Electrical Resistivity of Carbon Black Filled High-Density Polyethylene Composites

MYONG-GOO LEE, YOUNG CHANG NHO

Radioisotopes Radiation Application Team, Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong, Taejon 305-600, South Korea

ABSTRACT: The electrical resistivity of high-density polyethylene (HDPE) loaded with carbon black (CB) blends was evaluated as a function of the blending time and the melt index of HDPE. The relationship between the positive temperature coefficient effect and the room temperature volume resistivity was investigated. The positive temperature coefficient effect and reproducibility were improved significantly when the blending time of HDPE and CB was comparatively long. The effects of ^{60}Co γ-ray and electron beam irradiation on the positive and negative temperature coefficient behavior of the blends were studied. The effect of thermal aging on the volume resistivity was studied to ascertain the structural stability. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2440–2446, 2002

Key words: positive temperature coefficient; negative temperature coefficient; irradiation; melt index; high-density polyethylene; carbon black

INTRODUCTION

Polyethylene (PE) filled with carbon black (CB) is a prototypical composite that displays resistance switching. These materials can exhibit either a positive temperature coefficient (PTC) effect or a negative temperature coefficient (NTC) effect .[1–10] The main feature of a PTC material is that its electrical resistivity increases with the increase of the temperature when the filler concentration is moderate. Sometimes the material has the NTC effect that the resistivity decreases as the temperature increases. The electrical resistivity effect is a result of the thermal expansion of the polymer matrix and the formation of conducting pathways in the filler phase. Even though crosslinked high-density PE (HDPE) composites filled with CB have been used as thermistors, current limiters, overcurrent protectors, and self-regulating heaters in industry for many years, the mechanism for the PTC and NTC effects is not fully understood.[11–16] The lack of electrical reproducibility and the NTC effect are two main drawbacks to the application of PTC materials, and many scientists investigated the mechanism of electron transport and studied the stability and practicality of these materials.[17] Many experimental results showed that the electrical reproducibility of the materials during heating and cooling cycles can be improved by doping different sized CBs or by crosslinking; the latter is especially effective.[18,19] The electrical conduction process in CB/polymer composites is complicated and dependent on a large number of parameters, such as the filler concentration, CB particle size and structure, filler–matrix interactions, and processing techniques. It was reported that the PTC effect and reproducibility are both improved significantly when the polymer and CB are blended for a long time.[20,21] The increase in blending time

causes the absorption of the polymer on the CB surface to increase and finally to give the PTC effect. This absorption forms a bound polymer around the CBs and it obstructs the conduction of particles, so that the resistivity increases with the mixing time when the CB concentration is constant. Until now, there were no data available to evaluate the relationship between the melt index and volume resistivity as a function of temperature, as well as the irradiation effect of γ rays and electron beams (EBs) on the volume resistivity. This article examines the influence of the melt index and blending time on the volume resistivity of a HDPE/CB system. In addition, the irradiation effect on the PTC and NTC is evaluated when a γ ray and EB were used for the crosslinking of composites containing HDPE and CB. The structural stability of HDPE/CB systems after continuous thermal aging was also studied.

EXPERIMENTAL

HDPEs (SK Corporation) with melt indices of 0.04, 0.3, 0.8, and 5 g/10 min were selected as the polymer matrices in this work. The CB used was Raven 420™ purchased from Columbian Chemicals. Its average size was 86 nm, its surface area was 28 m²/g, and its dibenzoyl peroxide absorption was 75 mL/100 g. The CB and polymers were mixed in a Brabender at 170°C for 6, 12, 18, 24, and 30 min. The composition thus produced was sandwiched between a pair of copper foils (25 μm thick), which served as electrodes. The thickness of the sample was approximately 0.5 mm. The samples were irradiated using a γ-ray source at a rate of 10 kGy/h in air. The EB irradiation was done at a conveyer speed of 5 m/min and an acceleration energy of 1 MeV; the absorbed dose was adjusted by varying the electric current. The absorbed dose ranged from 10 to 180 kGy. The volume resistivities of the samples were consecutively measured with a digital multimeter and an insulating resistance tester at progressively elevated temperatures. All of the resistivities reported in this work are direct current resistivities. The composition of the HDPE/CB composites was 50:50 (w/w). The melting behavior of the composites was determined using differential scanning calorimetry (DSC, Perkin–Elmer DSC-7). The weight of the samples for DSC measurements was 2–3 mg. The samples were heated to 200°C at a heating rate of 10°C/min. The degree of gel was determined by the extraction method. The irradi-ated sample (200 mg) was enclosed in a stainless steel net (200 mesh), extracted with xylene for 48 h, and dried in a vacuum to a constant weight at 60°C. The degree of gel refers to the total amount of insoluble material involving crosslinked PE and CB trapped in the crosslinked PE.

RESULTS AND DISCUSSION

When 50:50 HDPE/CB was blended in a Brabender, the effect of the melt indices and the mixing time on the electrical resistivity was given as a function of temperature (Fig. 1). The melt indices of the HDPEs used in these experiments are 0.04, 0.3, 0.8, and 5 g/10 min. The samples were irradiated with γ rays. The absorbed dose was 120 kGy. Figure 1 shows the electrical resistivities of HDPE/CB composites as a function of temperature with blending times of 6, 12, 18, 24, and 30 min. In the tested melt index range, Figures 1(a) and (b) show that the PTC intensities increased with the increase of the melt indices when the blending time are a short 6 and 12 min, respectively. However, the PTC intensities decreased with an increase in the melt indices as shown in Figure 1(c–e) as the blending time was extended to 18, 24, and 30 min, respectively. The PTC magnitudes varied with the melt indices and mixing time of the composites. The CB aggregates are gradually broken by the shear force of the polymers during the blending at the melting temperature. This process makes the particles disperse in the matrix well. However, the distribution is destroyed when the sample is heated to high temperatures for the measurement of resistivity, because of the van der Waals force between the two particles and a decrease of the shear modulus of the matrix polymer. At the same time, the movement of the polymer chains and the expansion of the matrices make some CB aggregates and particles break away from the conducting networks at temperatures near the melting point of the polymer. The enlargement of the distance between the two particles causes an increment in the resistivity. We assume that the PTC intensity is affected by the two factors discussed above. The expansion coefficients of five kinds of HDPE are nearly the same; therefore, the diversity of the PTC magnitudes of the HDPE/CB compounds is mainly caused by the difference of the degrees of CB accumulation. As is well known, the shear modulus and viscosity of the matrix polymer are both reduced when the melt index
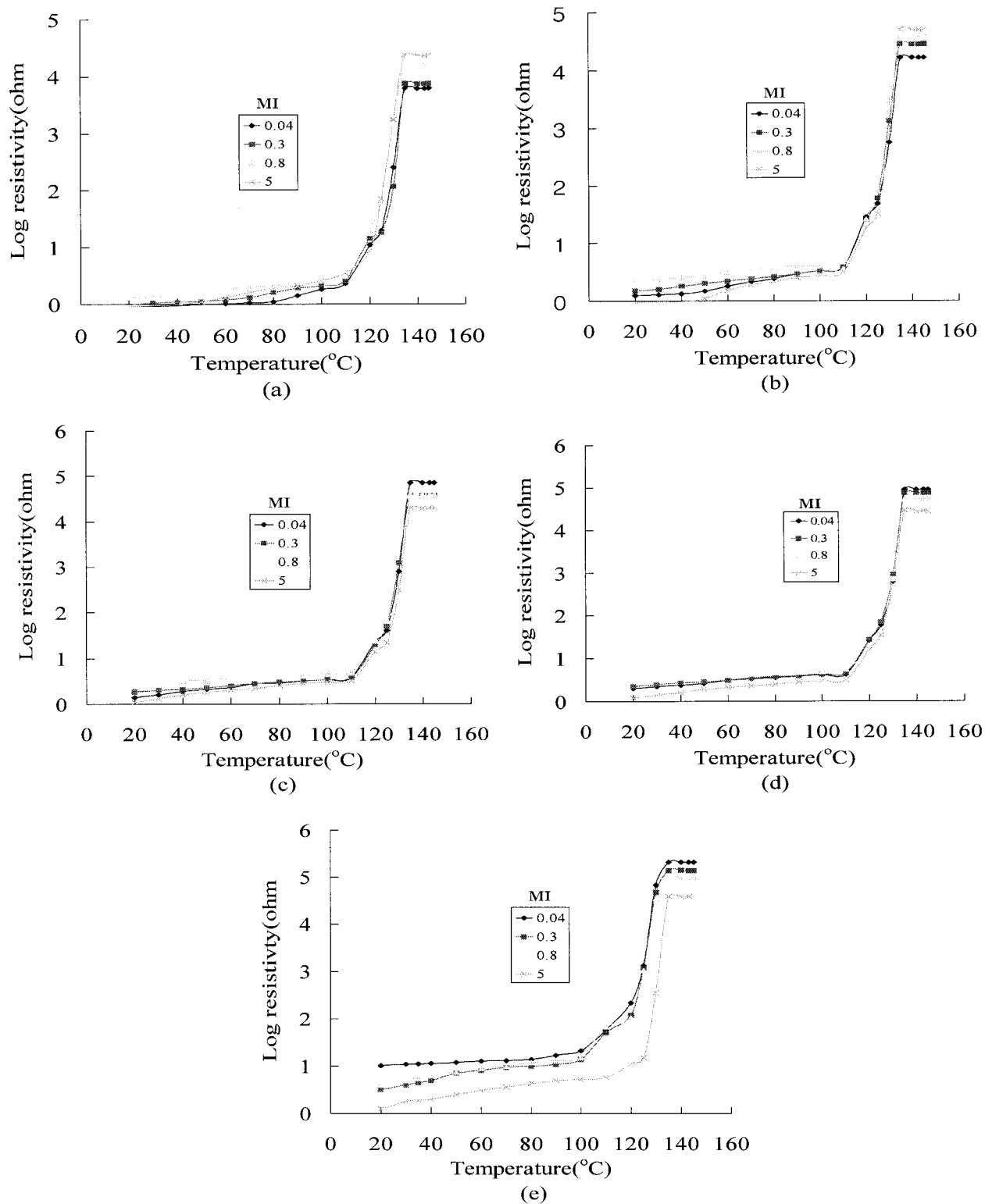
Figure 1 The effect of the melt indices of HDPE on the log resistivity at various mixing times of (a) 6, (b) 12, (c) 18, (d) 24, and (e) 30 min. The carbon black and polymers are mixed at 170°C and 50 rpm.

increases and this makes the movement of CB easy. Therefore, the absorption of polymer on the CB surface is more easily increased in a short blending time as the melt index increases. This absorption forms a bound polymer around the CBs and produces an abnormal increase in the volume resistivity at room temperature and in the PTC. The restraint of flocculation of the CB aggregates by polymer–filler bonding can be explained by another experiment. The PTC effect can be greatly influenced by the mixing time when HDPE and CB were blended for a long time. The mixing times of the samples used in this experiment are 6, 12, 18, 24, and 30 min. As the mixing time of the samples increases, the CB particles are better dispersed. This result is related to the fact that the increased mixing time of the composites leads to the disappearance of the network structure of the CBs. The increment of the bound polymer, which is the physical and chemical absorption of the polymer on the CB surface, makes the room temperature resistivity of the compound increase. This absorption forms a bound polymer around the blacks and it obstructs conduction of the particles. Thus, the room temperature resistivity increases with mixing time when the CB concentration is constant.

The crosslinking structure enhances the electrical reproducibility and declines the NTC effect of the composites. The influences of the γ-rays and EB irradiation dose on the PTC and NTC effects are shown in Figure 2. With an increase of the γ-ray radiation dose the PTC intensity decreased slightly, and the samples have NTC effects at irradiation doses ranging from 0 to 70 kGy. When the EB was used for crosslinking of the HDPE/CB composite, the composites show the NTC effects at irradiation doses ranging from 0 to 30 kGy. This indicates that, although the slightly crosslinked networks of the polymer at a low absorbed dose limit the movement of CB particles to some extent, they cannot completely prevent reagglomeration of CB particles in the vicinity of the melting point. Above 70 kGy the NTC effect is eliminated, illustrating that the crosslinked network is fully formed in this case and thus can effectively stabilize the PTC functions of the material. These results are due to the facts that crosslinking enhances the shear modulus of polymers and CBs are strongly attached to crosslinked HDPE networks. This strong attachment to crosslinked networks reduced the freedom of movement of CB particles at the polymer melting region.
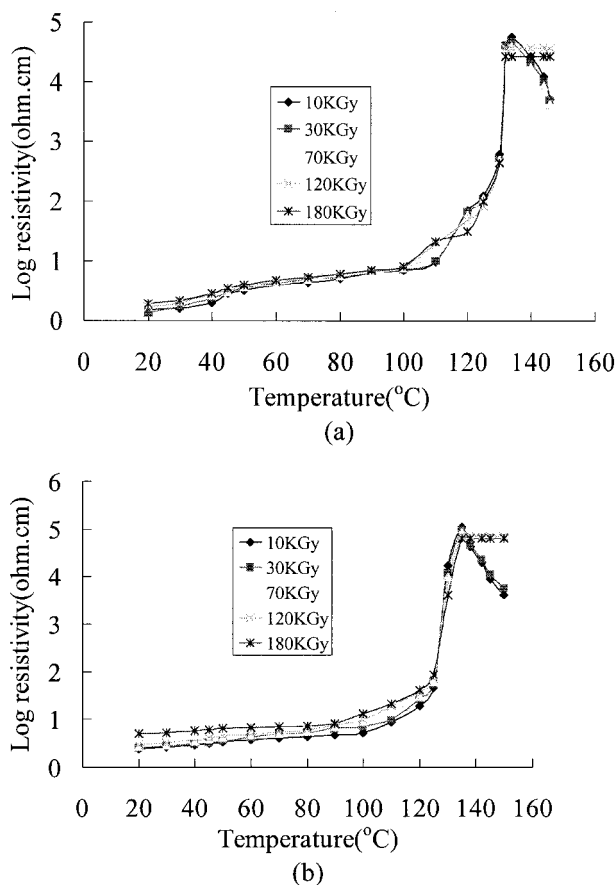
Figure 2   The influence of the irradiation dose on the PTC and NTC effects of the HDPE (melt index = 0.3)/CB blend. The processing conditions are 170°C and 50 rpm for 18 min and with (a) γ rays and (b) EBs.

Figure 3 shows the influence of the γ-ray and EB irradiation doses on the gel content when the HDPE/CB composite with different melt indices was irradiated at 10, 30, 70, 120, and 180 kGy. As can be seen, the degree of gel content increased with increasing γ-ray and EB irradiation doses up to 76 and 84%, respectively. The gel content of the EB irradiated compound was higher than that of the γ-ray irradiated compound. This difference between the γ-ray and EB irradiation effects can be explained by the dose rate effect. The mean dose rate of EB is 1,000–10,000 times higher than γ rays. When the compound is crosslinked with the irradiation source, a shorter time is required to accomplish the radiation modification of the polymers or its composites at a higher dose rate. It is well known that the irradiation of polymeric materials in the presence of air always results in some damage to their structure and properties, because of the radiation induced oxidative degra-

(a)

(b)
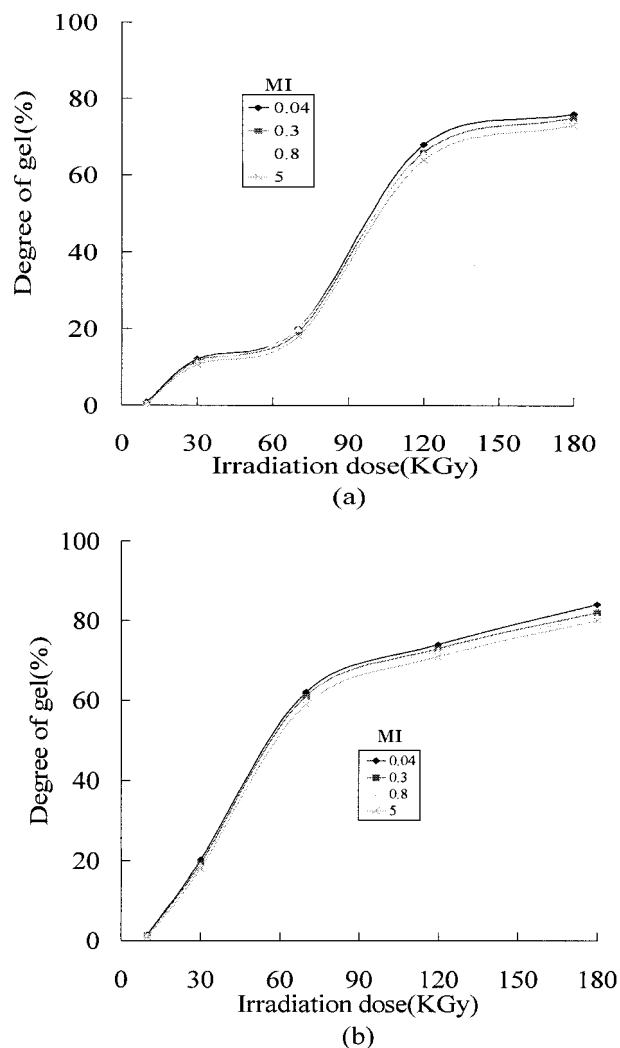
Figure 3 The effect of the irradiation dose on the degree of gel of matrix polymers irradiated with (a) γ rays to a total dose of 10, 30, 70, 120, and 180 kGy and (b) EBs to a total dose of 10, 30, 70, 120, and 180 kGy.

dation effect. It is expected that a higher dose rate and a shorter radiation time will result in a smaller radiation induced oxidative degradation effect on the compound. It is reasonable that the EB irradiated compound eliminated the NTC effect at a low dose while the γ-ray irradiated compound did not. Therefore, γ-radiation induced crosslinked networks of the polymer at a high absorbed dose limit the movement of CB particles. When the compounds irradiated with γ rays and EBs have a total dose above 120 and 70 kGy, respectively, the NTC effect is eliminated and the PTC intensity improves, demonstrating that the crosslinked network is fully formed at this time and thus can effectively stabilize the PTC effects of the composites.

Figure 4 is a plot of the log resistivity of the composites as a function of the thermal aging time in air. It was shown that the room temperature resistivity and PTC anomaly increased with increasing aging time at 140°C, but the PTC begins to fall at around 150 h. Because the presence of oxygen causes thermal aging to occur, a decrease in the PTC anomaly at 250 h can be attributed to the thermal degradation of HDPE in the presence of oxygen. To know the effect of the thermal aging behavior of the composites, a DSC calorimeter was used to study the melting behavior of the 50:50 HDPE/CB composites with various thermal aging times. The thermoanalysis of the samples aged at 140°C was investigated by DSC at a heating rate of 10°C/min, and the re-

(a)

(b)
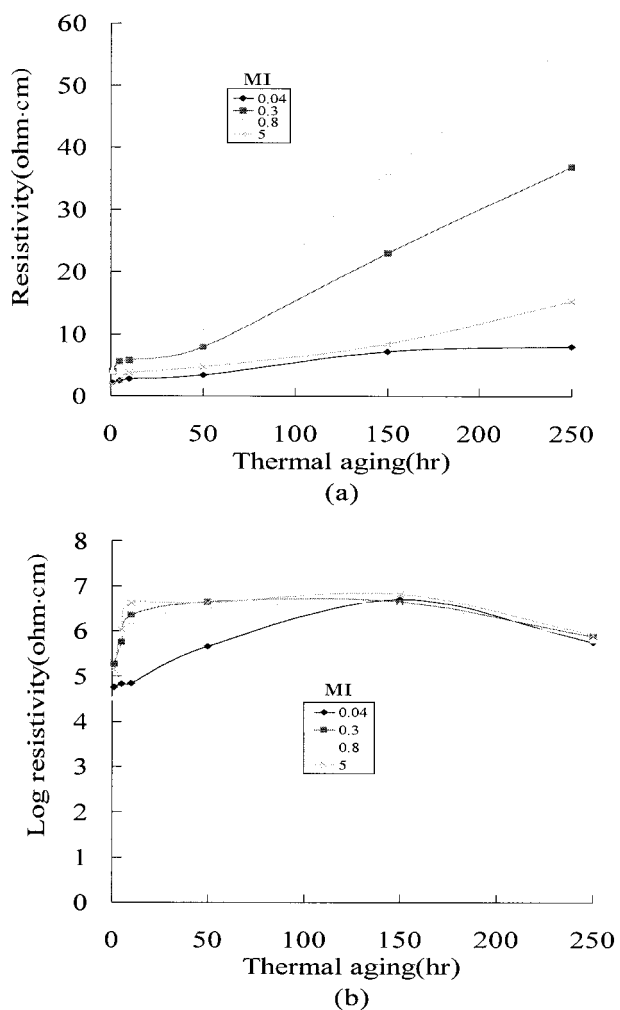
Figure 4 The log resistivity of the composites as a function of the thermal aging time at 140°C: (a) room temperature resistivity and (b) resistivity at maximum (PTC anomaly). The absorbed dose is 120 kGy.

sults are shown in Figure 5. The aging times are 150 and 250 h. The increase in aging time led to a decline of fusion in the DSC curve as shown in Figure 5. Clearly, the fusion peak of the 250-h aged sample was much lower than that of the unaged sample. It was found that the change in the PTC effect during aging is a direct result of the changes in the crystalline structure of the composites during aging. This indicates that there is a loss of crystallites as aging proceeds.
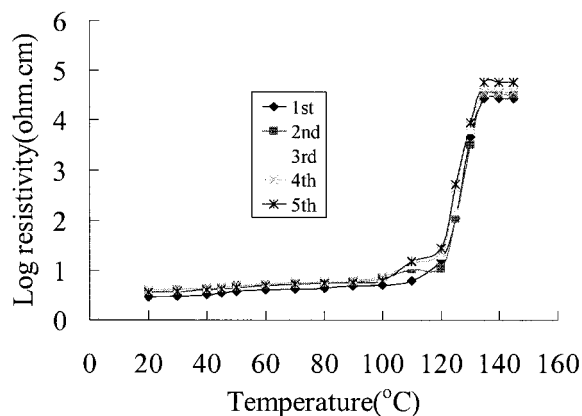
Figure 6 shows that the electrical reproducibility of HDPE (melt index = 0.3)/CB is improved by radiation induced crosslinking compared with the unirradiated compound. These results are because the crosslinking enhances the shear modulus of the polymers and the CBs are strongly attached to crosslinked HDPE networks. This restricting function not only makes the CBs redistribute during the movement and expansion of the matrix at high temperatures but also takes the particles back to their original positions while the sample is cooled. Therefore, the reproducibility was significantly improved and the NTC phenomenon was practically eliminated for the radiation induced crosslinked compound.

CONCLUSIONS

The PTC effect is remarkably improved with an increase of mixing time when the compounds are mixed for a long time during the preparation process. The increment of the bound polymer, which is the physical and chemical absorption of the polymer on the CB surface, makes the room tem-
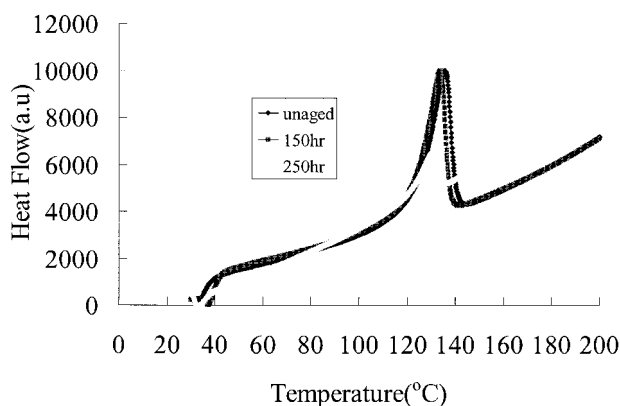
Figure 5 The effect of continuous thermal aging on the DSC curve. The sample is HDPE (melt index = 0.04)/CB composite. The absorbed dose is 120 kGy, and the thermal aging temperature is 140°C.
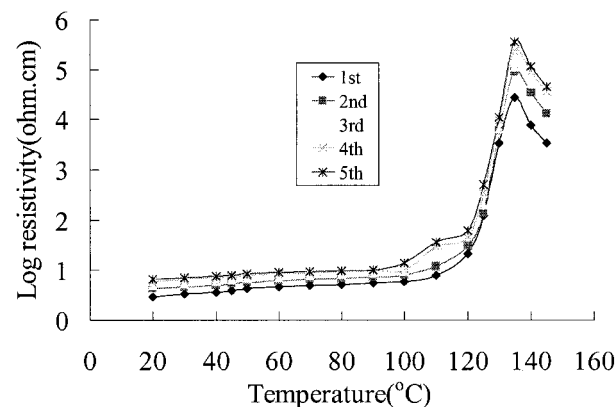
Figure 6 The effect of the radiation dose on the electrical reproducibility of the HDPE (melt index = 0.3)/CB composite (a) irradiated with γ rays to a total dose of 120 kGy and (b) unirradiated.

perature resistivity of the compound increase. Radiation crosslinking significantly improves the reproducibility and makes the NTC effect vanish for CB filled HDPE. When the compounds irradiated with γ rays and EBs have a total dose above 120 and 70 kGy, respectively, the NTC effect is eliminated compared with the low absorbed dose sample. This illustrates that the crosslinked network is fully formed at this time and thus can effectively stabilize the PTC effects of the composites. The electrical reproducibility significantly improves for the radiation induced crosslinked compound.

REFERENCES

1. Meyer, J. Polym Eng Sci 1973, 13, 462.
2. Meyer, J. Polym Eng Sci 1974, 14, 706.

3. Narkis, M.; Ram, A.; Flashner, F. Polym Eng Sci 1978, 18, 649.

4. Voet, A. Rubber Chem Technol 1981, 54, 42.

5. Narkis, M.; Ram, A.; Stein, Z. Polym Eng Sci 1981, 21, 1049.

6. Aneli, D. N.; Topchishvili, G. M. Int Polym Sci Technol 1986, 13, 91.

7. Klason, G.; Kubat, T. J Appl Polym Sci 1978, 22, 163.

8. Newnham, R. E.; Ruschan, G. R. J Am Ceram Soc 1991, 74, 463.

9. Masao, S. Macromolecules 1999, 32, 3534.

10. Kizkpatrick, S. Rev Mod Phys 1973, 45, 574.

11. Sichel, E. K.; Gittleman, I. J.; Sheng, P. Phys Rev B 1978, 18, 5712.

12. Hirano, S.; Kishimoto, A. Appl Phys Lett 1998, 73, 3742.

13. Strumpler, R.; Maidorn, G.; Rhyner, J. J Appl Phys Lett 1997, 81, 6786.

14. Lee, J. C.; Takayuki, I.; Toshio, N. J Appl Polym Sci 1998, 69, 193.

15. Mather, P. J.; Thomas, K. M. J Mater Sci 1997, 32, 1711.

16. Mingyin, Z.; Wentao, J.; Xinfang, C. J Appl Polym Sci 1996, 62, 743.

17. Xiao-Su, Y.; Guozhang, W.; Yi, P. Polym Int 1997, 44, 117.

18. Wentao, J.; Xinfang, C. J Appl Polym Sci 1997, 66, 1885.

19. Hao, T.; Xinfang, C.; Yunxia, L. Eur Polym J 1997, 33, 8.

20. Karasek, L.; Meissner, B. J Mater Sci 1994, 52, 1925.

21. Karasek, L.; Sumita, M. J Mater Sci 1996, 31, 281.