

Positive Temperature Coefficient Behavior of Polymer Composites Having a High Melting Temperature

Jung-il Kim, Phil Hyun Kang, Young Chang Nho

Radiation Application Research Division, Korea Atomic Energy Research Institute, P.O. Box 105, Yusong, Daejeon 305-600, South Korea

Received 5 June 2003; accepted 11 September 2003

ABSTRACT: The positive temperature coefficient (PTC) behavior of polymers having a high melting temperature, such as nylon, polyvinylidene fluoride, polyester, and polyacetal, was investigated. Carbon black and nickel powder were used to investigate the influence of their conductive fillers on PTC intensity. The polymer/filler composite was irradiated with gamma rays at dosages of 50, 100, and 150 kGy for the purpose of reducing the negative temperature coefficient (NTC) of a conductive composite. It was found

that the PTC temperature depended on the melting point of the polymer matrix. The crosslinking structure enhanced the electrical stability and decreased the NTC effect of the composites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 394–401, 2004

Key words: composites; radiation; crosslinking; irradiation; fillers

INTRODUCTION

Polymer resins are excellent electrical insulators. However, they can become conducting composites when blended with some kinds of conductive particles. These conducting polymer composites are used for many applications such as heaters, electrodes, and positive temperature coefficient (PTC) composites.^{1,2}

In recent years, polymer PTC composites have been receiving more attention because of their advantages such as lower resistivity at room temperature, easy fabrication, and lower cost than that of the ceramic composites. Moreover, these composites are used in other applications, such as self-controlled heaters, current limiters, and overcurrent protectors or sensors. The lack of electrical reproducibility and the negative temperature coefficient (NTC) effect are the two main drawbacks for the application of PTC materials.^{3,4}

Although the PTC and NTC phenomena have been studied extensively during the last few decades, there is no satisfactory theory to explain the PTC phenomenon. The explanation based on the tunneling effect is widely accepted. According to this mechanism, electrons pass through the thin gaps between the adjacent conductive particles, aggregates, and agglomerates at a practical magnitude to the electric field. The gap

width dominates the electrical properties rather than the length of the particle chain because the current is an exponential function of the gap width.^{5–10} Lin et al. explained these PTC phenomena with the Links–Nodes–Blobs (L–N–B) model.¹¹

Polymer PTC composites are generally composed of semicrystalline polymers and conductive particles such as carbon black (CB). The switching temperature means the temperature at which the interruption of the conduction path in the composite occurs, and is related to the PTC characteristics. The resistivity at the switching temperature is characterized by the PTC intensity, generally defined as the ratio of the maximum resistivity to the resistivity at room temperature.^{12–15}

In many studies, it has been well established that the PTC behavior of these composites depends not only on the properties of CB such as particle size, aggregate shape, and dispersion state, but also on the characteristics of polymers such as chemical structure, crystallinity, and the processing conditions.^{16–20} A number of studies investigated PTC composites composed of polyethylene and carbon black. However, there have hardly been any studies on PTC composites having a higher switching temperature than the HDPE/CB composites. Accordingly, this study focused on the PTC composites that were prepared from polymers having a higher melting point than that of polyethylene. We investigated PTC behavior when different conductive fillers were dispersed in the polymer resins, and then the composites were irradiated with gamma rays at dosages of 50, 100, and 150 kGy.

Correspondence to: Y. Nho (ycnho@kaeri.re.kr).

Contract grant sponsor: Nuclear R&D Program, Ministry of Science and Technology, Korea.

TABLE I
Characteristics of Matrix Resins

Matrix resin	Traditional name	Density (g/cm ³)	Melting temperature (°C)	Melt index (g/10 min)
Polyamide	Nylon-11	1.026	198	—
Polyamide	Nylon-12	1.010	178	—
Polyvinylidene-fluoride	PVDF	1.74	171	—
Polyacetal	Delrin 100P	1.34	175	1.0
Polyester	Hytrel 5526	1.20	203	7.5

EXPERIMENTAL

Materials and sample preparation

Nylon-11, nylon-12, polyvinylidene fluoride (PVDF), polyesters, and polyacetal resins were used for polymer matrices, and were supplied by the Aldrich Chemical Co. (Milwaukee, WI) and Dupont Co. (Wilmington, DE). Their characteristics are listed in Table I. Two different carbon blacks (Raven 420 and Sevacarb MT) (Raven 420 and Sevacarb MT) (Columbian Chemicals Co., Georgia) and nickel powders (Inco Co., New Jersey) were used as conductive fillers. Their characteristics are listed in Table II. The polymers and conductive filler were mixed in a Brabender plastograph (twin-screw, 60 rpm) at 10°C above the polymer melting temperature for 15 min. The mixtures were sandwiched between a pair of nickel foils (0.04 mm thick), which served as electrodes. The thickness of the sample was approximately 0.5 mm. The composites were then irradiated by γ -ray of ⁶⁰Co up to total doses of 50, 100, and 150 kGy at a dose rate of 10 kGy/h in a nitrogen gas atmosphere.

Physical testing of samples

The composites were placed in an oven to measure the electrical resistivity, and the oven was heated at a heating rate of 3°C/min. The electrical resistivity was measured with a digital multimeter (model 2000; Keithley Instruments, Taunton, MA) and four cables were used for the connection between the sample and the multimeter. A computer system equipped with a GPIB card was used for automatic data acquisition.

A cyclic endurance test of PTC composites was used to investigate electrical reproducibility by applying a

current of 33.3 amps, 60 V for 10 s, followed by a resting period of no current of voltage for 300 s.

WAXD (wide angle x-ray diffraction) measurements were done on a diffractometer (Rigaku D/MAX-2000 X-Ray diffractometer, Japan), using a rotating Cu-anode X-ray source ($\lambda = 0.15406$ nm) operating at 40 kV and 40 mA. The diffractometer was equipped with Soller slits in both the incident and reflected beams. The data were collected in the 2θ range of 1.5–70°, in steps of 0.04° and a scanning rate of 4 s per point. The crystallinity was evaluated for all samples by comparing the area under the diffraction peaks using a computer program called JADE.

The percentage of crosslinking in the irradiated PTC sample was determined by measuring the insoluble content using the extraction method. The samples were extracted with boiling solvents (*m*-cresol, DMF, and heptane) for 24 h, then dried at room temperature for 8 h, and finally dried under a vacuum at 80°C to a constant weight.

RESULTS AND DISCUSSION

PTC behavior according to the polymer matrix of conductive composites

Figure 1 shows the resistivity as a function of temperature for the various polymer composites loaded with 50 wt % of Raven 420 carbon black (afterward CB). For all the polymer/CB composites, the resistivity increased steadily as the temperature was raised, and increased more rapidly near the melting temperature when the polymer crystal started to melt. When the temperature of the composite approached the melting

TABLE II
Characteristics of Conductive Fillers

Conductive powder	Particle size (μ m)	Specific surface area (m ² /g)	Apparent density (g/cc)	Company	Remarks
Carbon Black (Raven 420)	0.086	28	0.75	Columbian Chemical	Furnance type
Carbon Black (Sevacarb MT)	0.30	7.0	0.41	Columbian Chemical	Furnance type
Nickel (255)	2.2–2.8	0.7	0.4	Inco	Filamentary type

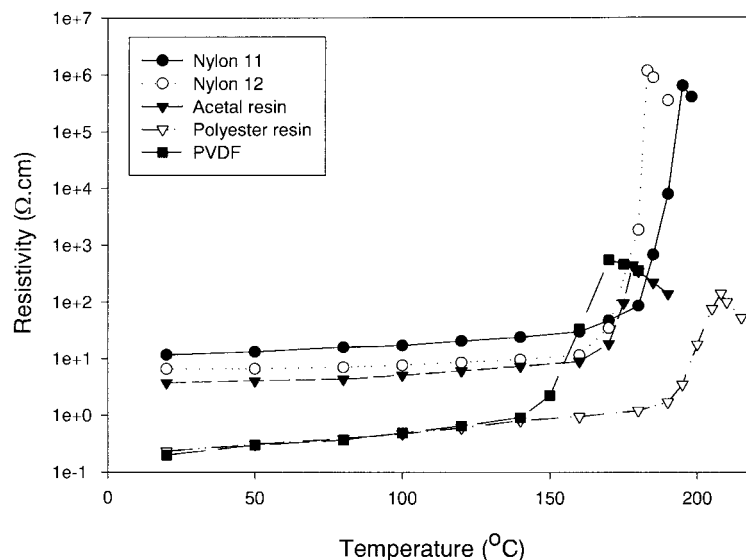


Figure 1 Resistivity of various resins/carbon black (50/50 wt %) composites as a function of temperature.

point of polymer resins, the conduction paths formed by the CB interface were damaged because of the partial melting of the polymer crystallites; thus the resistivity of the composites increased drastically. The resistivity reached a peak value above the melting temperature, and then decreased with a further increase in temperature, which is called the NTC effect. There was a steep increase in the resistivity near the melting point of each polymer. The nylon-12 composite had the largest PTC intensity of about 2.0×10^5 , although the polyacetal and polyester composites had small PTC intensities. These various PTC intensities were attributed to the difference of crystallinity in the polymer matrix. The larger the crystallinity of the

polymer matrix is, the larger the expansion of the polymer becomes when the polymer crystal starts to melt; that is, the conduction path in the composite was effectively interrupted.¹²⁻¹⁴ In these experiments, the crystallinities of the used polymers were measured by X-ray diffractometer at room temperature as shown in Figure 2. As can be seen, the specific crystal peaks of polymer were observed and then were computed. The degrees of crystallinity of the polymer matrices were 48.06% (nylon-11), 48.30% (nylon-12), 38.62% (polyacetal resin), 36.26% (polyester resin), and 40.91% (PVDF), respectively. From these data, it was confirmed that the PTC intensity was proportional to the crystallinity of polymer.

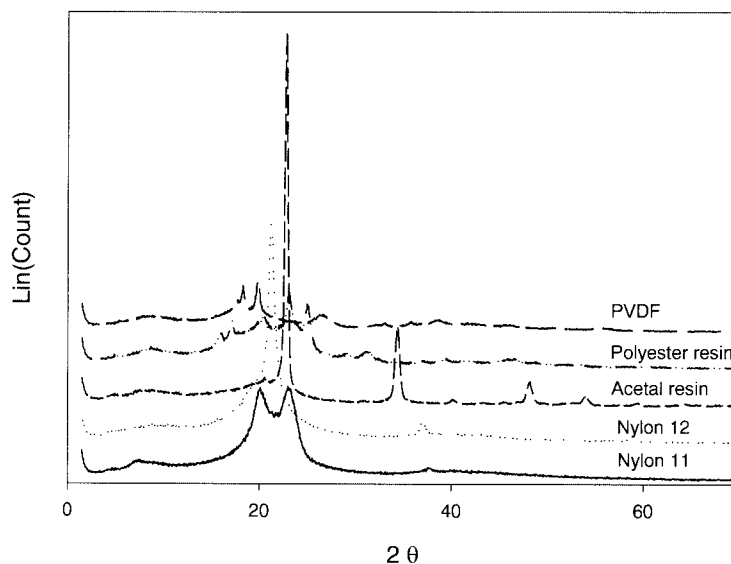


Figure 2 X-ray diffraction patterns of various polymers.

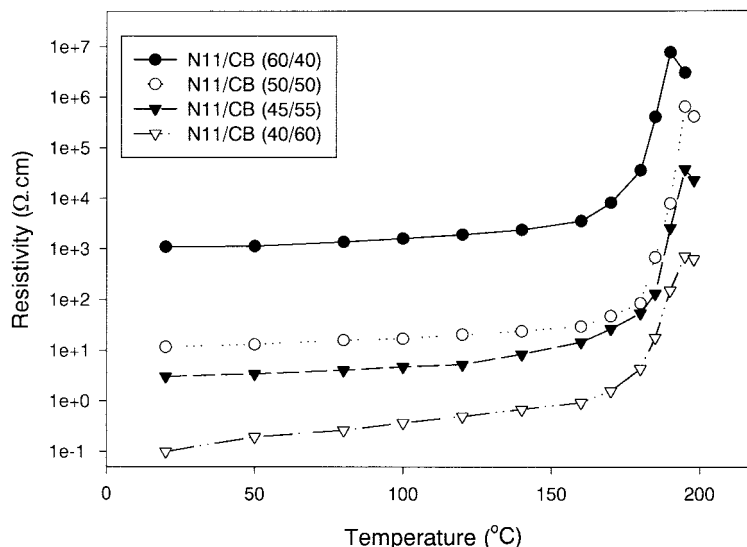


Figure 3 Resistivity as a function of temperature for the nylon-11/carbon black (CB) composites containing various CB wt % concentrations.

Figures 3 and 4 show the influence of carbon black contents on the resistivity. As shown in these figures, the room-temperature resistivity decreased as the CB contents in the composites increased. The composites had a high PTC intensity at about 50 wt % content of the CB. As the CB contents were further increased, the PTC intensity lessened with the NTC effect contracting. When the CB contents of conductive composites reached about 60 wt %, the NTC behavior disappeared. In this case, it is supposed that the flow of polymer is limited because of an extreme loading of the CB.

The typical result for the influence of γ -ray irradiation dose on PTC behavior is shown in Figure 5.

Room-temperature resistivity and PTC intensity increased steadily with the irradiation dose. The composites showed NTC behavior for nonirradiation, whereas the NTC behavior of the composites was eliminated at an irradiation dose above 50 kGy. These results are attributed to the fact that the CB becomes trapped in the crosslinked polymer matrix as a result of irradiation. This strong trapping, binding, and attachment by the crosslinked polymer matrix reduces the freedom of movement of the CB particles at all temperature ranges, especially at and above the polymer melting temperature.²¹

Figure 6 shows the influence of γ -ray irradiation dose on the gel content, when the composites were

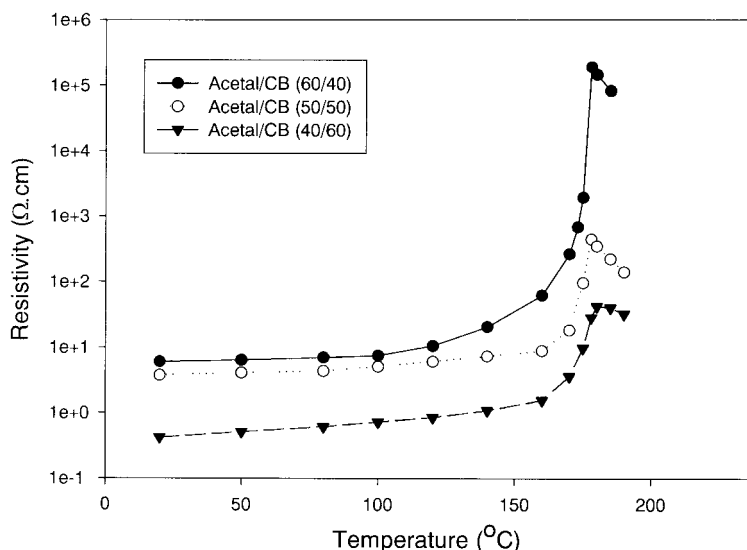


Figure 4 Resistivity as a function of temperature for polyacetal/carbon black (CB) composites containing various CB wt % concentrations.

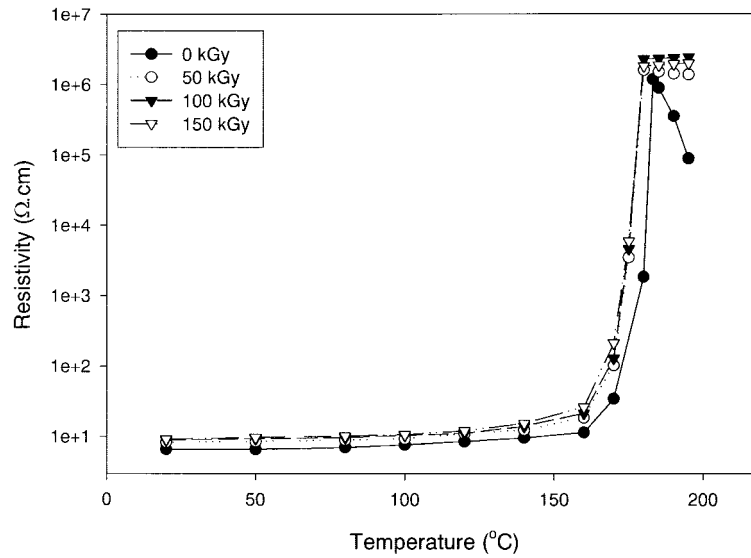


Figure 5 Resistivity as a function of temperature for nylon-12/carbon black (50/50 wt %) composites irradiated with 0, 50, 100, and 150 kGy.

irradiated at 0, 50, 100 and 150 kGy. The degree of gel content increased with increasing the γ -ray irradiation dose. It is apparent that the polymer matrix is crosslinked by irradiation and CBs become trapped in the crosslinked polymer matrix. The gel content of the PVDF composite was higher than that of the other composites, and that of the polyester composite was the lowest.

Influence of conductive fillers on PTC behavior

Mixtures of dispersed conductive carbon fillers in a polymer matrix show electrical resistivities ranging from insulators to semiconductors. The electrical con-

ductivity of such mixtures depends on the specific types of fillers such as particle sizes, structure, and surface chemistry. In this work, two CBs of different particle size and metallic nickel powder were used as conductive fillers, as shown in Table II. Figure 7 shows the resistivity as a function of temperature for nylon-12 composites loaded with the same 40% volume of conductive fillers. The nylon-12/Raven 420 CB composite indicated a lower room-temperature resistivity than that of the nylon-12/Sevacarb-MT CB composites. This is because the Raven 420 CB powder, which has a small particle size, more easily forms a conductive pathway. It is considered that room-temperature resistivity is affected by the size of the con-

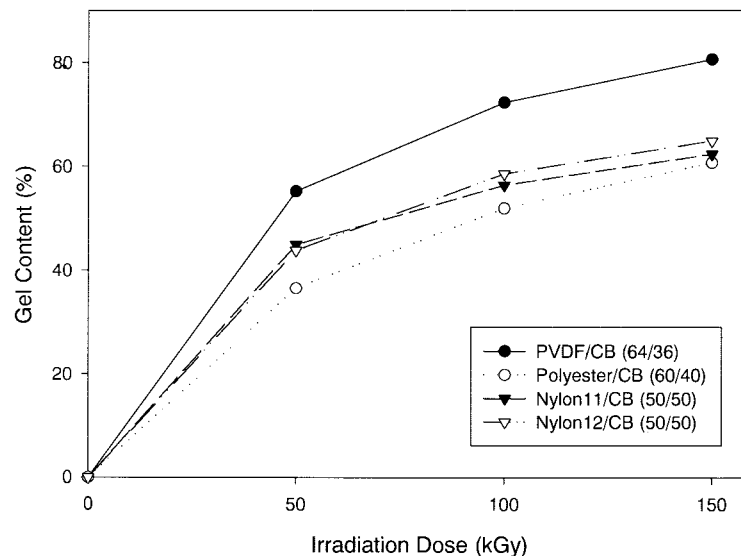


Figure 6 Gel contents as a function of irradiation dose for carbon black-filled composites.

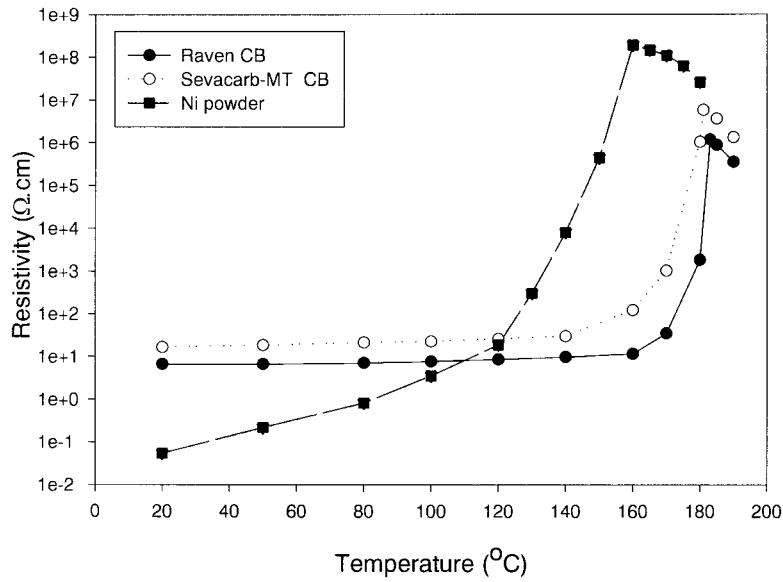


Figure 7 Resistivity as a function of temperature for nylon-12 composites involving various conductive fillers.

ductive filler as well as the kinds of conductive particles. On the other hand, the nickel powder composite indicated the lowest room-temperature resistivity and the highest PTC intensity. Moreover, the resistivity of nickel composite increased rapidly with increasing temperature, and its switching temperature was lower than that of carbon black composites. The influence of the content of nickel powder on the resistivity is depicted in Figure 8, which shows that the room-temperature resistivity of the composites was increased and the switching temperature was decreased as the nickel powder contents decreased. Furthermore, the resistivity was increased steadily as the temperature

was increased from room temperature to 100°C, and it decreased suddenly above the melting temperature.

Figure 9 shows the influence of γ -ray irradiation dose on PTC/NTC behaviors of nickel powder/nylon-12 composites. As shown in Figure 9, the NTC behavior was reduced above the 50-kGy radiation dose. These results are attributable to the crosslinking of nylon-12 by irradiation.

A cyclic endurance test of the PTC composites was used to investigate electrical reproducibility by applying a current of 33.3 amps, 60 V for 10 s, followed by a resting period of no current of voltage for 300 s. Figure 10 shows the results of the cyclic electrical

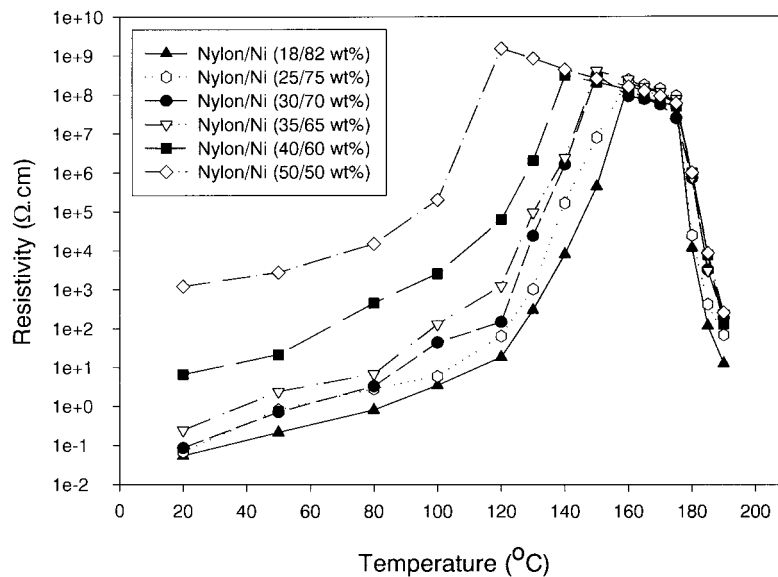


Figure 8 Resistivity as a function of temperature for nylon-12/Ni composites.

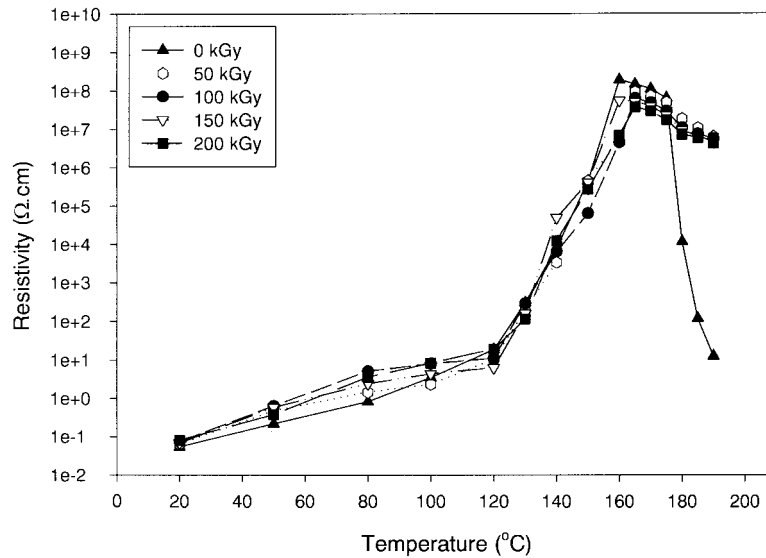


Figure 9 Resistivity as a function of temperature for nylon-12/Ni composites (18/82 wt %) irradiated with 0, 50, 100, 150, and 200 kGy.

stability test of the PTC composites. The room-temperature resistivity of the PTC composites irradiated by γ -ray was more stable than the unirradiated composites, and the CB composites had a more stable room-temperature resistivity than the nickel powder composites. It was supposed that the electrical stability was significantly improved by the crosslinking induced by γ -ray irradiation, with the CB having a better electrical stability than that of the nickel powder.

CONCLUSIONS

We investigated PTC behavior when different conductive fillers were dispersed in various polymer resins,

and then the composites were irradiated with gamma rays at dosages of 50, 100, and 150 kGy. These various PTC intensities had a close relation with the crystallinities of the polymer matrices. In the same kinds of carbon black, the composites loaded with a large particle size of carbon black exhibited a high room-temperature resistivity and large PTC intensity. Nickel powder composites showed the lowest room-temperature resistivity and the highest PTC intensity. The PTC temperature of nickel powder composites was decreased as the nickel powder contents decreased. As the composites were irradiated with γ -ray, the NTC behavior disappeared and the electrical stability was significantly improved.

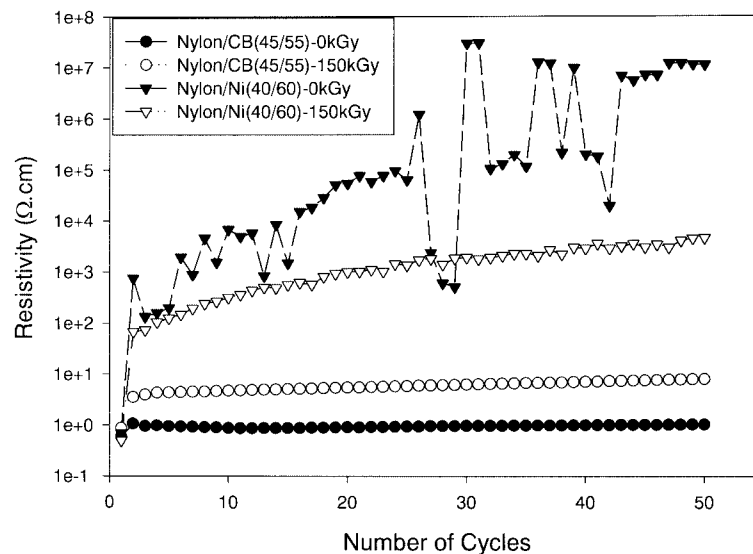


Figure 10 Resistivity as a function of the repeated cycles of overcurrent for nylon-12/CB composites.

This work was supported by the Nuclear R&D Program from the Ministry of Science and Technology, Korea.

References

1. Meyer, J. *Polym Eng Sci* 1973, 13, 462.
2. Tang, H.; Chen, X.; Luo, Y. *Eur Polym Mater* 1996, 32, 963.
3. He, X.; Wang, L.; Chen, X. *J Appl Phys* 2001, 80, 1571.
4. Kohler, F. U.S. Pat. 3,243,753, 1966.
5. Tang, H.; Piao, J.; Chen, X.; Luo, Y.; Li, S. *J Appl Polym Sci* 1993, 48, 1795.
6. Ohe, K.; Naito, Y. *Jpn J Appl Phys* 1971, 10, 99.
7. Narkis, M.; Ram, A.; Flashner, F. *J Appl Polym Sci* 1978, 22, 163.
8. Narkis, M.; Ram, A.; Stein, Z. *J Appl Polym Sci* 1980, 25, 1515.
9. Sumita, M.; Abe, H.; Kayaki, H.; Miyasaka, K. *J Macromol Sci B* 1986, 25, 171.
10. Sumita, M.; Sakata, K.; Asai, S.; Miyasaka, K.; Nakagawa, H. *Polym Bull* 1991, 25, 265.
11. Lin, C. R.; Chen, Y. C.; Chang, C. Y. *Macromol Theory Simul* 2001, 10, 219.
12. Jia, W.; Chen, X. *J Appl Polym Sci* 1994, 54, 1219.
13. Yang, G.; Teng, R.; Xiao, P. *Polym Compos* 1997, 18, 477.
14. Yang, G. *Polym Compos* 1997, 18, 484.
15. Chan, C. M.; Cheng, C. L.; Yuen, M. F. *Polym Eng Sci* 1997, 37, 1127.
16. Lee, J. C.; Nakajima, K.; Ikehara, T.; Nishi, T. *J Appl Polym Sci* 1997, 65, 409.
17. Narkis, M.; Ram, A.; Flashner, F. *Polym Eng Sci* 1984, 29, 1639.
18. Aneil, D. N.; Topchishvili, G. M. *Int Polym Sci Technol* 1986, 13, T/91.
19. Kim, J. I.; Kang, P. H.; Nho, Y. C. *J Ind Eng Chem* 2002, 8, 380.
20. Narkis, M.; Ram, A.; Stein, Z. *Polym Eng Sci* 1981, 21, 1049.
21. Lee, M. G.; Nho, Y. C. *Radiat Phys Chem* 2001, 61, 75.