Effect of Irradiation and Thermal Aging on PTC Characteristics
of Conductive Carbon Black-Filled Polyethylene Composites

Phil Hyun Kang   and   Young Chang Nho

Korea Atomic Energy Research Institute

P.O. Box 105, Taejon 305-600, South Korea

Abstract

Effect of irradiation and thermal aging on PTC(positive temperature coefficient) characteristics of a conductive high density polyethylene/carbon black (HDPE/CB) composite was investigated. HDPE with a melt index of 0.35 was selected as the polymer matrix in this work. Carbon black with an average particle size 86 nm was used. The CB and polymer were mixed in a Brabender Plastograph at 160°C for 15 min. The CB/polymer blend thus produced was sandwiched between a pair of copper foils(0.04 mm thick), which served as electrodes. The thickness of the sample was approximately 0.5 mm. The HDPE/CB sheet was irradiated with gamma rays to a dosage of 60kGy, 120kGy and 180kGy to examine the behavior of the NTC(negative temperature coefficient) of the conductive composite. The conductive HDPE/CB composites preferably needs an antioxidant which stabilize the composites against thermo-oxidative degradation because they should be resistant to the severe condition of high temperature. Various types of anti-oxidants were added into the HDPE/CB. Thermal aging of PTC samples was conducted in an oven at 150°C for 140hr in air. The electrical properties of HDPE/CB composites were examined to determine the effect of antioxidants on the degradation of polymer. It was found that the peak resistivity of the compositions depended on the time of thermal aging treatment and the presence of antioxidants.

1. Introduction

Carbon black-polyethylene 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). 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 thus hindering the electrical conduct[1-3]. The lack of electrical reproducibility and the NTC effect are two main drawbacks to the application of PTC materials. Therefore, an effort to improve the various performances of PTC materials, especially the mechanisms of the PTC and NTC effects, has been made in depth[4-5]. 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. 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 reporting either irradiation crosslinking at room temperature or peroxide chemical crosslinking in a molding operation at room temperatures above the PE melting point[6]. Narkis reported that the PTC intensity is affected not only by the species of polymer and carbon black, but also by the processing conditions[7]. However, they did not explain the influence of antioxidant or other additive on PTC behavior of HDPE/CB in detail. In general, an endurance test of polymer switch was carried out to confirm the reliability of the self-resetting performance. We carried out an endurance test with repeated thermal cycle by heating the samples and cooling in an oven. The variations of the resistivity were observed by measuring the electrical resistivity at the time of each heat imposition. In order to improve the thermal stability of the PTC composition on exposure to successive thermal cycles, the composition preferably needs an antioxidant in addition to the radiation crosslinking. Accordingly, this study focuses on the effect of irradiation and thermal aging on PTC characteristics of a conductive high density polyethylene/carbon black composite when various types of anti-oxidants were added into the HDPE/CB.

2. Experimental

2.1. Materials and sample preparation

The base material used in this study was high density polyethylene (HDPE 5200B) supplied by Honam Petrochemical Corporation, Korea in powder form. It has a density

of $0.963g/cm^3$ and melting index of 0.35g/10min. The conducting filler was a commercial CB(Raven 420, supplied by the Columbia Chemicals Company, USA) with an average 86nm diameter particle size, BET(determination method developed by Brunauer, Emet, and Teller) of $28m^2/g$, and DBP(Dibutyl Phthalate absorption measurement method) of 75cc/100g determined with a particle size analyzer. Two types of commercial antioxidants were used in the study; one was a Octadecyl-3-(3,5-ditert.butyl-4-hydroxyphenyl)propionate(tradename, Irganox1076) supplied by CIBA-GEIGY Ltd., Swiss and the other was an Bis(2,4-di-butylphenyl)pentaerythritol Diphosphite(tradename, Ultranox626) supplied by GE Specialty Chemicals, Inc, USA. Dicumyl peroxide(DCP) used as a crosslinking agent was obtained from Aldrich Chemical Company, Inc., USA. Carbon black, HDPE, and antioxidants or dicumyl peroxide were mixed in a Brabender Plastograph at 160°C for 15min. The content of antioxidant and Dicumyl peroxide was 0.5% and 0.25%, based on the weight of the composite, respectively. The composition thus produced was sandwiched between a pair of copper foils(0.04mm thick), which served as electrodes. The thickness of the sample was approximately 0.5mm. The copper foil was supplied by Fukuda Metal Foil & Powder Co., Ltd. The PTC samples were irradiated by γ–rays to total doses of 60, 120, and 180 kGy at a dose rate of 10 kGy/hr at room temperature in nitrogen. Thermal aging treatment of PTC samples was conducted in an oven at 150°C for 24, 140hr in air.

2.2. Measurements of sample

As shown in Figure 1, the electrical resistivity was measured with a digital multimeter (Keithley Instruments model 2000). The PTC samples were placed in an oven to measure the electrical conductivity at various temperatures and 4 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. The crystal melting temperature of HDPE was measured using differential scanning calorimetry(DSC) (DSC-7 Series Thermal Analysis System, Perkin Elmer). Heating runs were conducted from 50 to 200 at a rate of 10 /min in nitrogen. The weight of the sample was around 3 mg. The heat of fusion was obtained by integrating the area under the endothermic peak. The percentage crystallinity of the specimen was determined by

assuming a value 288 J/g for the heat of fusion for a fully crystalline polyethylene material. The degree of crosslinking in the irradiated PTC sample was determined by measuring the insoluble content using the extraction method. The samples were extracted with boiling xylene for 24hr, then washed with ethanol, and finally dried under a vacuum at 80 to a constant weight. WAXD was obtained with a rotating Cu-anode X-ray source. The intensity curve was measured on the 2 theta scale, and the crystallinity was evaluated for all samples by comparing the area under the diffraction peaks. The thermal mechanical analysis was conducted on a TMA-943 system(Dupont mdel, USA). Temperature scans were from 30-150°C. A specimen of HDPE was studied using an expansion probe. The probe was lowered onto the samples and the initial height was recorded. The expansion was measured as 5°C/min in nitrogen. Dynamic mechanical testing has long been employed in the study of the viscoelastic response of polymers. The measurements were taken from –150 to150^{o}C, at a heating rate of 2°C/min. The loss tangent(tanδ) was measured for all samples.

3. Results and discussion

3.1. The effect of radiation crosslinking on PTC behavior

Figure 2 shows the PTC and DSC melting curves of a CB/HDPE/Ir1076(50:49.5:0.5) composite relative to irradiation condition. The resistivity began to increase when lamellar crystals started to melt and abruptly increased when the temperature approached T $_{max, DSC}$ regardless of irradiation condition. For non-irradiated conductive composite, it reached the maximum around T $_{max, DSC}$ and started to decrease gradually after that temperature as a result of the reagglomerization of CB particles in the molten polymer phase(NTC). When the composites were irradiated at 120kGy, the irradiated conductive composite had a higher peak resistivity compared with the non irradiated composite. Also the NTC behavior seen with the non-irradiated disappeared. The endothermic peak temperature is shifted to a higher temperature with an increase in the absorbed dose. The radiation crosslinking enhanced the PTC intensity. The increase of the PTC intensity is caused by reactions of free radicals of polymer with the chemical groups of CB[8]. The covalent bonds enhanced the binding force between polymer and

CB. NTC effect decreases for the crosslinked compound. These results are due to the effect that crosslinking enhances the shear modulus of polymers and that CBs are strongly attatched to crosslinked polyethylene networks. This strong attatchment to crosslinked network is, thus, expected to reduce the freedom of movement of carbon particles at high temperature. Figure 3 shows the TMA thermogram of HDPE/CB(50:50) with temperature. In polymeric materials, the thermal transitions are accompanied by changes in the isobaric expansivity of the material. These changes are measured using thermo-mechanical analysis. TMA measures the change in length of a material over a temperature range. As shown in Figure 3, the value of the dimension change of the specimen is observed when the temperature increases. The thermal expansion coefficient of the specimen decreased with increasing irradiation dose. The difference in expansivity of the sample at the same temperature can be described by the crosslinking network of the polymer caused by the irradiation effect. Figure 4 shows the viscoelastic response of the HDPE/carbon black composite relative to absorbed dose. The tanδ value at –120°C decreases as the irradiation increases. The result means that the dynamic modulus increases when the irradiation dose increases. Figure 5 shows the degree of crosslinking in the HDPE/CB composite relative to the absorbed dose. The degree of crosslinking in the irradiated PTC sample was determined by measuring the insoluble content using the extraction method. The degree of crosslinking in the polymer increased with the irradiation dose up to 180kGy. The radiation crosslinking in the composite significantly improved the reproducibility and declined the NTC behavior of the carbon black filled HDPE above its melting point. The influence of irradiation doses on the crystalline structure was shown in Figure 6. From the X-ray diffraction pattern in Figure 6, it was found that the observed half-width of the (110) and (220) peaks almost remains unchanged. There is no significant difference in X-ray profiles of non-irradiated and irradiated blend.

3.2. PTC behavior of thermal aged carbon black/HDPE composite

The overall resistivity of CB/HDPE and CB/HDPE/DCPcomposite before thermal aging is shown in Figure 7. For the composite with dicumyl peroxide, the peak resistivity was above 10^6 Ωcm. The room temperature resistivity of the CB/HDPE is

lower than that of CB/HDPE/DCP. The PTC intensity of CB/HDPE is considerably reduced compared to CB/HDPE/DCP. The addition of dicumyl peroxide affects the electrical behavior generally in such a manner that the room temperature resistivity and PTC intensity become higher. Figures 8-9 show resistivity changes of carbon black-filled HDPE relative to temperature and antioxidants after thermal aging treatment. As shown in Figure 8, the thermal aged samples exhibited a higher resistivity at room temperature, a more abrupt and intensive PTC switch behavior, compared to non-thermal aging samples. The peak resistivity of all samples were above 10^6 Ωcm. The difference between Irganox 1076 and ultranox 626 as an antioxidant on the resistivity of the composite after the thermal aging was not large(Figure 8). But there is significant difference in resistivity curve of conductive composite without antioxidant and with antioxidant in Figure 9. A dramatic decrease in the PTC intensity of composite without antioxidant was observed as thermal aging time increases. This shows that the composition preferably needs an antioxidant which stabilizes the composition against degradation, e.g. thermo-oxidative degradation of polymer. Figure 10 shows initial resistivity changes of carbon black-filled HDPE versus aging time after thermal aging treatment at 150°C. Initial resistivity of the carbon black-filled HDPE increased with an increase in the thermal aging time. For samples blended with Irganox 1076 and Ultranox 626, the resistivity change according to thermal aging time was lower than that of composite without antioxidant. Figure 11 shows resistivity ratio of the conductive composite after thermal aging. Resistivity ratio is defined as the ratio of the resistivity after thermal aging to the resistivity at room temperature. The resistivity ratio increased with an increase in the thermal aging time. The resistivity ratio of the composite without antioxidant was higher than that of the composite with antioxidant. This shows that antioxidants cause the electrical properties of the conductive composite to become more stable on thermal aging treatment. Threfore, in order to improve the thermal stability of the conductive polymer composition on exposure to successive thermal cycles, it is preferred that addition of antioxidant is needed. From the result of thermal aging treatment, it was found that the addition of antioxidant in CB/HDPE composition was effective to reduce resistivity change of conductive polymer composition.

4. Conclusions

The effect of irradiation and thermal aging treatment on PTC characteristics of a conductive high density polyethylene/carbon black composite was studied. The radiation crosslinking enhanced the PTC intensity. This result is due to the effect that crosslinking enhances the shear modulus of polymers and that CBs are strongly attatched to crosslinked polyethylene networks. There was a significant difference in resistivity curve of conductive composite without antioxidant and with antioxidant. A dramatic decrease in the PTC intensity of composite without antioxidant was observed as thermal aging time increases. It was found that addition of antioxidant in CB/HDPE composition was effective to reduce resistivity change in conductive polymer composition.

References

1. F. Kohler, U.S. Pat. 3,243,753. "Resistance element"(1966).

2. B. Wartgotz and WM. Alvino, "Conductive polyethylene resins from ethylene copolymers and conductive carbon black," *Polymer Eng. Sci*.p.63(1967).

3. K. Ohe and Y. Naito, " New resistor having an anomalously large positive temperature coefficient,"*Japan J Appl Phys*. **10**, p.99(1971).

4. J. Meyer, "Stability of polymer composites as positive-temperature-coefficient resistors,"*Polymer Eng and Sci* .**14**, p.706(1974).

5. J. Meyer, "Glass transition temperature as aguide to selection of polymers suitable for PTC materials,"*Polymer Eng Sci*.**13**, p.462(1973).

6. H. Tang , J. Piao , X. Chen , Y. Luo, and S. Li, "Studies on the PTC/NTC effect of carbon black filled low density polyethylene composites" *Eur. Polym. J.* **8**, p.1383(1997).

7. M. Narkis, A. Ram and Z. Stein, "Effect of crosslinking on carbon black/polyethylene switching materials," *J. Appl Polym Sci.* **25**, p.1515(1980).

8. H. Tang , J. Piao , X. Chen , Y. Luo, and S. Li, "The positive temperature coefficient phenomenon of vinyl polymer/CB composites" *J. Appl Polym Sci.* **48**, p.1795(1993).
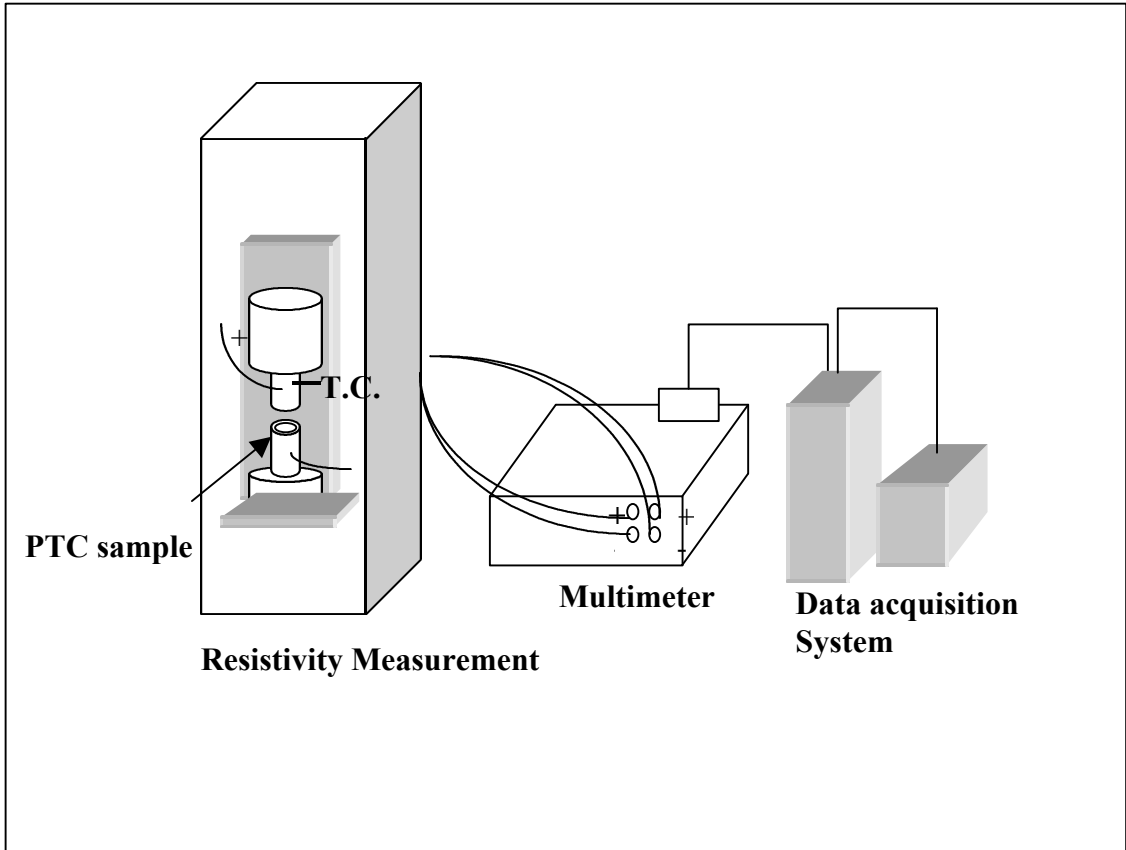
Figure 1. Schematic diagram of electrical resistivity of Carbon black/HDPE composite.
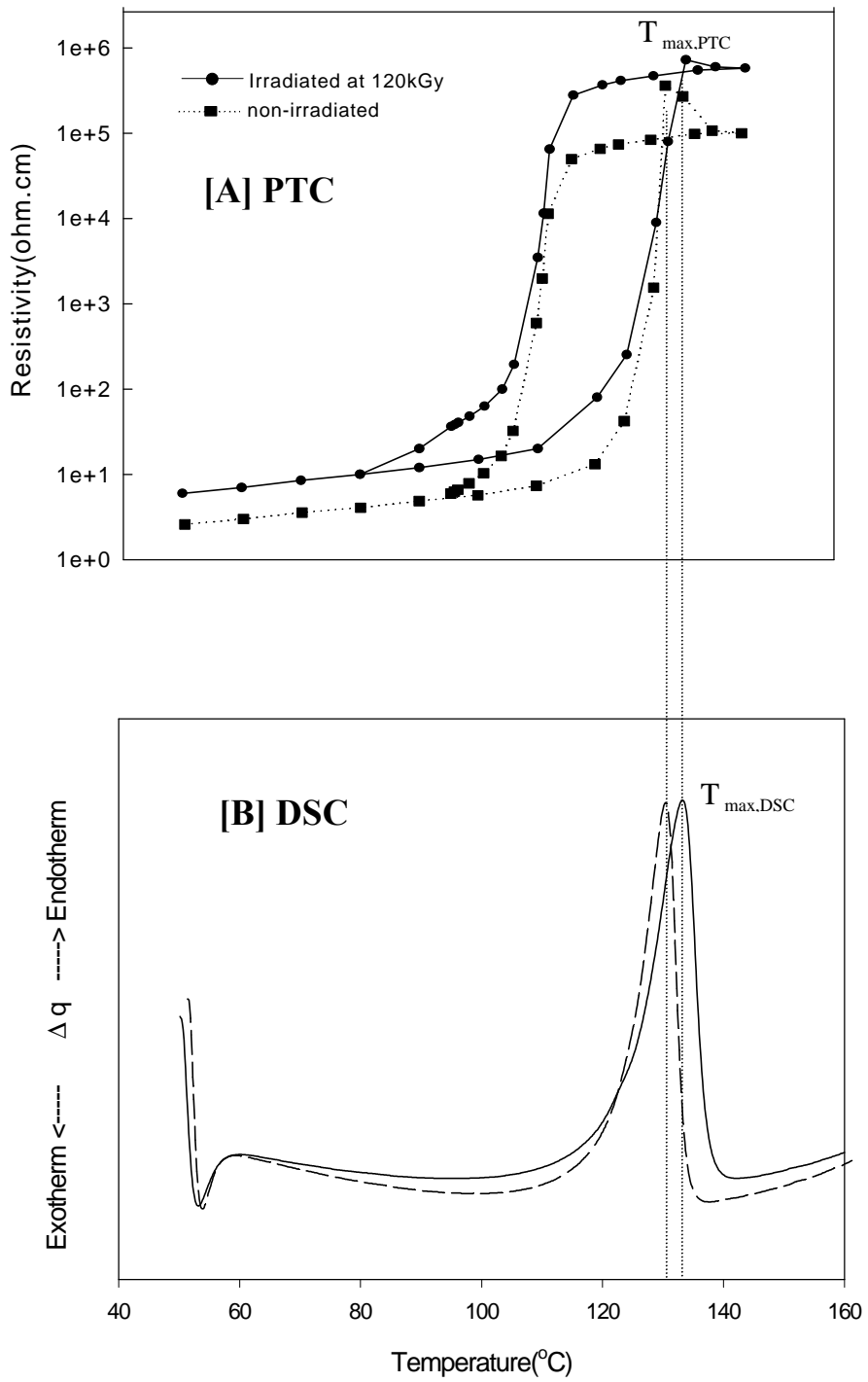
Figure 2. Comparison between PTC curves and DSC melting curves of CB/HDPE/Ir1076 (50:49.5:0.5)relative to irradiation condition.
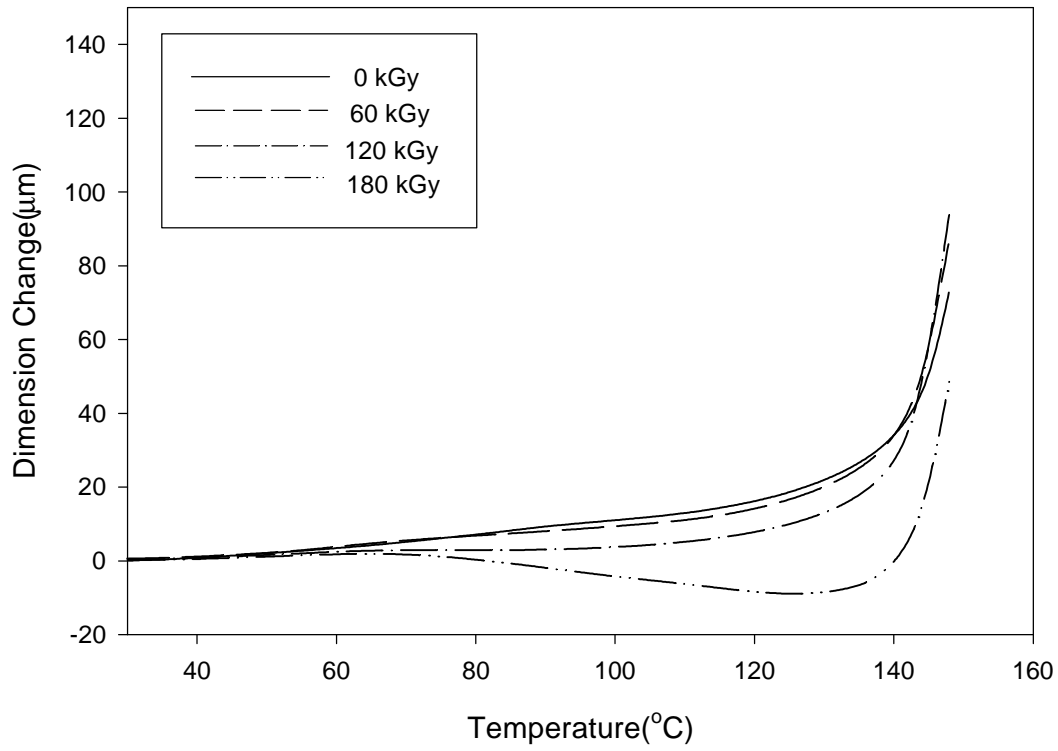
Figure 3. TMA curves of CB/HDPE(50:50) relative to absorbed dose.
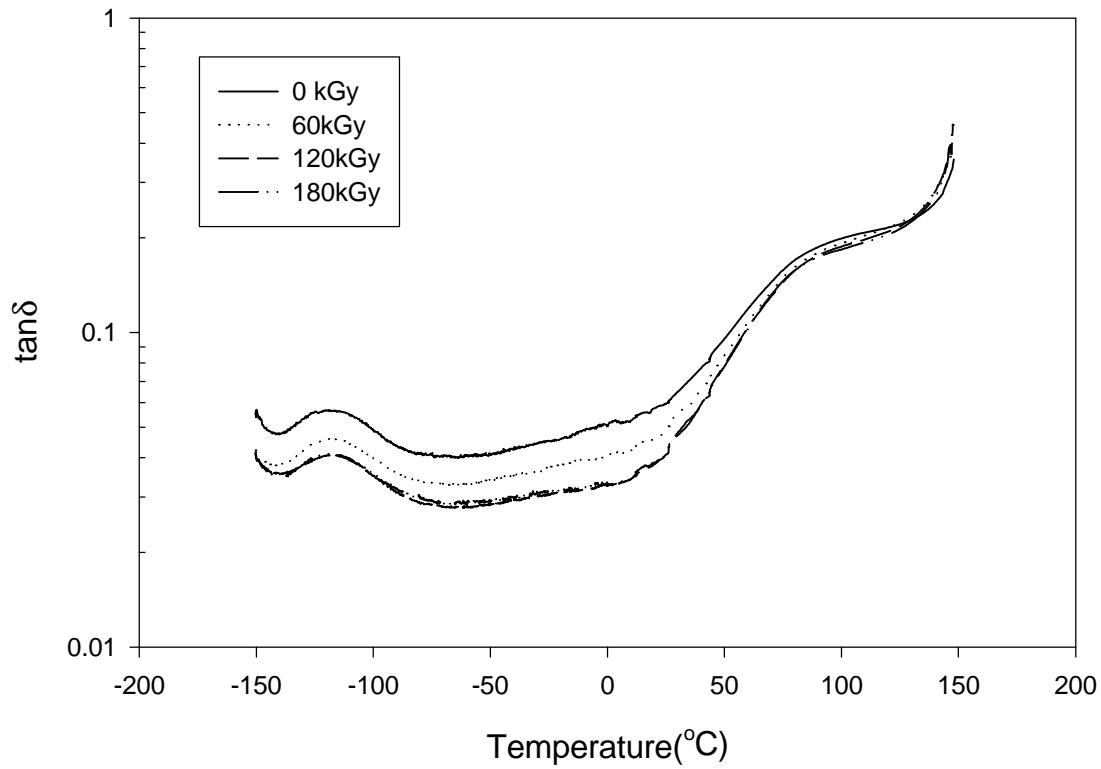
Figure 4. Loss factor(tand) as a function of temperature for iraadiated CB/HDPE(50:50) blend.
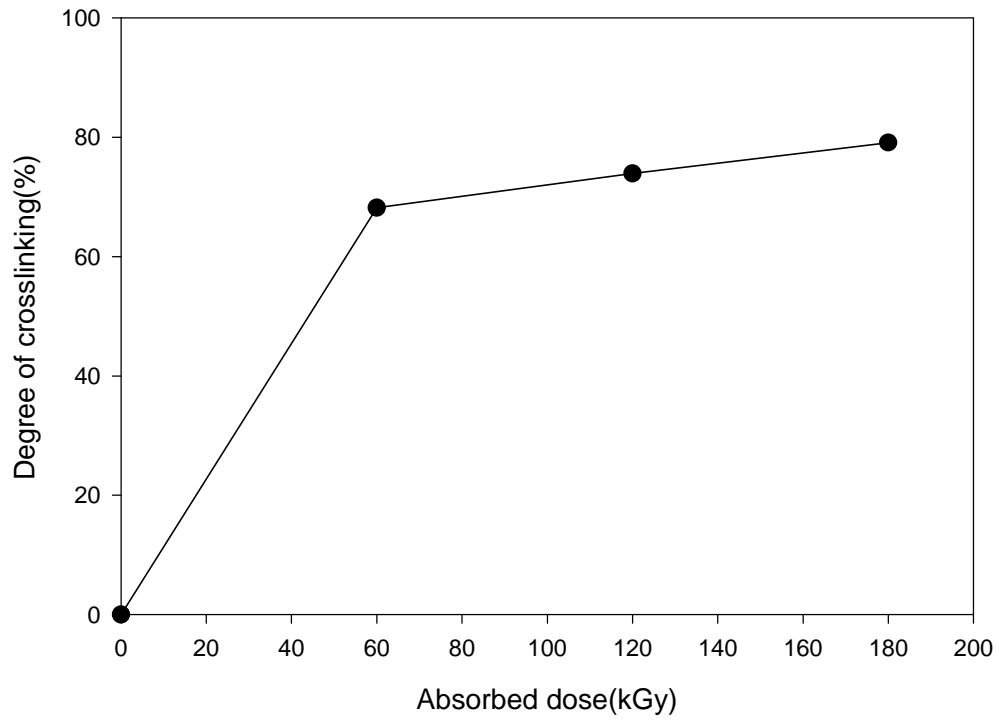
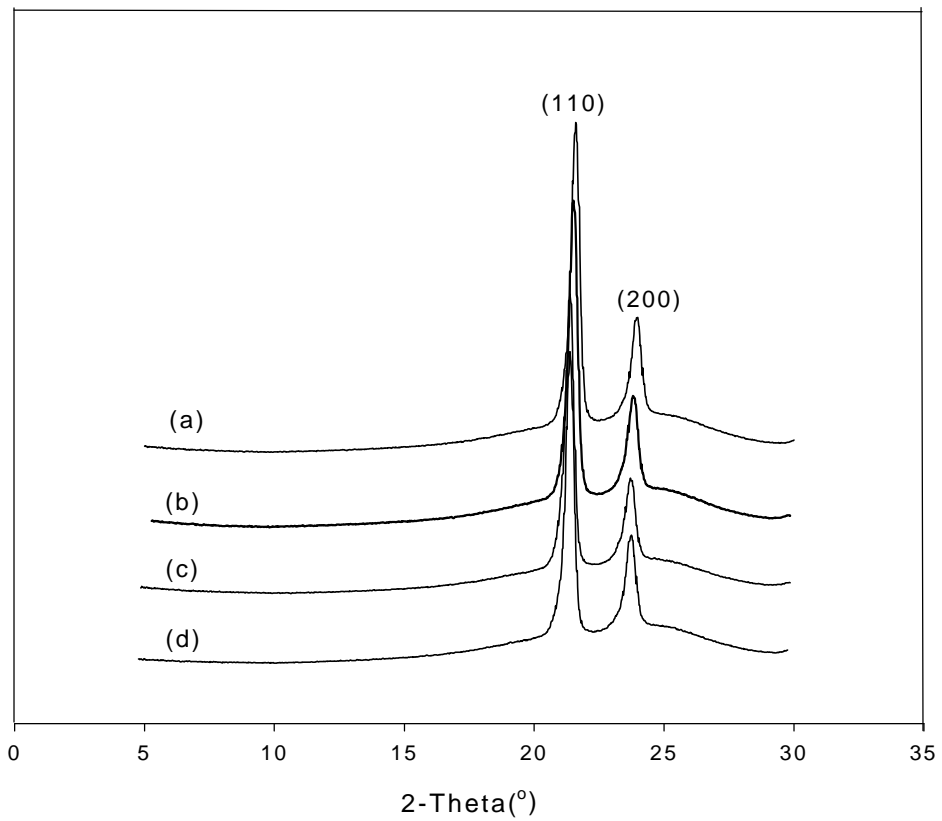Figure 5. Degree of crosslinking of CB/HDPE(50:50) relative to absorbed dose.

Figure 6. X-ray diffraction patterns of the CB/HDPE(50:50) composites under different doses of g-ray radiation dose for (a) 0kGy, (b)60kGy, (c)120kGy, and (d)180kGy.
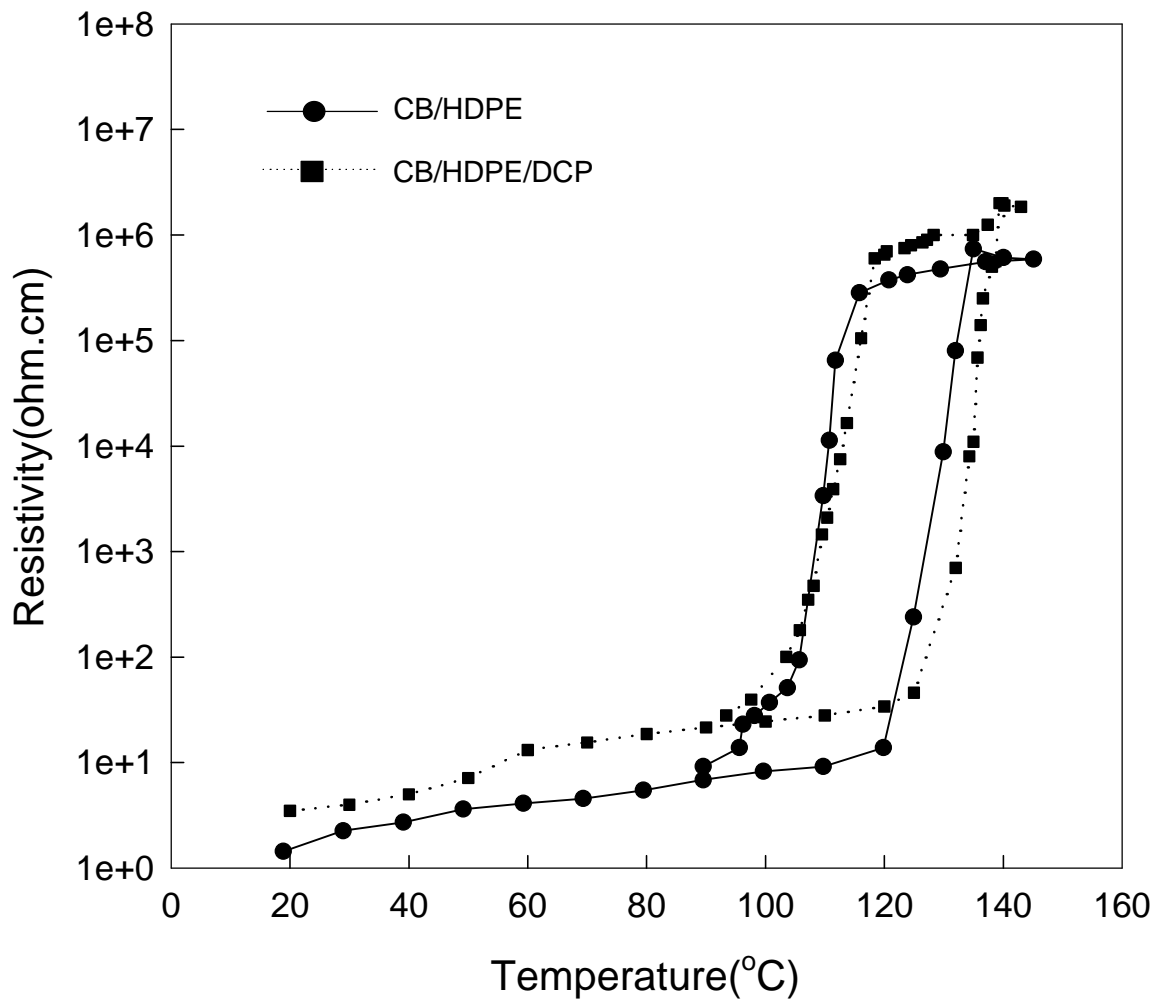
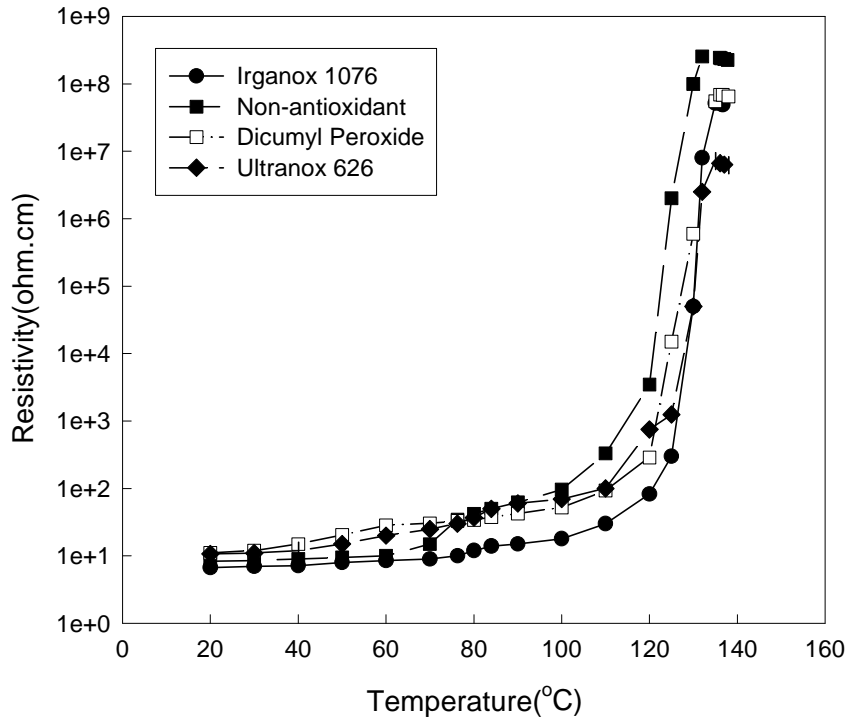Figure 7. Resistivity of CB/HDPE(50:50) and CB/HDPE/DCP(50:50:0.25) before thermal aging at 150°C.

Figure 8. Resistivity of carbon black filled HDPE versus temperature after thermal aging at 150°C for 24hr.
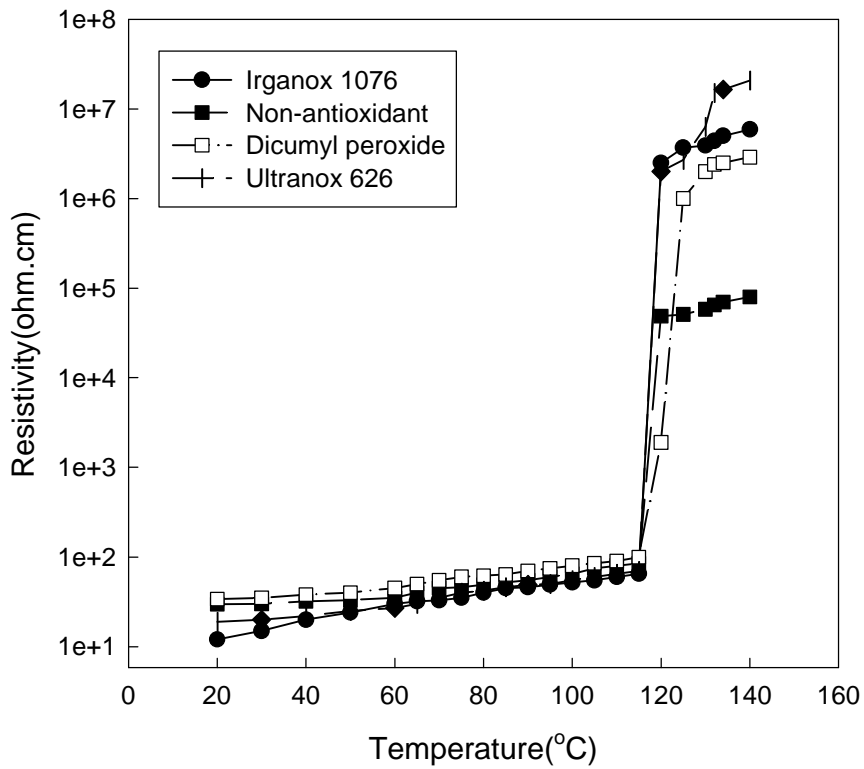

Figure 9. Resistivity of carbon black filled HDPE versus temperature after thermal aging at 150°C for 140hr.
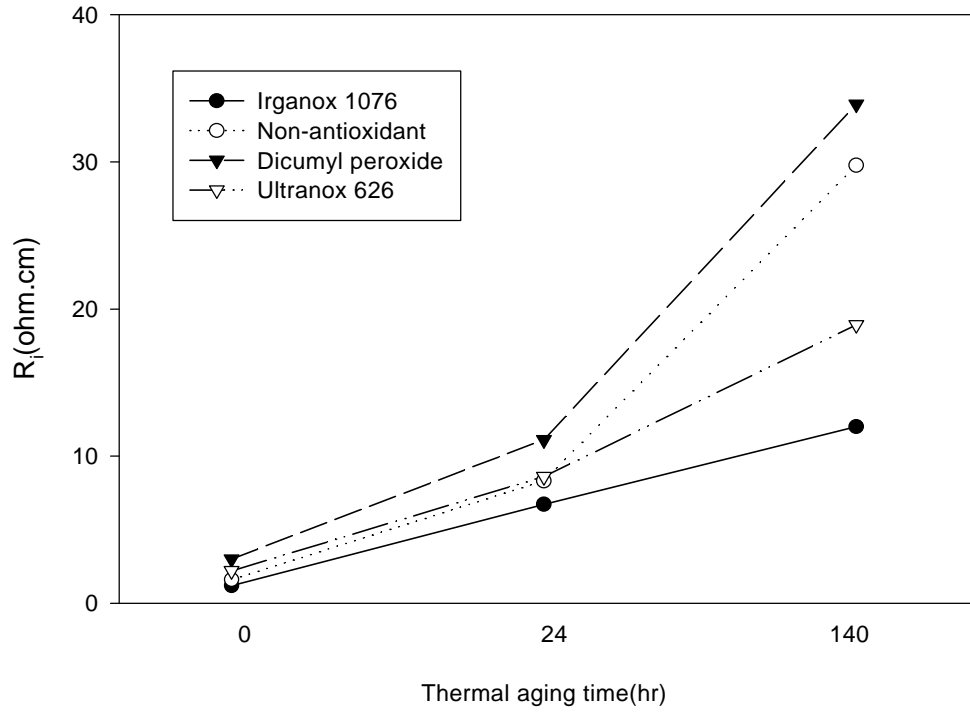
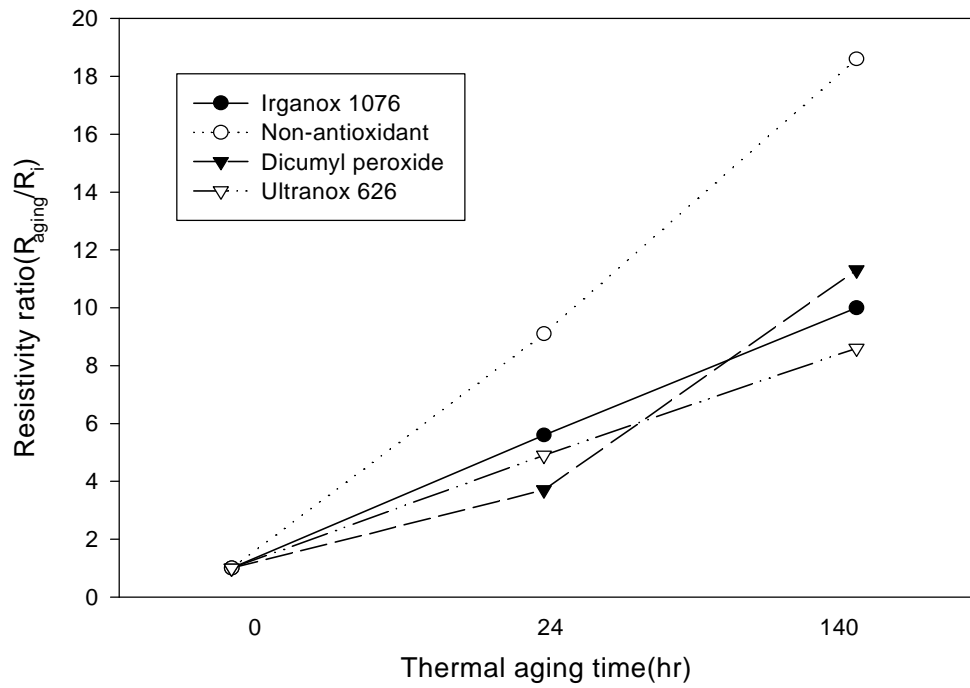Figure 10. Initial resistivity of carbon black filled HDPE versus aging time after thermal aging treatment at $150^{o}C$.

Figure 11. Resistivity ratio of carbon black filled HDPE versus aging time after thermal aging treament at $150^{o}C$.