial PTC resistance effect that is mainly caused by two factors. The first is the percolation threshold, which is defined as the critical volume fraction of filler at which conducting paths begin to form throughout the composites. The second is the volume expansion coefficient at the melting point of the matrix. From our own experiences,[3,4] one problem encountered during preparation is how to balance the electrical and mechanical properties and processing conditions. The high loading level of filler for low room temperature resistivi-

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Table I Polymers Studied and Their Physical Data

Polymers	MFR (g/10 min)	ρ (g/cm^3)	T_m (peak, °C)	H (J/g)
PE, Qilu 2480	0.14	0.943	126.7	135
EVA, UE 631	2.0	0.946	85.5	19

ties bring about a high viscosity of melts and brittleness of the final products and also sacrifices the PTC effect. An additional drawback of using thermoplastic matrices (e.g., PE) is that a strong negative temperature coefficient (NTC) effect is observed at temperatures above the PTC transition due to thermal-induced movement of the conducting particles to form a new network across the medium. To alleviate this problem, the composites are usually crosslinked through either chemical or radiation treatment.[5]

The purposes of this experimental study are to balance the processing conditions with the electrical and mechanical properties by composition modification and to eliminate the NTC after the PTC by either chemical or radiation crosslinking or both.

EXPERIMENTAL

Two types of commercial polymers were used as matrices in the study; one was a PE (tradename Qilu 2480) as base material and the other was an ethylene vinyl acetate (EVA, tradename UE 631) with a VA content of 18% as a modification component. Their melt flow rate (MFR) and their densities are listed in Table I. All compositions studied had a constant 2 wt % content of additives, including stabilizers, antioxidants, and processing aids. The conducting filler was a commercial CB with an average 42-nm diameter particle size, BET (determination method developed by Brunauer, Emmet, and Teller) of 63 m^2/g, and DBP (Dibutyl Phthalate absorption measurement method) of 3.3 mL/g determined with a particle size analyzer.

The incorporation of CB into the polymers was completed by shear milling on a two-roller mixer at 150°C for 15 min. The shear roller gap was 0.5 mm. Prior to the mixing, all components were dried at 80°C for 24 h under a vacuum. The fact that the samples prepared gave good reproducible data implied that an equilibrium state was achieved through the mixing.

The milled pieces were then compression molded under 5.3 MPa at 180°C for 10 min into samples of approximately 2-mm thickness. The compression direction was perpendicular to the shear. By compression molding, the samples were also electroded with copper meshes on both sides. This kind of electrode proved to possess very good adhesive strength to the PE based materials, even when the samples were tested in a wide range of temperatures and by repeated temperature cycles.

The electric resistivity was measured in the thickness direction. Low resistivity measurements were performed on a 7150P Digital Multimeter; high resistivity measurements were made with a ZC36 High Resistance Electrometer. Resistivity as a function of temperature was measured with a computer controlled apparatus of our own design.

Thermal, mechanical, and rheological measurements, as well as the processing procedures, such as blending, chemical, and radiation crosslinking, are described directly in the following text insofar as necessary.

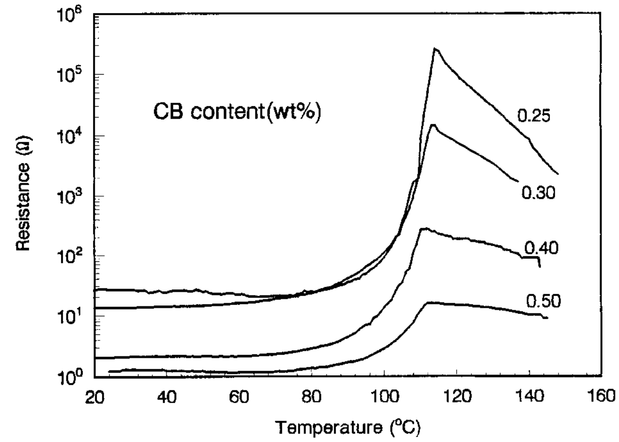

Figure 1 Resistance R plotted against temperature T for CB–PE binary composites.

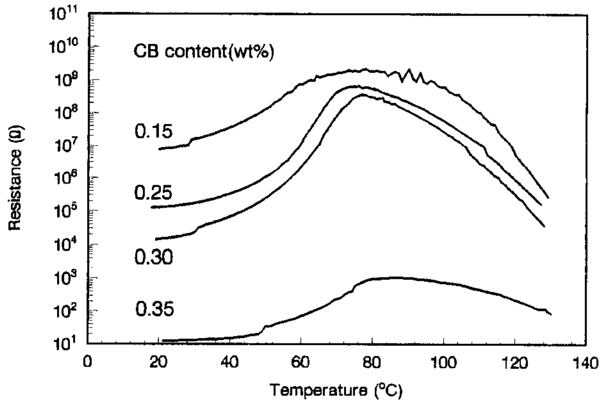

Figure 2 Resistance R plotted against temperature T for CB–EVA binary composites.

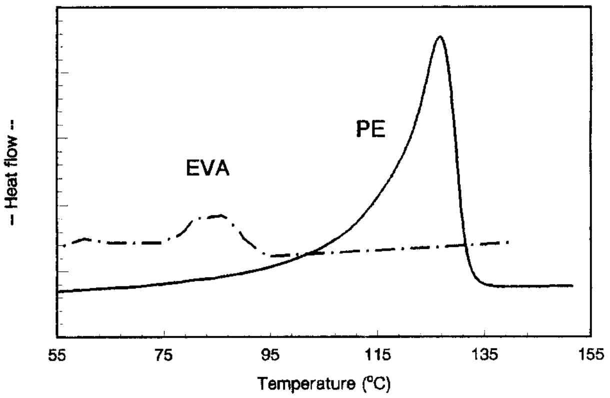

Figure 4 Melting behavior for PE and EVA studied by means of DSC.

RESULTS AND DISCUSSION

Electric and Thermal Properties

The presence of a PTC transition is of great importance in dealing with these composites. Figures 1 and 2 illustrate the resistance (R) as a function of temperature (T) for several compositions in the CB–PE and CB–EVA binary systems, respectively. In composite samples with lower content of filler, the room temperature resistance is relatively high and there is only a low PTC effect (see Fig. 2). As the filler concentration is increased, a significant PTC effect is observed. A further increase in CB content decreases room temperature resistance and also reduces the PTC effect. All of the PTC anomalies are observed near the melting point of the polymer matrix.

To select the composites with high PTC intensity ρ_{PTC} [$=\log(\rho_{\max}/\rho_r)$] and relatively low room temperature resistivity, ρ_r, a ratio of $\rho_{\mathrm{PTC}}/\log \rho_r$ is introduced that might also serve as a criterion to evaluate the PTC behavior. The results are presented in Figure 3, together with percolation curves for the CB–PE and CB–EVA systems. A comparison of the two systems shows that the CB–EVA system has a broader percolation curve, a higher critical weight fraction, a higher room temperature resistivity for CB content well past the critical point, and lower ratio of $\rho_{\mathrm{PTC}}/\log \rho_r$ than the CB–PE system. These differences may be ascribed to the polar attribute of EVA that often puts conductive fillers into better wettability and dispersion in the polymer matrix. It is not difficult to believe that if the polymer completely wets the surface of the filler, the high resistance "skin" will eliminate the percolative connectivity and result in a high resistance. Many previous works[6–9] have testified that such kinds of skin effects may change the conductivity mechanism and alter the particle–particle contact geometry, which leads to a high critical weight fraction and broad percolation curve.

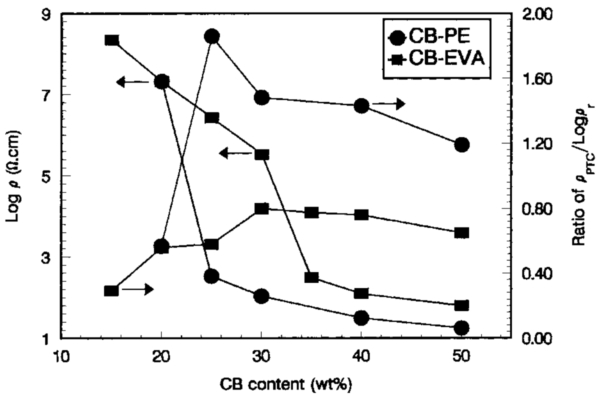

Figure 3 Room temperature resistivity ρ_r and ratio of $\rho_{\mathrm{PTC}}/\log \rho_r$ as function of CB content for CB–PE and CB–EVA binary composites.

The mechanism for the PTC anomaly in semicrystalline polymers is generally attributed to the relatively large change in specific volume of the polymer at its melting temperature. Thus, the melting behavior of the base polymers should be responsible for the PTC behavior of the composites. Figure 4 illustrates the melting behavior for the PE and the EVA polymers used in this study, and Table I reports the melting temperatures (T_m) and melting enthalpies (H), respectively, determined by differential scanning calorimetry (DSC, heating rate of 10°C/min in N_2) measure-

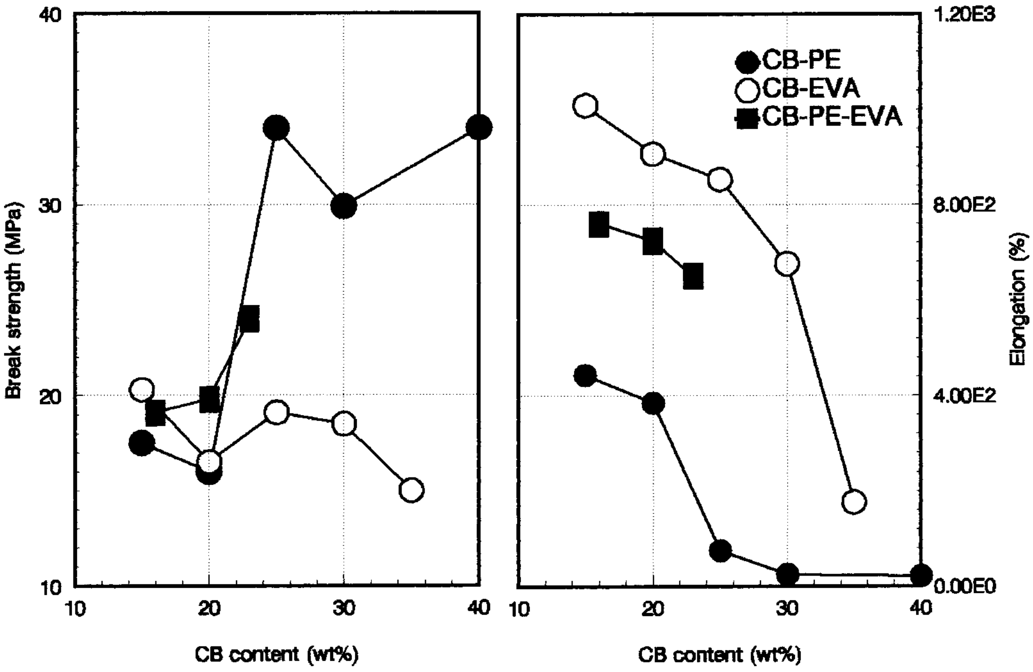

Figure 5 Mechanical properties of PE, EVA, and PE–EVA blend that are dependent on CB content.

ments. There is, in fact, a similarity in the temperature running between the PTC transition behavior and the melting behavior. The poorly defined PTC transition for the CB–EVA composites corresponds to the poorly defined melting behavior of the EVA matrix, whereas both the PTC effect of the CB–PE composites and the melting peak of the PE matrix are significantly clear. The fact that there is no clearly defined PTC transition at the melting point for the EVA based composites leads one to believe that EVA alone cannot be used as the matrix polymer for the PTC materials.

Figures 1 and 2 show that the NTC transitions immediately follow the PTC transition. The NTC effect is presumably due to reaggregating of CB particles in the polymer melt and repairing of the disconnected conducting pathways.[10] The details of this effect are not yet well understood. The NTC intensity seems to be proportional to the previous PTC effect, especially for the CB–EVA system.

Mechanical Properties and Processing Conditions

To produce flexible self-regulating heaters and related devices, the balancing of electrical and mechanical properties and processing conditions of filled conductive composites is of great significance. For the CB–PE and CB–EVA binary systems studied, Figure 5 and Table II show that the mechanical properties vary from one to the other with the alteration of the polymer types. The composition-dependence of the elongation at break, ε_b, decreases generally with the increase of CB loading, while the break strength, σ_b, for the CB-PE increases. The elongation values for the two systems, however, lie at significantly different levels.

To balance the properties, EVA was mixed with the PE-CB system to form a trinary system (approximate ratio of EVA : PE of 1 : 3) through a conventional compounding technique. By this

Table II Mechanical Properties of PE, EVA, and Their Composite Dependent on CB Content

CB (wt %)	PE, Qilu 2480		EVA, UE631		PE-EVA System	
	σ_b	ε_b	σ_b	ε_b	σ_b	ε_b
15	17.0	444	20.3	1009	—	—
20	15.9	384	16.5	907	19.8	724
25	34.0	74	19.1	853	—	—
30	29.9	24	18.5	676	—	—
35	—	—	15.0	176	—	—
40	34.0	21.3	—	—	—	—

σ_b (MPa) are the break strengths and ε_b (%) is the elongation at break.

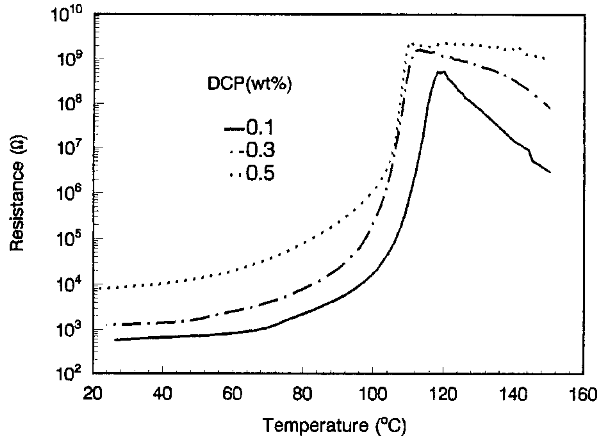

Figure 6 Resistance R plotted against temperature T for CB–PE–EVA–ZnO multicomponent system crosslinked by using DCP with different contents.

modification, the break strength of the blend became higher than that of the CB–PE system, especially at low CB content; the elongation at break was greatly improved in contrast to the original CB–PE binary system. The quantitative data are also listed in Figure 5 and Table II.

Not only the mechanical, but also the processing conditions of the CB-PE binary system can be positively changed. A further study on blending processability by means of torque measurement showed that the maximum shear torque was reduced from 3070 mg for the CB–PE system to 2000 mg for the CB–EVA–PE system, the equilibrium torque was reduced from 1750 to 1200 mg, the equilibrium time for plasticating was reduced from 6.0 to 3.5 min, and the shear heat-induced temperature was reduced from 10 to 5°C. A torque rheometer was used for this study.

It is well known that EVA has been widely used in the modification of PE for better flexibility, toughness, and resistance to environmental stress cracking. Our results demonstrate that the EVA–PE blend can also serve as a better matrix material for applications like flexible self-regulating heaters, due to its mechanical and processing properties.

Crosslinking Treatment

To enhance the thermal stability and to alleviate the NTC effect, the CB–PE–EVA trinary system prepared was filled with zinc oxide (ZnO) or talc and then chemically crosslinked by using dicumyl peroxide (DCP) as the crosslinking and grafting agent. A small amount of the peroxide was directly mixed with the materials during the compounding at 150°C for 15 min. Under these conditions, the peroxide, which had a decomposition half-life of 20–25 min[11], was kept stable. Primary radicals were produced by the thermal decomposition of DCP at 180°C during the compression molding. These, in turn, extracted one of the H atoms, thus saturating themselves and transferring the radical state to the polymer chain. DSC measurements indicated that, for a DCP range from 0.1 to 0.5 wt %, there was no melting peak for the EVA component registered in the thermogram of this crosslinked multicomponent system, which may suggest that the EVA component is very compatible with the PE matrix and there should only be one single PTC transition caused by the PE component present in the resistance–temperature curves. Figure 6 gives the results of these resistance–temperature measurements.

As shown in Figure 6, increasing the DCP content from 0.1 to 0.5 wt % (i.e., increasing the degree of chemical crosslinking) leads to an obvious increase in room temperature electrical resistance, a decrease in the PTC effect, a shift of the PTC transition to lower temperatures, and a reduction of the NTC effect. A summarized description of the influence of this crosslinking on the PTC as well as NTC intensity is shown in Figure 7 and Table III for CB–PE–EVA systems filled with ZnO and talc. The decrease in the ratio of $\rho_{PTC}/\log \rho_r$ must be seen as necessary at this composition by this chemical crosslinking operation.

Table IV shows the change in mechanical prop-

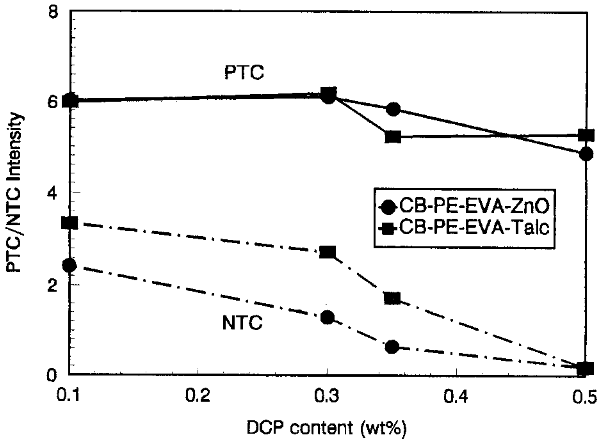

Figure 7 The intensity of the (—) PTC and (---) NTC effects as a function of DCP content for CB–PE–EVA composites filled with ZnO and talc.

Table III Electrical Properties of CB–PE–EVA Composites Filled with ZnO and Talc Dependent on DCP Content

DCP (wt%)	CB–PE–EVA–ZnO				CB–PE–EVA–Talc			
	ρ_r (Ω cm)	ρ_{PTC}	ρ_{NTC}	η	ρ_r (Ω cm)	ρ_{PTC}	ρ_{NTC}	η
0.1	5.2×10^3	6.03	2.42	1.62	7.1×10^3	5.99	3.34	1.56
0.3	1.1×10^4	6.11	1.30	1.51	5.3×10^3	6.2	2.73	1.67
0.35	3.5×10^4	5.85	0.64	1.29	2.6×10^4	5.23	1.72	1.18
0.5	6.8×10^4	4.88	0.18	1.01	5.7×10^4	5.29	0.18	1.11

CB : PE : EVA : ZnO(talc): additive = 20 : 52 : 13 : 13 : 2. η denotes the ratio of $\rho_{\mathrm{PTC}}/\log \rho_r$.

erties that are dependent on the composition and crosslinking treatment. The mechanical properties of these two systems were balanced, although the ZnO or talc fillers generally cause material brittleness. At sufficiently high crosslinking degrees, the material had excellent temperature stability. After three to four heating cycles, the room temperature resistivity and the PTC intensity stayed unchanged. More cycles and long-term aging did not show any degradation of the properties.

On the other hand, radicals can also be created by radiation crosslinking. For this purpose, a highly penetrating source, Co^{60}, was used. At room temperature, crosslinking agent-free samples with base composition of CB–PE–EVA–ZnO were irradiated in air at a constant dose rate of 0.5 Mrad/h for 36 h. Figure 8 shows that the NTC effect is mostly eliminated and the room temperature resistance is only slightly increased. Significant improvement is also achieved in the thermal stability of the PTC transition.

A disadvantage of the addition of EVA and ZnO to the primary CB–PE composite with subsequently crosslinking is the significant increase of room temperature resistance. This effect can be better demonstrated in Figure 9 by comparing a primary CB–PE system with a CB–PE–EVA–ZnO multicomponent system. Both of them are first chemically crosslinked by using 0.1 wt % DCP (curves 1) and then radiation crosslinked (curves 2). The increase in the resistance seems to be a compromise that must be accepted.

CONCLUSION

1. A diversity of polymer matrices may result in different percolation curves. Composites for a CB–EVA system show broader percolation curves than for the CB–PE system. Low room temperature resistance can be achieved at and especially above the critical weight fraction.
2. The PTC effect appears near the melting point of the semicrystalline polymer. The thermal expansion of the polymer at the melting point is believed to cause the PTC transition by separating the contacting

Table IV Mechanical Properties of Different Compositions of Crosslinked and Uncrosslinked Systems

System	DCP (wt %)	CL	σ_Y	σ_b	ε_b
CB–PE–EVA	0	No	21.6	19.8	724
CB–PE–ZnO	0	No	—	28.7	41.3
CB–PE–ZnO	0.1	Yes	—	30.2	48.0
CB–PE–EVA–ZnO	0.1	Yes	24.0	17.9	548
CB–PE–EVA–talc	0.1	Yes	23.0	17.9	549

CL, the chemical crosslinking using DCP. σ_Y are the yield strengths.

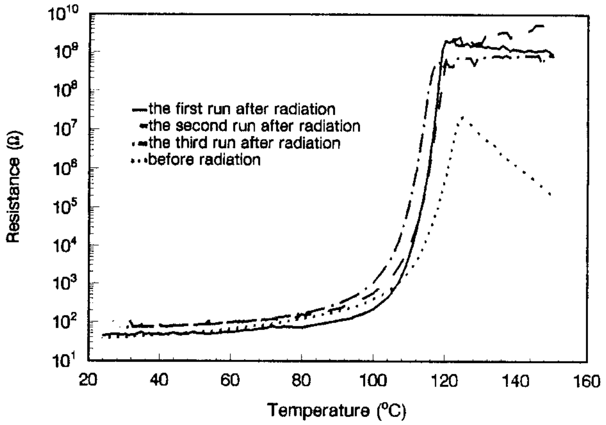

Figure 8 Comparison of resistance and temperature plots for CB–PE–EVA–ZnO multicomponent system uncrosslinked and crosslinked by radiation.

conductive CB aggregates. The PTC intensity depends on the volume fraction. In the range near the critical weight fraction, the PTC intensity reaches its maximum in the intensity–weight fraction plot.

3. The polymer-based conductive composites may exhibit at the same time low room temperature resistivity and high PTC intensity by special composition design, for instance, a semicrystalline polymer matrix, having a very high thermal expansion coefficient, filled with CB slightly higher than its critical percolation value.
4. An accompanying effect when increasing the filler content is an increase in the mechanical strength and a decrease in the elongation at break. The brittleness caused by high loading of the filler can mostly be balanced by adding a flexible component such as EVA. By this composition modification, namely with a CB–PE–EVA trinary base system, the mechanical properties and the processing conditions can be positively changed.
5. Chemical and radiation crosslinking are both effective in eliminating the NTC effect after the PTC transition and in enhancing the thermal stability. In most cases, the PTC intensity is also increased due to this

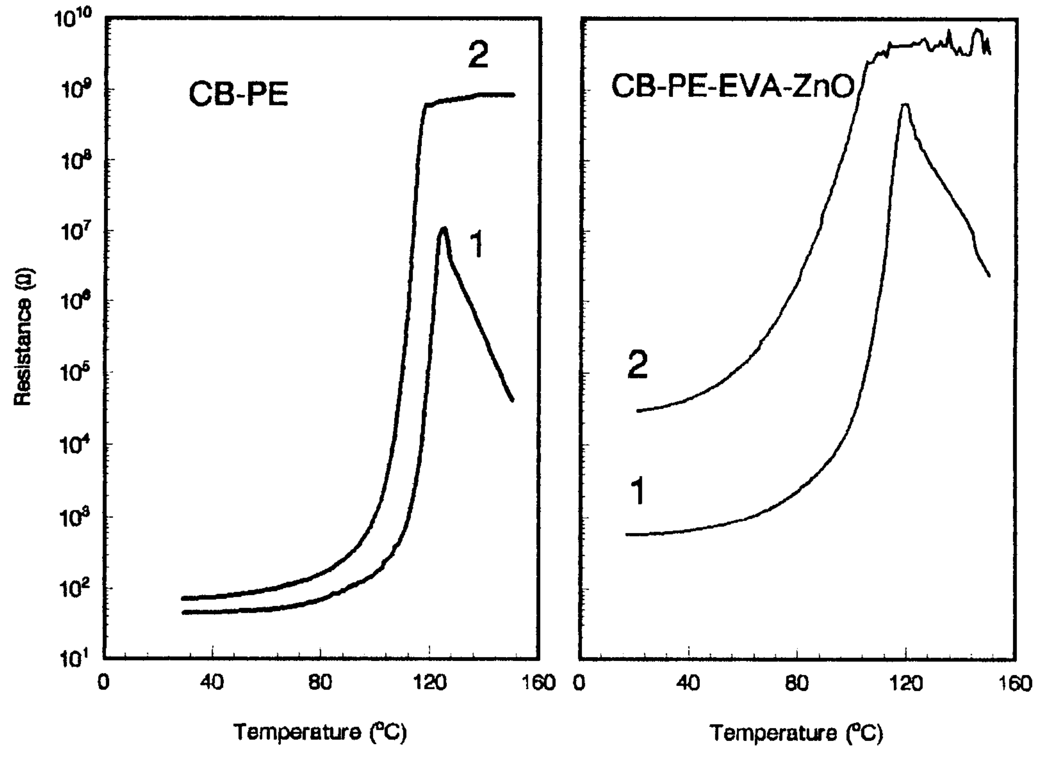

Figure 9 Comparison of resistance and temperature plots for CB–PE and CB–PE–EVA–ZnO systems first crosslinked by using 0.1 wt % DCP (curve 1) and then radiation crosslinked again (curve 2).

treatment. A drawback of the crosslinking treatment is that the room temperature resistivity increases. Therefore, more efforts to balance the electrical (low room temperature resistivity, large PTC intensity) and mechanical (high strength, high toughness) properties, and in particular, to enhance the long-term stability of these properties, are needed.

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