Influence of Irradiation Conditions on the Electrical Behavior of Polyethylene–Carbon Black Conductive Composites

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ABSTRACT: The temperature-dependent resistivity behavior of carbon black–loaded polyethylene (PE) composites irradiated both at room temperature and 170°C above the PE melting point was studied. The irradiation doses were varied. At a given loading level, irradiation at room temperature corresponded to an energy treatment on a low-resistive, solid, three-phase composite system, while at a high temperature it corresponded to a treatment on high-resistive, viscous, two-phase system. The irradiation condition had a complicated influence on the electrical response to temperature. The resulting composite structure was analyzed by using differential scanning calorimetry, gel fraction, and wide-angle X-ray diffraction. The results were then discussed by comparing them with those of the unirradiated sample. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 494–499, 2000

Key words: electron beam irradiation; PTC and NTC; crosslinking; crystalline structure

INTRODUCTION

Carbon black–polyethylene (CB-PE) composites exhibit a sharp resistivity increase with a rise in temperature in the polymer melting region (PTC, positive temperature coefficient) followed by a rapid resistivity decrease (NTC, negative temperature coefficient).[1–3] The composite PTC effect can be at least partly explained by the rapid expansion of the system undergoing melting, thereby increasing the gaps between particles and aggregates and thus hindering the electrical conduct.[4–6] Another factor to be considered is the fine distribution of the particles and/or aggregates in the polymer phase. An inhomogeneous distribution is expected since CB particles have been preferentially rejected from spherulites during their formation and growth. Upon heating, the "frozen" distribution will start to change in the vicinity of the commencement of the melting region by movements of CB. As the viscosity is reduced, an enhanced redistribution process is taking place toward a more uniform distribution, permitting more and more particles or aggregates to participate in the conductive process. The NTC effect is thus presumably caused by the movements in the molten polymer and formation of a new distribution of better uniformity and conductivity.[7] Crosslinking has been proven to be an effective way to reduce dramatically the freedom of movement of the CB at high temperatures and thus in practice to eliminate the NTC effect. Already there exist a number of references report-

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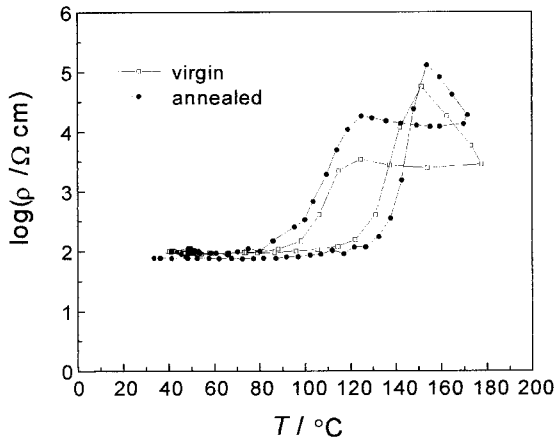
ing either irradiation crosslinking at room temperature, or peroxide chemical crosslinking in a molding operation at temperatures above the PE melting point.[7–9] The present article reports on a study on temperature-dependent resistivity behavior of CB-loaded PE composite samples that have been electron beam irradiated at different energy doses and temperatures.

EXPERIMENTAL

Composite samples were made by mixing polyethylene (HD-PE2480; Qilu Petroleum Company, China) with CB (acetylene black; Chun An Chemical Company, China) (65 : 35 in weight) in a Bandury-type mixer at 170°C for 15 min, then mixed again on a two-roll mill at the same condition. Plates were compression molded at 170°C for 10 min. And finally samples 1.5 × 1.5 × 0.2 cm^3 in size were cut from the plates.

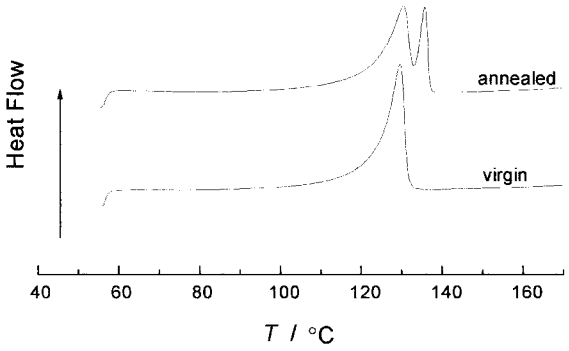
Electron beam irradiation was carried out using a BF-5 electron accelerator at a dose rate of 360 kGy/h in air at 25°C (noted as *RT*) and 170°C (*MT*), respectively. The electron energy and the beam current were 3 Mev and 200 μA, respectively.

Thermal analysis was performed using Perkin–Elmer DSC-7, with a scanning rate of ±10°C/min. Overall resistivity was measured using a 7150 Plus digital multimeter in the thickness direction of the samples, whose surfaces were painted with silver paint. Resistance was automatically recorded against temperature with a computer-controlled apparatus of our own development, at a rate of ±10°C/min. The gel fraction of the samples was determined through the ratio of the weight of insoluble fraction after extraction with reflux boiling xylene in an extractor for 72 h and the weight of the sample before extraction.



Resistivity – Temperature Behavior of a Virgin and an Annealed PE/CB Composite Sample in Comparison

Figure 1 Comparison of resistivity–temperature behavior of a virgin and an annealed PE–CB composite sample.



DSC Traces of a Virgin and an Annealed PE/CB Composite Sample in Comparison

Figure 2 Comparison of DSC traces of a virgin and an annealed PE–CB composite sample.

RESULTS AND DISCUSSION

Through the preexperiments, an annealing procedure as follows was on settled to avoid the thermal history: each sample (whether irradiated or not) was first isothermally annealed at 170°C for 5 min, then at 125°C for 36 h, and finally slowly cooled down to room temperature in air.

The effect of annealing on the overall resistivity is shown in Figure 1. The annealed sample exhibits a lower resistivity at room temperature, a more abrupt and high-intensity PTC switch behavior, and a higher transition temperature, suggesting that good thermal–electric switch properties were achieved by the isothermal treatment.

Figure 2 reports the influence of annealing on the heat flow of the polymer by means of DSC. As can be seen, an additional high-temperature peak appears in the DSC trace for the annealed sample, which is often observed and reported as a result of the special thermal behavior of PE.[10] Thermal analysis data reveal that both the crystallinity and the melting enthalpy of the annealed

Table I Influence of Irradiation Condition on the Polymer Phase in Terms of Melting Enthalpy and Crystallinity

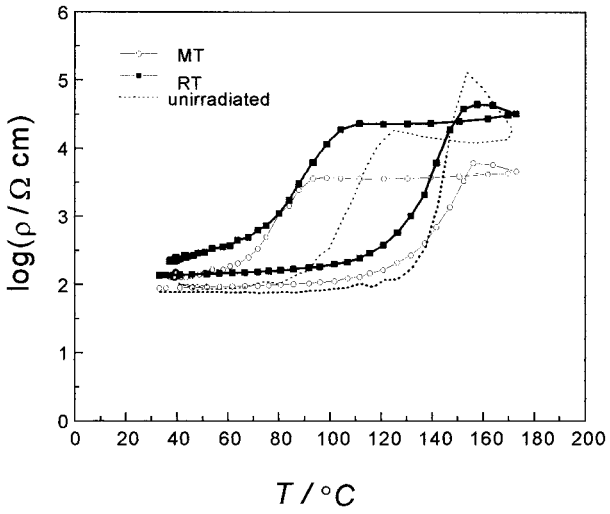
Irradiation Condition Dose (kGy)/Temperature	Polymer Melting Enthalpy (J/g)	Polymer Crystallinity (%)
Virgin, unirradiated	109	57
Annealed, unirradiated	135	71
Irradiated at 20/RT	108	57
Irradiated at 20/MT	106	56
Irradiated at 200/RT	88	47
Irradiated at 200/MT	81	43
Irradiated at 400/RT	91	48
Irradiated at 400/MT	60	32

samples are higher than those of the virgin samples (Table I). Therefore, the intensified PTC switch behavior can be ascribed to the variation of the crystalline structure caused by the annealing. On the other hand, the annealing seems likely to have a minimal effect on the NTC behavior (Fig. 1) because the NTC occurs in a temperature range higher than the melting point.

Table I also lists the thermal analytical data for the samples irradiated at different doses, either at room temperature (RT) or at 170°C (MT). Compared with the unirradiated samples, both the enthalpy and crystallinity of the irradiated samples decrease with the energy doses. Particularly the high-temperature exposure of the samples to the radiation affects the crystalline structure so seriously that enthalpy and crystallinity are all lower than those of the RT samples at the given doses.

Because the crystalline structure of the polymer phase primarily controls the PTC transition behavior, it is understood that the electrical response will change with the irradiation conditions. This is demonstrated in Figures 3 and 4 for doses of 20, 200, and 400 kGy. In all the figures a reference curve of an unirradiated sample is also shown for comparison.

Under the condition of 20 kGy (Fig. 3), the room temperature resistivity of the MT sample is slightly higher than that of the unirradiated one, but it is still lower than that of the RT sample. The PTC intensity is considerably reduced compared to both the unirradiated and the RT/irradiated one. The electron beam radiation affects the electrical behavior generally in such a manner that the PTC switching rate becomes lower, the PTC intensity smaller, and the heating–cooling



Temperature Dependent Resistivity Behavior of PE/CB Composite Samples Irradiated at RT and 170°C (MT), respectively, in Comparison with the Unirradiated

Figure 3 Temperature-dependent resistivity behavior of PE–CB composite samples irradiated at RT and 170°C (MT), respectively, in comparison with the unirradiated samples.

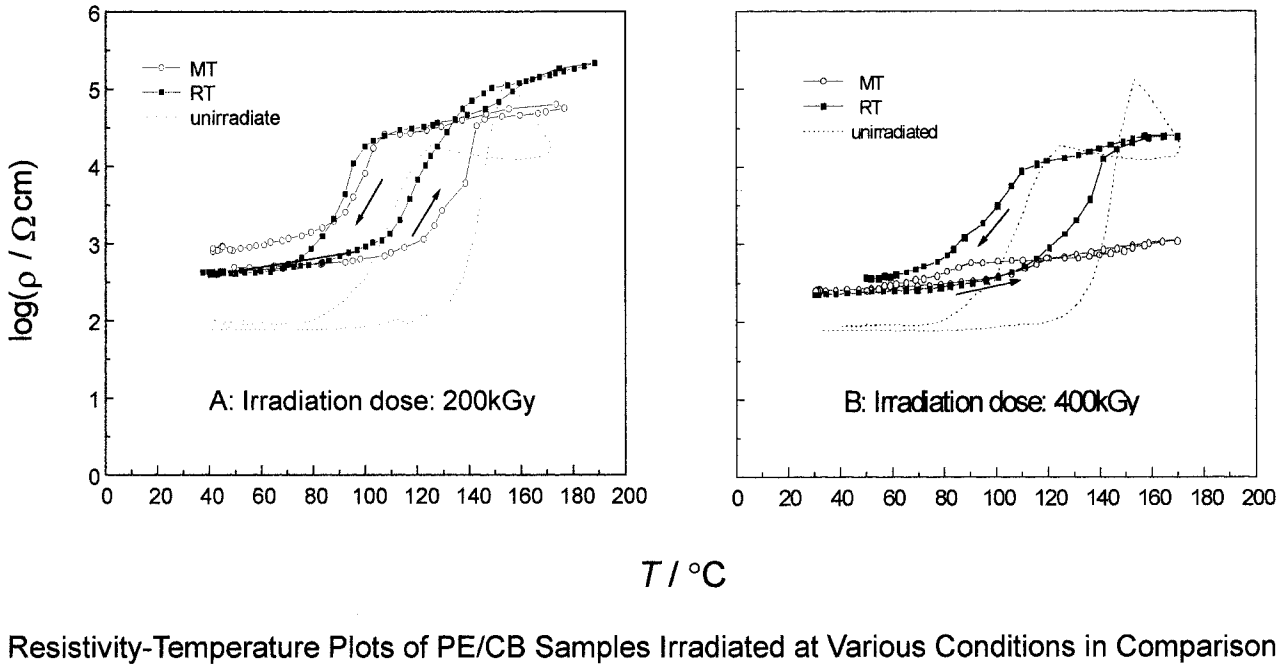


Figure 4 Comparison of resistivity–temperature plots of PE–CB samples irradiated under various conditions.

hysteresis loop gets wider for both the RT and MT samples. The NTC intensity decreases also for the both irradiated samples, as well as the NTC decreasing rate.

At an energy dose of 200 kGy or 400 kGy (Fig. 4), the NTC effect disappears completely. In the temperature range where the NTC effect was expected, the resistivity increases again. This behavior holds true for the both temperatures. Under this condition, the initially thermoplastic polymer can develop to a more densely crosslinked system. Evidence for this is shown in Figure 5. For all the irradiation doses investigated in this experiment except the 20 kGy/RT condition, irradiation results in gel fractions equal to or higher than 80%, exhibiting high crosslinking densities. Thus, in Figure 4 the third PTC stage observed in both the RT and MT samples above the PTC jump can be attributed to the compact effect caused by the high-dose irradiation crosslinking.

Irradiation temperature also has a significant effect on the resistivity behavior. At room temperature there exists a low-resistive (for the given filler volume fraction), solid, three-phase system of CB and semicrystalline PE. If the composite is irradiated, the crosslinking will take place preferentially in the amorphous intergranulate region, where the CB aggregates naturally concentrate. Therefore, a CB-rich, interlinked conductive structure can be formed, which behaves like larger conductive aggregates. An example is the composite treated at RT/20 kGy (Fig. 3). However, a 170°C irradiation corresponds to a high temperature treatment on a two-phase system of solid CB and molten PE, which is also high resistive (in the NTC stage for the given filler volume fraction). The crosslinking can occur to any greater extent, thus stopping the particles and aggregates from moving and fixing the resistive state. Therefore, the PTC jump is lowered a great deal. This is also demonstrated in Figures 3 and 4, particularly in Figure 4(b), for the MT samples.

Irradiation can also attack the polymer structure, thus influencing the electrical behavior of the composites. At 20 kGy, DSC traces of both the RT and MT samples are similar (Fig. 6), but the gel fraction data (Fig. 5) are quite different. Therefore, the crosslinking effect is thought to be dominant. The low-temperature peaks are probably due to CB-induced crystallization by annealing.[11] However, particularly at 400 kGy, the gel fraction data are similar (Fig. 5), but the DSC traces are quite different (Fig. 6). Therefore, high-temperature, high-dose irradiation-induced polymer degradation cannot be excluded. At present it

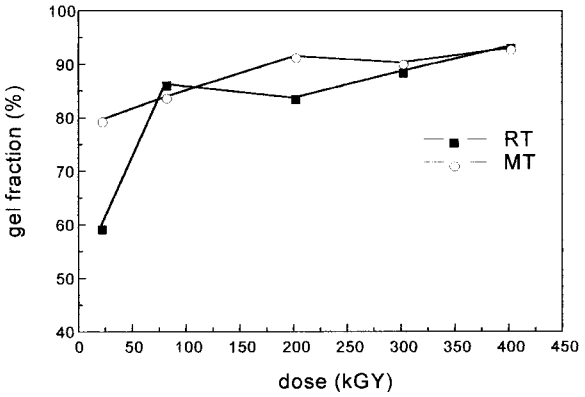


Figure 5 Comparison of gel fraction of irradiated PE–CB composite samples at RT and 170°C as function of energy doses.

is only possible to speculate on the likely difference between the conductive structures, with respect to the irradiation doses and temperatures.

Electrical reproducibility of the composites is of great practical concern. High-dosage irradiation can improve reproducibility significantly; however, high-dose irradiation at MT at the very least sacrifices the PTC intensity to a large extent. Therefore, a compromise between the electrical properties and the irradiation conditions at an optimum dosage and temperature has to be taken into consideration by a systematic investigation. Detailed results will be presented elsewhere.[12]

The influence of irradiation doses and temperatures on the crystalline structure can also be found in the X-ray diffraction pattern in Figure 7. A high-dose and high-temperature treatment apparently produces a higher ratio between the amorphous and crystalline areas. However, no additional information is provided by the WAXD compared to the DSC study.

CONCLUSION

The influence of electron beam radiation of varied irradiation doses and temperatures on temperature-resistivity behavior and the polymer structure of annealed carbon black–loaded polyethylene composites was studied. Radiation at a dose of 20 kGy makes the PTC switching rate lower, the PTC intensity smaller, and the heating–cooling hysteresis loop wider for both the RT and MT samples, while high-energy radiation eliminates the NTC effect completely. Moreover, it causes a third stage of PTC. Room temperature irradiation was found to be generally milder against the polymer phase than was the 170°C treatment. It results in a reproducible electrical behavior by stopping the CB particles and aggregates from mov-

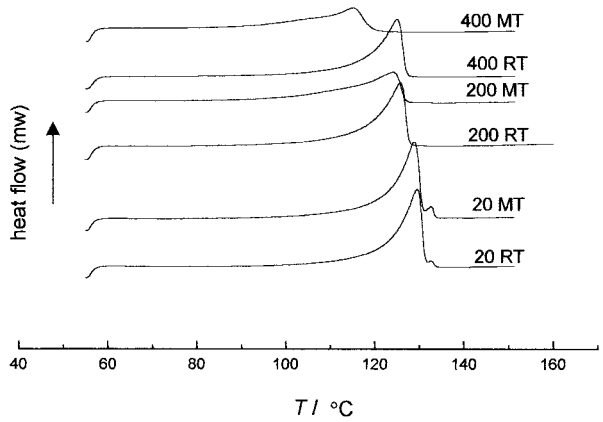
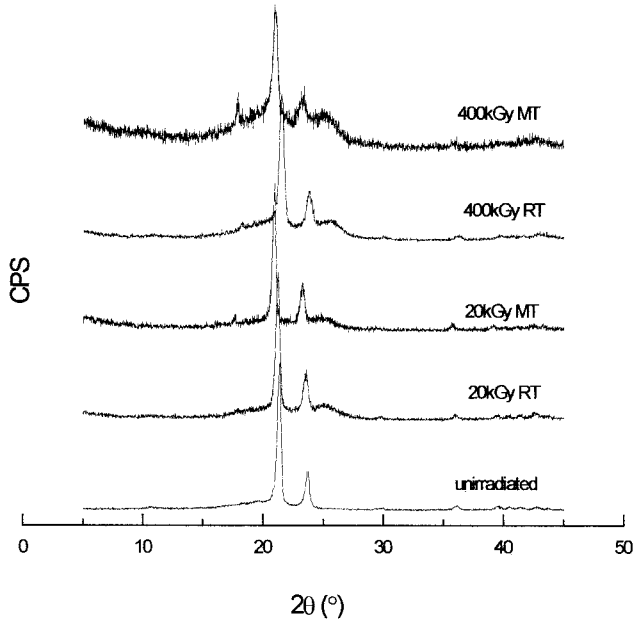


Figure 6 DSC traces of PE–CB composite samples irradiated at various energy doses and temperatures.



WAXD Pattern of PE/CB Composite Samples
Irradiated at Various Energy Doses and Temperatures

Figure 7 WAXD pattern of PE–CB composite samples irradiated at various energy doses and temperatures.

ing. The high-temperature one significantly reduces the PTC intensity because of its higher crosslinking densities compared to those treated at room temperature.

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