

Effects of Thermal Ageing Treatment and Antioxidants on the Positive Temperature Coefficient Characteristics of Carbon Black/Polyethylene Conductive Composites

Jong Seok Park,² Phil Hyun Kang,¹ Young Chang Nho,¹ Dong Hack Suh²

¹Radioisotopes/Radiation Application Team, Korea Atomic Energy Research Institute, Daejeon 305-600, South Korea

²Department of Industrial Chemistry, Hanyang University, Haengdang-1-Dong, Seongdong-Ku, Seoul 133-791, South Korea

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ABSTRACT: 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) or negative temperature coefficient (NTC). The CB-filled semicrystalline polymer composites ideally need antioxidants, which stabilize the composites against thermooxidative degradation, because they should be resistant to the severe conditions of high temperature. The characterization of PTC materials is affected by the crystallinity of the polymer, and the crystallinity of the polymer is changed with thermal ageing treatment. Thermal ageing of PTC samples was conducted in an oven in the range 50–140°C, in air. The composites, containing 0.5–3%

(by weight) Irganox 1076 (Ciba-Geigy), were irradiated under nitrogen at room temperature with different doses of gamma rays from a ⁶⁰Co source. The resulting composites were analyzed by differential scanning calorimetry, gel fractionation, X-ray diffraction, and dynamic mechanical analysis. The conductivity of the composites depended on the amounts of antioxidants and the duration of the thermal ageing treatment. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2316–2322, 2003

Key words: polyethylene (PE); composites; crosslinking; antioxidants; thermal properties; ageing

INTRODUCTION

The positive temperature coefficient (PTC) phenomenon of carbon black (CB)-filled polymers has been of interest for a number of years. The sudden increase in resistivity of these polymers with temperature is explained by the PTC. In general, it has been well accepted that the strong PTC effect of CB-filled semicrystalline polymer composites is caused by an increase in the average interparticle or aggregate distance of CB, which is created by the large thermal expansion that occurs as a result of the melting of the polymer crystals.^{1–4} In contrast, the resistivity decrease is explained by the negative temperature coefficient (NTC). It has been suggested the NTC effect of CB-filled semicrystalline polymer composites is caused by the formation of a flocculated structure when the viscosity of the polymer is sufficiently low at elevated temperature,^{5–7} but the NTC effect of CB-filled polymer composites has not been elucidated in detail.

PTC materials are being put to good use in a number of applications, such as a self-controlled component of temperature or heat.⁸ The lack of electrical reproducibility and the NTC effect are two main drawbacks to the application of PTC materials. The

switching temperature and the resistivity increase at the switching temperature (switching effect) need to be understood for the successful design of materials for useful products. The switching temperature is the temperature at which the interruption of the conduction of the path in the composite takes place and is related to the PTC characteristics. The switching effect is characterized by the PTC intensity and is generally defined as the ratio of the resistivity at the switching temperature to that at room temperature.^{9,10} The NTC effect is, thus, presumably caused by movement in the molten polymer and the formation of a new distribution of better uniformity and conductivity. Crosslinking has been proven to be an effective way to significantly reduce the freedom of movement of CB particles at high temperature,¹⁰ and irradiation produces crosslinking.¹¹ According to the principles of radiation chemistry, the polymer will be excited under irradiation, and then active species (e.g., cations, anions, or radicals) can be generated from the excited polymer. In this way, the properties of the irradiated materials can be changed.¹² The structure of the conductive composites, particularly that of CB-filled polymer composites,^{13,14} is affected by thermal ageing treatment. Enhancing the reproducibility of the structures of CB-filled semicrystalline polymer composites is one of the main problems in the development as PTC materials. The composites probably need antioxidants,

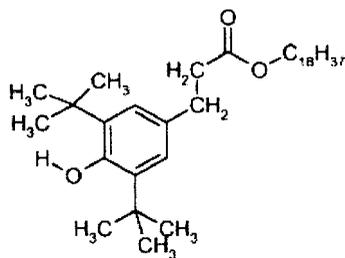


Figure 1 Structure of Irganox 1076R.

which stabilize the composites against thermal oxidative degradation, because they should be resistant to the severe conditions of high temperature. As thermal oxidative degradation proceeds, the amount of the degraded products increases and the crystallinity of the polymer decreases, resulting in a decline in the performance of the PTC materials.^{15,16} In this paper, we report the findings of our study on the effect of the thermal ageing and an antioxidant on the electrical properties of CB-filled semicrystalline polymer composites. The effects of γ -ray irradiation on the elastic modulus, crystallinity, and crosslinking percent were also examined.

EXPERIMENTAL

Sample preparation

A commercial grade of high-density polyethylene (HDPE; Hivorex 5200B) was used throughout this study and was supplied by Honam Petrochemical Corporation (, Korea). HDPE has a density of 0.963 g/cm³ and a melting index of 0.35 g/10 min. The CB (RavenTM420, Columbian Chemicals,) has an average size of 86 nm and a surface area of 28 m²/g. The antioxidant Irganox 1076 was purchased from Ciba-Geigy (). The structural formula of Irganox 1076 [octadecyl-3-(3,5-diterbutyl-4-hydroxyphenyl)-propionate] is shown in Figure 1. The ratio of CB in all composite samples was the equivalent of 50 wt %. The HDPE, CB, and antioxidants were mixed in a Brabender Plastograph at 160°C for 15 min. The composition thus produced was sandwiched between a pair of copper foils (0.04 mm thick; Fukuda Metal Foil & Powder Company, Ltd.,), which served as electrode. The thickness of the sample was \sim 0.5 mm. Thermal ageing treatment of PTC samples was conducted in an oven at 50–140°C for 480 h in air.

Measurements of the samples

The electrical resistivity was measured with a digital multimeter (model 2000, Keithley Instruments,), and four cables were used for connection between the sample and the multimeter. A computer system equipped with a GPIB card was used for automatic

data acquisition. The resistance of the specimen was read for each temperature point at the end of each step.

The crystal melting temperature of HDPE was measured by differential scanning calorimetry (DSC; DSC-7 Series Thermal Analysis System, Perkin Elmer,). Heating runs were conducted from 30 to 180°C at a rate of 10°C/min in nitrogen. The weight of the sample was \sim 3 mg. The heat of fusion was obtained by integrating the area under the endothermic peak.

X-ray diffractometry (XRD; D-MAX-III B X-ray diffractometer, Rigaku) in the range $2\theta = 5\text{--}30^\circ$, was used for analysis of the crystallinity of HDPE. The dynamic-mechanical properties were investigated with a dynamic-mechanical analyzer (DMA; DMA 2980, TA Instrument Company). The samples were measured from -150 to 150°C at 1 Hz at a heating rate of 5°C/min. The crosslinking percent of PTC sample was determined by measuring the insoluble content by the solvent extraction method. The samples were extracted with boiling xylene for 24 h and then dried under a vacuum at 80°C to a constant weight.

RESULTS AND DISCUSSION

Radiation effects of CB-filled semicrystalline polymer composites

The mechanism for eliminating the NTC effect is not yet fully understood. However, the absence of the NTC effect in CB-filled semicrystalline polymer composites is related to the crosslinking of the polymer. There already exist several references reporting either irradiation crosslinking at room temperature in air or peroxide chemical crosslinking in a molding operation.^{5,7,12} The influence of irradiation appears as crosslinking and degradation as well as a change in elastic modulus of the polymer. The resistivity of HDPE (50 wt %)/CB(50 wt %) composites as a func-

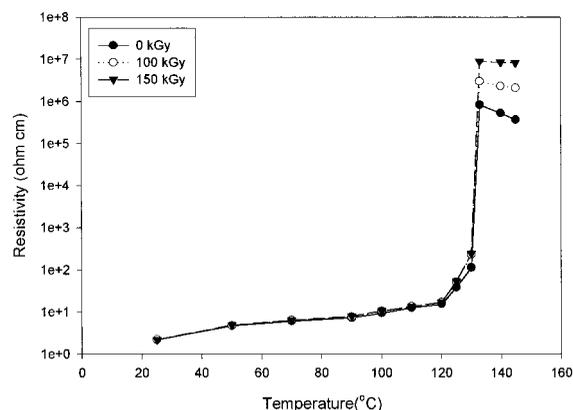


Figure 2 The resistivity of HDPE/CB(50/50 wt %) composites as a function of temperature with increasing irradiation dose.

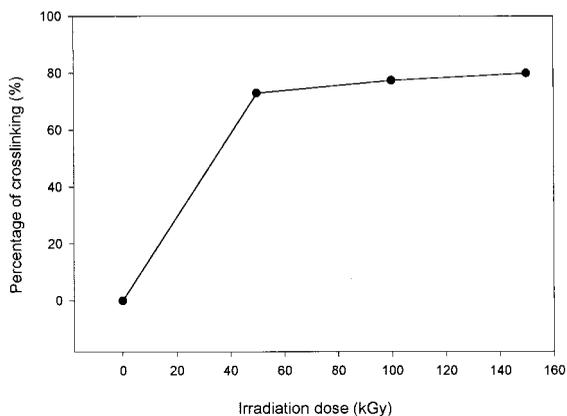


Figure 3 The percentage of crosslinking of HDPE/CB (50/50 wt %) composites relative to absorbed dose.

tion of temperature with increasing γ -ray radiation dose is shown in Figure 2. The PTC intensity increased slightly and the NTC effect was almost eliminated in the irradiated samples, whereas NTC behavior was still present in the non-irradiated samples.

The percentage of crosslinking in the irradiated HDPE/CB samples, determined by measuring the in-

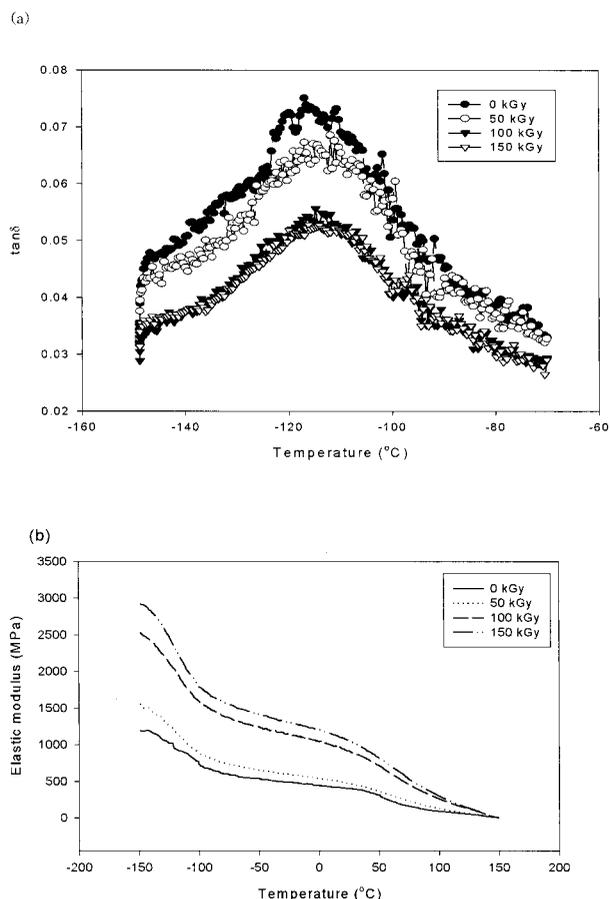


Figure 4 Comparison of (a) $\tan \delta$ and (b) elastic modulus (E') of HDPE/CB (50/50 wt %) composites with increasing irradiation dose.

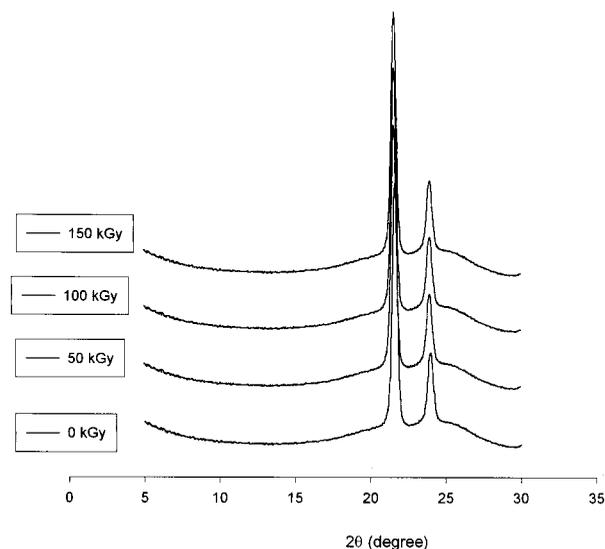


Figure 5 The XRD analysis of HDPE/CB (50/50 wt %) composites with increasing irradiation dose.

soluble content by the solvent extraction method, is shown in Figure 3. The percentage of crosslinking in the polymer increased with the irradiation dose up to 150 kGy. It can be seen that the γ -rays induce a crosslinking of the polymer and that the NTC effects are eliminated with increasing the crosslinking of the polymer.

The temperature dependence of the loss factor ($\tan \delta$) and elastic modulus (E') of the control and irradiated samples are shown in Figure 4. Non-irradiated HDPE/CB composites exhibited the highest $\tan \delta$ in this study. Following γ -ray irradiation, there was an increase in the elastic modulus of the composites, and relaxation was observed near -120°C . These results are due to crankshaft movement of methyl groups in the main chain of the polymer.^{12,17} The decrease in the $\tan \delta$ and increase in E' of the HDPE/CB composites with increasing irradiation dose are due to the crosslinking of the polymer. Indeed, a decrease in molecular mobility is a characteristic that is associated with the crosslinking of the material caused by γ -ray radiation. These results prove that high doses of irradiation induce further crosslinking of the materials (Figures 2–4).

The XRD patterns of the HDPE/CB composites according to irradiation dose are shown in Figure 5. No changes of crystalline peaks were observed in irradiated samples (50, 100, and 150 kGy) compared with those in the non-irradiated sample. These XRD results indicate that the crystallinity of the polymer was little affected by the crosslinking induced by γ -ray irradiation. Perhaps the crosslinked portion of the irradiated polymer occurred mainly in the amorphous phase rather than in the crystalline phase. The results show that irradiation mainly increased the percentage of

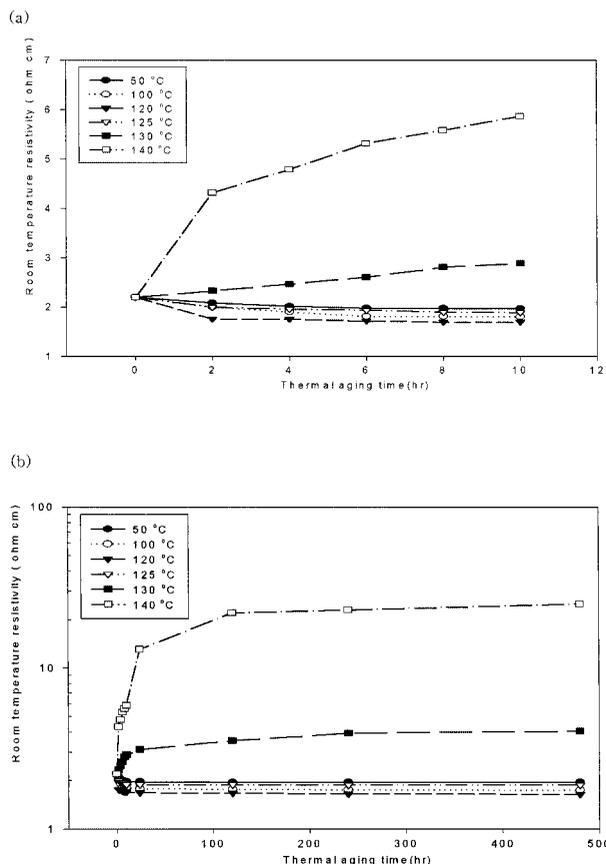


Figure 6 Room temperature resistivity of HDPE/CB (50/50 wt %) composites irradiated at 150 kGy according to increasing time for (a)10 h and (b) 480 h at different thermal ageing temperatures.

crosslinking of the polymer rather than degradation (Figures 2–5).

Effect of thermal ageing treatment on crystallinity of the conductive composites

The room temperature resistivity of HDPE/CB composites with increasing thermal ageing time (10 and 480 h) at different thermal ageing temperatures is shown in Figure 6. The conductive composites were thermally aged in an oven from 50 to 140°C in air. The room temperature resistivity of the conductive composites decreased slightly between 50 and 125°C. In particular, the sample exposed to thermal ageing treatment at 120°C had the lowest resistivity. However, the resistivity started to increase steadily at 130°C and drastically increased at temperatures >140°C with increasing thermal ageing time.

The resistivity of the composite irradiated at 150 kGy as a function of temperature is shown in Figure 7. The resistivity increased steadily as the temperature was raised from 25 to 120°C, as the polymer crystal started to melt. When the temperature approached the melting point of HDPE, the resistivity of the compos-

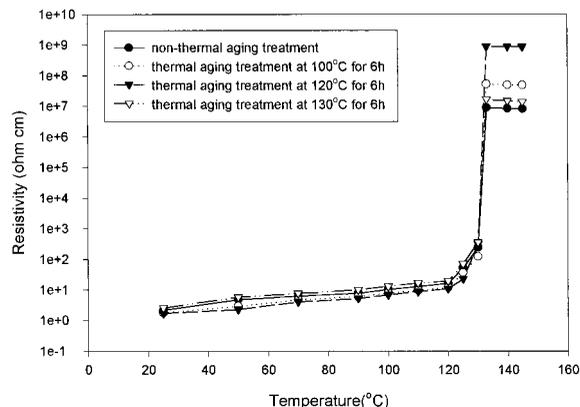


Figure 7 Resistivity of HDPE/CB (50/50 wt %) composites irradiated at 150 kGy as a function of temperature according to different thermal ageing temperatures.

ite drastically increased and reached a peak value at ~133°. The HDPE/CB composite that was thermally aged at 120°C for 6 h and irradiated at 150 kGy had the lowest room temperature resistivity and the highest PTC intensity. The HDPE/CB composite with thermal ageing treatment at 100°C for 6 h and irradiation treatment at 150 kGy exhibit lower room temperature resistivity and higher PTC intensity than similar composites that were not thermally aged. The PTC intensities increased with increasing thermal ageing temperature but decreased at 130°C.

DSC and XRD methods were used to analyze this thermal ageing effect on the composites irradiated at 150 kGy. The XRD patterns of composites irradiated at 150 kGy are plotted according to thermal ageing temperature in Figure 8. These results indicate that the crystallinity of polymer was affected by thermal ageing temperature: the crystallinity of polymer increased with thermal ageing treatment

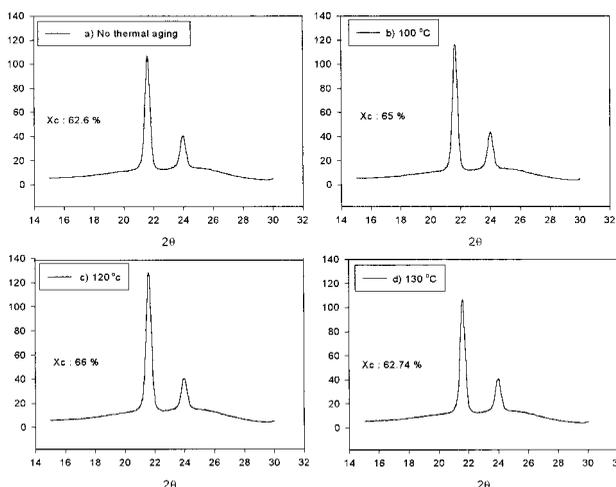


Figure 8 XRD peaks of HDPE/CB (50/50 wt %) composites irradiated at 150 kGy according to different thermal ageing temperatures for 6 h.

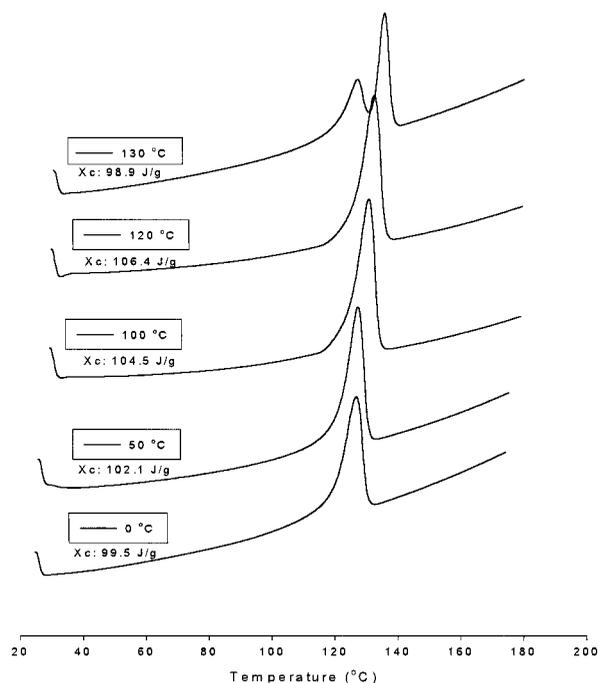


Figure 9 DSC curves of HDPE/CB (50/50 wt %) composites irradiated at 150 kGy according to increasing thermal ageing temperatures for 6 h.

up to 120°C, reached a peak of crystallinity at 120°C, and decreased at 130°C. The DSC curves of the HDPE/CB composite irradiated at 150 kGy according to thermal ageing temperature, shown in Figure 9, show the same the result as did the data in Figure 8; that is, the melting enthalpy of polymer increased with thermal ageing treatment up to 120°C, reached a peak with thermal ageing treatment at 120°C, and decreased with thermal ageing treatment around the melting point of the polymer at 130°C. The room temperature resistivity and PTC intensity were affected by the crystallinity of the polymer (Figures 6–9). The crystallinity of the polymer increased with thermal ageing treatment below the melting point of the polymer but decreased with thermal ageing treatment above the melting point of the polymer. The polymer had the highest crystallinity and melting enthalpy with thermal ageing treatment at 120°C. The CB particles are randomly dispersed in the amorphous phase of the polymer.⁷ The amorphous phase of the polymer decreases according to increasing the crystalline phase of the polymer. Therefore, the gap of CB particles in the amorphous phase of the polymer became narrower, it was easier for the composites to form a conductive pathway, and the room temperature resistivity of the composites decreased. When the conductive composites were thermally aged above the melting point of the polymer, the crystallinity of polymer decreased because of the severe degradation of the polymer by

oxygen at the high temperature.¹⁵ The PTC intensity is also affected by the crystallinity of the polymer. With the thermal expansion that results from the melting of the polymer crystals, the gap of CB particles in its polymer matrix drastically broadens and the resistivity of the conductive composites rapidly increases.¹⁸ Therefore, the PTC intensity of conductive composites becomes higher as the crystallinity increases

Reproducibility of the conductive composites

Enhancement of the reproducibility of the conductive composites is one of the important things in the development as PTC materials.¹⁴ Ideally, the composites should be stabilized against thermooxidative degradation by antioxidants because antioxidants can withstand the severe conditions of high temperature. In this work, we used Irganox 1076 (Ciba-Geigy) as a phenolic-type antioxidant. The reproducibility of the room temperature resistivity of the conductive composites containing Irganox 1076 is shown in Figure 10. The resistivity was measured after samples were heated from 25 to 145°C at a rate of 2°/min and steadily cooled up to 25°C in air. The composite without antioxidant had the highest resistivity at room temperature after one cycle. The resistivity at room temperature decreased with increasing amounts of antioxidant, but the composites had almost the same resistivity values following the addition of >1 wt % antioxidant. The resistivity of the composites did not increase further after two cycles.

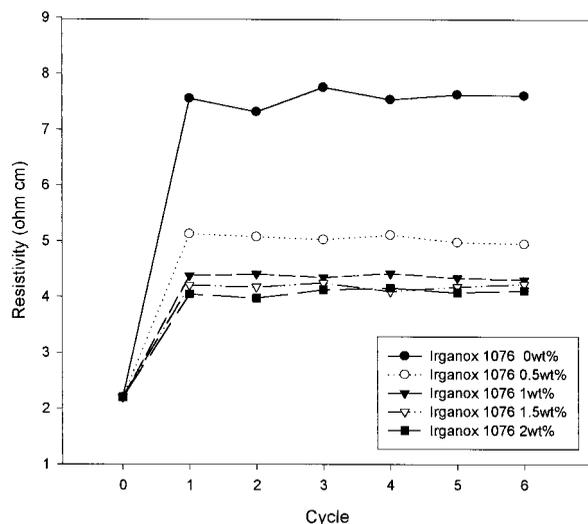


Figure 10 Reproducibility of the room temperature resistivity of the irradiated conductive HDPE/CB composites with increasing amounts of Irganox 1076 (amount of CB is always 50 wt %).

The percentage of crosslinking of the conductive composites versus amount of antioxidant is shown in Figure 11. The percentage of crosslinking in the polymer decreased with increasing amounts of antioxidant. The percentage of crosslinking of the composite containing 0.5 wt % antioxidant was slightly smaller than that of the composites without antioxidant. As shown in Figure 12, the peak resistivity of the composite containing antioxidant decreased and NTC behavior appeared with increasing amounts of antioxidant. However, the peak resistivity and the percentage of crosslinking of the composite containing 0.5 wt % antioxidant had almost the same values as the composites without antioxidant. It can be seen that the peak resistivity of the conductive HDPE/CB composites is proportional to the percentage of the crosslinking of the polymer (Figures 11 and 12). The reproducibility of the composites was improved by the addition of antioxidant, but the percentage of crosslinking and the peak resistivity of the conductive composite were decreased. Finally, the percentage of crosslinking and the peak resistivity of the composite containing 0.5 wt % antioxidant were almost unaffected.

CONCLUSIONS

The effects of irradiation, thermal ageing, and antioxidant on the PTC characteristics of conductive HDPE/CB composites were investigated. The percentage of crosslinking of the conductive HDPE/CB composites was increased with increasing doses of γ -rays irradiation, and the crystallinity of the polymer was almost unaffected by γ -ray irradiation. The room temperature resistivity and PTC intensity were affected by crystallinity of the polymer. The

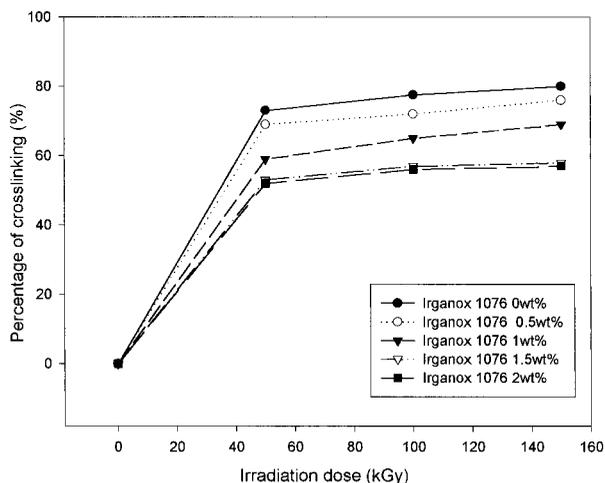


Figure 11 The percentage of crosslinking of the conductive HDPE/CB composites according to increasing amounts of Irganox 1076 (amount of CB is always 50 wt %).

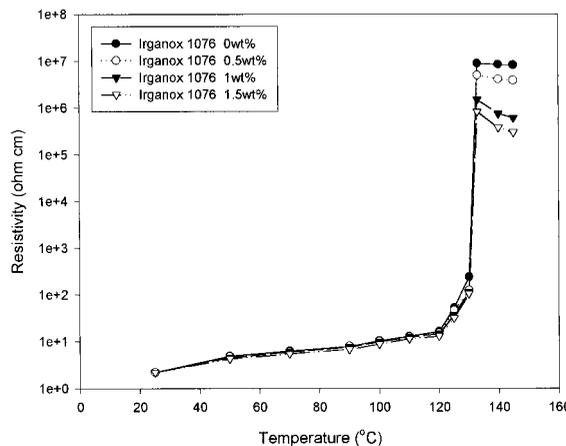


Figure 12 Resistivity of conductive HDPE/CB composites irradiated at 150 kGy as a function of temperature according to increasing amounts of Irganox 1076 (amount of CB is always 50 wt %).

room temperature resistivity of the conductive HDPE/CB composites decreased from 50 to 125°C with increasing thermal ageing time. In particular, the conductive composites with thermal ageing treatment at 120°C had the lowest resistivity because the crystallinity of the polymer increased with thermal ageing treatment. The crystallinity of the polymer increased with thermal ageing treatment below the melting point of the polymer but decreased with thermal ageing treatment above melting point of the polymer. The peak resistivity decreased with increasing amounts of antioxidant, but the composites had almost the same peak resistivity in the cases of >1 wt % antioxidant, and the resistivity of the composites did not increase further after two cycles. The percentage of crosslinking in the polymer and the peak resistivity decreased and NTC behavior appeared with increasing amounts of antioxidant. But the peak resistivity and the percentage of crosslinking of the composite containing 0.5 wt % antioxidant had almost the same values as the composites without antioxidant.

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References

- Ohe, K.; Natio, Y. *Jpn J Appl Phys* 1971, 10, 99.
- Feng, J.; Chan, C. M. *Polymer* 2000, 41, 7279.
- Yi, X.; Wu, G.; Pan, Y. *Polym Int* 1997, 44, 117.
- Yi, X.; Wang, B.; Pan, Y. *J Mater Sci Lett* 1997, 16, 1381.
- Kang, P.H.; Nho, Y.C.J. *Ind Eng Chem.* 2001, 7, 199.
- Tang, H.; Liu, Z.Y.; Piao, J.H.; Chen, X.F.; Lou, Y.Z.; Li, S.H. *J Appl Polym Sci* 1994, 51, 1159.
- Lee, M.G.; Nho, Y.C. *Radiat Phys Chem* 2001, 61, 75.
- Wally, R.J. In *Proceedings of the National SAMPE Symposium Exhibition*; 1985, Vol. 30, p. 441.

9. Luo, S.; Wong, C.P. *IEEE Trans Components Packaging Technol* 2000, 23(1), 151.
10. Yi, X.S.; Zhang, J.F.; Zheng, Q.; Pan, Y. *J Appl Polym Sci* 2000, 77, 494.
11. Silverman, J.; Zoepfl, F.J.; Randll, J.C.; Markovic, V. *Radiat Phys Chem* 1983, 22, 583.
12. Pionteck, J.; Hu, J.; Pompe, G.; Albrecht, V.; Schulz, U.; Borsig, E. *Polymer* 2000, 41, 7915.
13. Luo, Y.T.; Wang, G.C.; Zhang, B.Y.; Zhang, Z. *P. Eur Polym J* 1998, 34, 1221.
14. Zhang, J.F.; Zheng, Q.; Yang, Y.Q.; Yi, X.S. *J Appl Polym Sci* 2002, 83, 3112.
15. Han, S.O.; Lee, D.W.; Han, O.H. *Polym Degrad Stab* 1999, 63, 237.
16. Andreucetti, N.A.; Sarmoria, C.; Curzio O.A.; Valles, E.M. *Radiat Phys Chem* 1998, 52, 177.
17. Celette, N.; Stevenson, I.; Davenas, J.; David, L.; Vigier, G. *Nucl Instrum Methods Phys Res* 2001, 185, 305.
18. Zhang, J.F.; Zheng, Q.; Yang, Y.Q.; Yi, X.S. *J Appl Polym Sci* 2002, 83, 3117.