카본블랙 충전 HDPE/EEA Copolymer 복합재료에 있어서 가교구조가 PTC 특성에 미치는 영향

이 건 주
LG전선(주) 전선연구소 고분자재료 기술그룹

Effect of Crosslinking on the PTC Stability Carbon Black Filled HDPE/EEA Copolymer Composite

Gun-Joo Lee
Research Lab., Polymeric Materials Technology Group, LG Cable Ltd.

Abstract - In order to apply for silane crosslinking process to PTC products, especially, self-regulating heater, silane crosslinked samples were compared with radiation crosslinked sample in terms of PTC characteristic and PTC stability. Silane crosslinked samples have lower PTC intensity than radiation crosslinked sample. It can be explained that multiple networks of silane crosslink restrict the movement of molecules in the composite as the sample is heating. As a result of heat cycles at 140℃, the changes of volume resistivity and PTC intensity for radiation crosslinked sample were higher than those of silane crosslinked samples. Whereas, in the case of heat cycles at 85℃, which is limiting temperature for self-regulating heater, both silane and radiation crosslinked samples show stable results without pronounce changes of resistivity up to five cycles.

1. Introduction

The importance of PTC (positive temperature coefficient) materials has been well understood in electric and electronic industries.[1,2] Especially, self-regulating heaters have become the most popular form of electric heat tracing products (protecting freezing and maintaining fluid at process temperature in pipeline or vessel) because this technology eliminates the possibility of heater burnout due to an inability to dissipate internally generated heat which is main cause of heater failure. Self-regulating heater, which adjusts its power output as a function of ambient temperature to maintain the system to a required temperature, is usually provided in the form of a strip consisting of two parallel bus wires embedded in a polymeric PTC core which serves as the heating element. One of the drawbacks of the heater is the decrease of power output due to the lack of PTC stability which refers a resistivity change under operating conditions.

Meyer investigated the PTC stability in carbon black filled high-density polyethylene (HDPE) with respect to the electrical degradation of the material. He concluded that the basic cause of the electrical degradation is a change in crystalline properties of the polymer matrix caused by oxidation and it can be improved by the incorporation of stabilizers to the PTC material.[3] Narkis has reported that the reproducibility of the PTC phenomenon, which means the PTC stability with heat cycling, could be improved by structure stabilization based on the use of a mixture of carbon blacks differing appreciably in their particle size.[4] It has been well known that the crosslinking of polymer molecules is an efficient method for the elimination of NTC (negative temperature coefficient) effect and the improvement of PTC stability in carbon black filled polymer system. Narkis[5], Tang[6] and Yang[7] et al. have used the electron beam irradiation (radiation crosslinking) and peroxide incorporation (peroxide crosslinking) to the composites for the studies of the effects of crosslinking on PTC characteristics.

Both electron beam irradiation and peroxide method have been used for a crosslinking of PTC products. However, it has been known that these processes are required a high cost investment for mass production. A crosslinking method by silanol condensation reaction of a silane-modified polymer (silane crosslinking) has been also used in cable manufacturing industry for a long time because of its economical advantage.

In this study, the effects of crosslinking on PTC characteristic and PTC stability in carbon black filled HDPE/ethylene-ethylacrylate copolymer (EEA) blend (70/30) composites were investigated. Especially, the silane crosslinking method was compared with radiation crosslinking method and was evaluated to adapt for PTC products by using heat cycle testing. Also, the relationship between PTC characteristic and crosslinking structure was discussed.

2. Experimental

2.1 Materials and sample preparation

HDPE (DGDK 3364, Union Carbide Co.), EEA (A710, Dupont-Mitsui Co.) and their blends (HDPE/EEA) were used as matrices. The HDPE had density of 0.945 g/cm^3, weight average molecular weight (Mw) of 150,000, and polydispersity index of 8.5. EEA contains 15% ethyl acrylate as comonomer and had density of 0.940 g/cm^3, Mw of 280,000, and polydispersity index of 5.3. The crystal melting temperature of HDPE and EEA, measured by differential scanning calorimetry (DSC), was 130℃ and 89℃, respectively. Black Pearls 460 (Cabot Co.) was used for conductive carbon black. The carbon black has average particle size of 29 nm, N_2 surface area of 84 m^2/g and DBP values of 102 cc/100g. Zinc oxide (ZnO), which has average particle size of 0.6μm , surface area of 4.5-6.0 ㎡/g , was also used to improve the dispersion of carbon black in the compounding process.

The compounds were prepared by two step process. Firstly, carbon black, ZnO were mixed with EEA resin for 10 min by using banbury mixer and then the mixture were pelletized. The maximum temperature during compounding was 150℃. Secondly, the mixture was continully melt blended with HDPE resin and was made into pellet form by using Buss kneader. The barrel temperature of the kneader was 150℃. The compound consisting of 30 phr carbon black and 9phr ZnO per 100parts of blend resin was extruded two parallel nickel-plated copper wires (7 strands, 0.45mm thickness per each strand) through a sheet die. The extruded strip, of which the electrodes were inserted on the opposite sides, had the dimensions of 12mm width, and 1.3mm thickness and the distance of electrodes was 7mm. For radiation crosslinking, the strip was irradiated by electron beam. The energy was 1.5MeV and the beam current was 40mA. For the preparation of silane crosslinking, the pellets made by Buss kneader mixed with vinyltrimethoysilane, dibutyltin dilaurate on a henschel mixer before the strip extrusion. The mixing was carried out for 15min at 120℃. The crosslinking networks were completed in 80℃ water bath for 4 hr.

The samples were jacketed with polymeric tubes to maintain dimensions when they were exposed to the crystal melting temperature of the matrix polymer. In the case of silane crosslinking process, because different grafting contents lead to different resistivity, each sample having different grafting content was subjected to heat treatment at 140℃ for 5-30min to have a resistivity range of 200-300 Ω.cm.

2.2 Measurements of properties

The electrical resistivity was measured with a digital multimeter (Keithley Instruments Model 197A). The samples were placed in the chamber to measure the electrical conductivity at various temperatures and two cables were used for connection between sample and multimeter. The computer system equipped with GPIB card was used for automatic data acquisition. GPC (gel permeation chromatography, Waters Model 150C) and, TMA (DuPont Model 2940) were used in characterization of the polymers. Crosslinking density was determined by measurement of gel content. Gel content was taken as the weight percentage of insoluble material after boiling in xylene for 24hr.

3. Results and discussion

3.1 Effect of irradiation and annealing on PTC characteristic

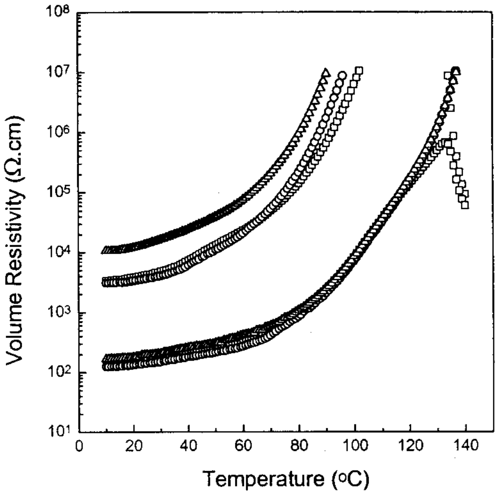

Fig.1. The effect of irradiation and annealing on PTC characteristic in carbon black filled HDPE/EEA composites: (□) non-irradiated, (○) irradiated,(△) annealed after irradiation.

Fig.1 shows the effect of irradiation and annealing on PTC characteristic in carbon black filled HDPE/EEA composites. Three kinds of samples, which include non-irradiated, irradiated, and annealed after irradiation, were compared in terms of temperature dependence of volume resistivity. The figure also compares two groups of samples differing in resistivity ranges. The annealed samples are treated at 140℃ for 5 min, cooled at the rate of 1℃/min. As expected, irradiation leads to remove NTC phenomenon in the composite. In previous paper[8], it was explained that NTC phenomon is due to the reagglomeration or networking induced by attraction (such as Van der Waals interaction) between carbon black aggregates. The elimination of NTC after irradiation has been well explained that crosslinking reduces the movement of the carbon black particles at a temperature above melting region of polymers.[5] Two interesting observations are found in the figure, that is, the volume resistivity at room temperatrue of the composite slightly decreases after irradiation, and then increases after annealing, respectively. It was reported that irradiation influenced the crystals of polymer, resulting in the decrease of melting temperature caused by increasing crystal defects.[9]

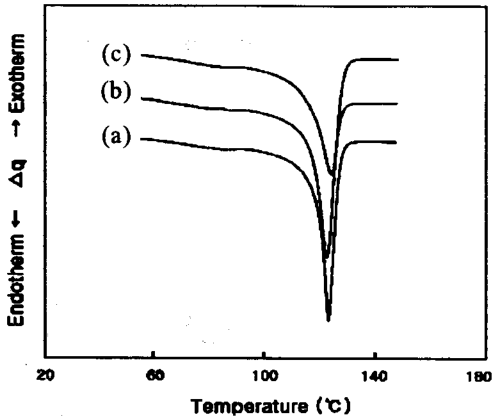

Fig.2. The effect of irradiation and annealing on DSC thermogram in carbon black filled HDPE/EEA blend composite:
(a) non-irradiated, (b) irradiated,
(c) annealed after irradiation.

Fig.2 compares DSC thermograms for non-irradiated, irradiated and irradiated/annealed samples. As a result, the heat of fusion of main melting peak was decreased from 63.6J/g to 62.4J/g after irradiation, and the peak temperature was also decreased from 125.3℃ to 124℃. In general, it was known that the conductivity in carbon black filled composite increases with increasing crystallinity of matrix polymer.[6,8] From above consideration, it is confirmed that the decrease of resistivity found in our experiment can not be explained by only the changes of melting peak temperature and crystallinity. On the other hand, it was found that surface temperature, measured with temperature indicating tape, of the strip was maintained 60-80℃ during irradiation. From the result, it is assumed that the relaxation of molecules, involving residual stress caused by rapid cooling in extrusion process, leads carbon black particles to rearrange, resulting in decrease of resistivity. Another observation is the increase of resistivity after annealing. Fig.2 shows the main peak is recovered by 1.5℃ after annealing and the heat of fusion is decreased to 59.8J/g. As far as only considering the change of heat of fusion, it can be explained that the increase of resistivity is due to the decrease of crystallinity after annealing. However, it still leaves how the increase of resistivity is explained with respect to melting temperature. It should be noted that radiation crosslinking is carried out in solid state, hence crosslinking reaction occurs in amorphous region, resulting that the crosslink junctions are distributed heterogeneously.[2,10,11] Consequently, it is presumed that crosslinking networks are acted as obstacles to form conduction paths during crystallization process of the composite. It is likely that the increase of PTC intensity after irradiation is also due to the heterogeneous distribution of crosslink junctions.

3.2 Comparison of radiation and silane crosslinking

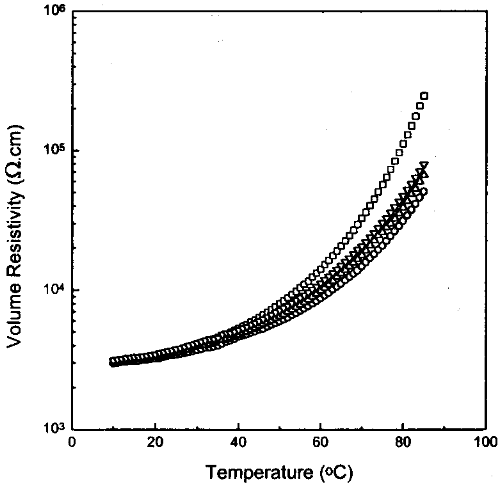

Fig.3. The volume resistivity versus temperature curves for carbon black filled HDPE/EEA composites with different crosslinking process and its density (gel%):
(□) radiation crosslinked (70),
(○) silane crosslinked (50),
(△) silane crosslinked (56),
(▽) silane crosslinked (63)

Fig.3 shows the effect of crosslinking process and crosslinking density (gel%) on PTC characteristic for carbon black filled HDPE/EEA composites. In the figure, one radiation crosslinked sample and three silane crosslinked samples differing in crosslinking density were compared, and this, the gel contents were 70% for radiation crosslinking, and 63%, 56%, and 50% for silane crosslinking, respectively. All samples were annealed at 85℃ for 5 min and cooled at the rate of 1℃/min for the same thermal history. It is clearly seen that the I_{85} value, defined as the resistivity ratio of 85℃ to 25℃, of radiation crosslinked sample has higher than those of silane crosslinked samples. Considering that the temperature range of experiment was from 10℃ to 85℃, it seems that the difference of crystal melting behavior between two crosslinking processes is not proper to explain the result.

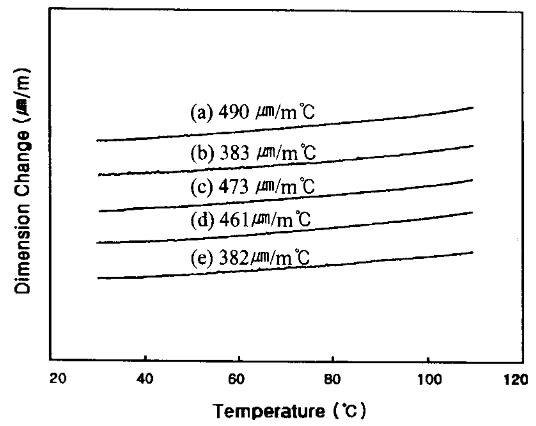

Fig.4. TMA thermogram for carbon black filled HDPE/EEA composites with different crosslinking process and its density (gel%):
(a) radiation crosslinked(70),
(b) non-crosslinked(50),
(c) silane crosslinked (63),
(d) silane crosslinked (56),
and (e) silane crosslinked (50)

Fig.4 shows TMA thermograms of five samples. The coefficient of thermal expansion (CTE) measured from 30℃ to 85℃ is 490, 384, 473, 461, and 382㎛/m℃ for radiation crosslinked, non-crosslinked, and silane crosslinked samples (the order of 63%, 56%, and 50%), respectively. It is observed that CTE increases with increasing crosslinking density, resulting in increasing I_{85} value. However, it is not enough to explain by only the difference of CTE as considered non-linearity of crosslinking density dependence on CTE. It should be noted that two groups of samples were subject to different reaction routes.[10~13] Therefore, it is expected that two groups of samples would have different network structures. It was reported that the multiple reactivity of the trifuctional silane-methoxy structure during the silane condensation reaction will also support multipul network formation.[11] Another assumption for the low values of I_{85} found in silane crosslinked samples is that multiple networks restrict the movements of molecules in composite as the sample is heating, resulting in breaking ineffectively conduction path.

Fig.5 shows the volume resistivity as a function of heat cycles at 140℃ for carbon black filled HDPE/EEA composites differing in crosslinking

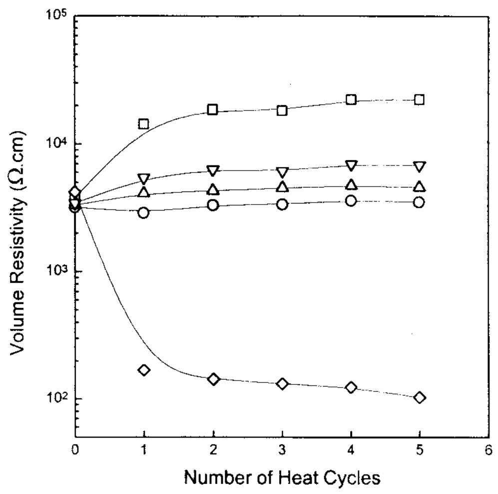

Fig.5. The volume resistivity as a function of heat cycle at 140℃ for carbon black filled HDPE/EEA composites with different crosslinking process and its density (gel%):
(□) radiation crosslinked (70),
(○) silane crosslinked (50),
(△) silane crosslinked (56),
(▽) silane crosslinked (63) and
(◇) non-crosslinked

process and crosslinking density, i.e., one radiation crosslinked sample (70 gel%), three silane crosslinked samples differing in crosslinking density (63, 56, and 50 gel%), and non-crosslinked sample. Heat cycle testing is effective method for evaluation of PTC products. In the test, the change of resistivity and PTC intensity after heat cycling is used as a measure of PTC stability. The heat cycle procedure was performed as follows: heating to 140℃ at the rate of 1℃/min, annealing at 140℃(or 85℃) for 5 min and then cooling to room temperature at the rate of 1℃/min. It is seen that the change of resistivity for radiation crosslinked and non-crosslinked samples are pronounced as compared those of silane crosslinked samples. In the case of radiation crosslinked sample, the volume resistivity increases from 3.8×10^3Ω.cm to 1.4×10^4Ω.cm after first cycle and then the slope of increasing gradually diminishes with cycles. The increase after first cycle for radiation crossliking is already explained for the comparison of irradiated and non-irradiated samples in Fig.1. The volume resistivity for non crosslinked sample abruptly decreases from 4.2×10^3Ω.cmto 1.7×10^2Ω.cm after first cycle and then slightly decreases with cycles. The decrease is due to the reagglormeration of carbon black aggregates during melting attributed Van der Waals interaction.[8] Unexpectedly, the changes of resistivity for silane crosslinked samples are lower than radiation crosslinked sample. It is attributed the fact that the grafting of vinyltrimethysilane onto polymer backbone occurs in melting state. Therefore, it can be explained that the variation of crosslink structure through heat cycles over melting temperature is small, resulting in decrease of resistivity with cycles.

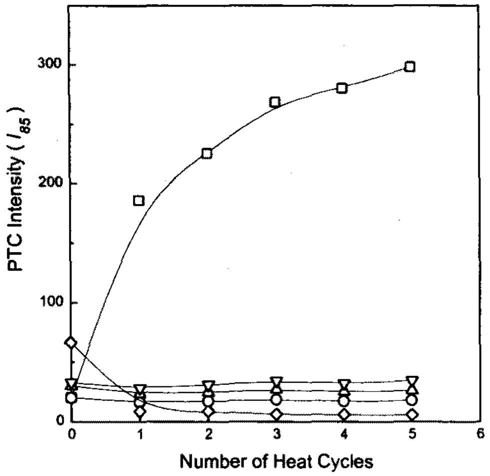

Fig.6. The PTC intsnsity(I_{85}) as a function of heat cycle at 140℃ for carbon black filled HDPE/EEA composites with different crosslinking process and its density (gel%):
(□) radiation crosslinked (70),
(○) silane crosslinked (50),
(△) silane crosslinked (56),
(▽) silane crosslinked (63) and
(◇) non-crosslinked

The PTC intensity (I_{85}) as a function of heat cycles at 140℃ for the samples is compared in Fig.6. The value of I_{85} for radiation crosslinked sample increases sharply from 20 to 186 after first cycle and keeps increasing. The value of I_{85} for non-crosslined sample decreases from 67 to 9 after first cycle and maintains same level. These changes are due that PTC intensity in the carbon black filled polymer composites depends on the resistivity of the composite. For samples with silane crosslinking, the values of I_{85} slightly decrease after first cycle, and then maintain up to five cycles. It is also likely due to the same reason as in the case of volume resistivity in Fig.5.

Fig.7 shows the volume resistivity as a function of heat cycle at 85℃ for carbon black filled HDPE/EEA composites differing in crosslinking process and crosslinking density. As shown in the figure, the effect of heat cycle at 85℃ is not pronounced. Although the variation is a little, the values of resistivity for all samples slightly decrease up to three cycles, and the slopes are similar except non-crosslinked sample. After third cycle, the volume

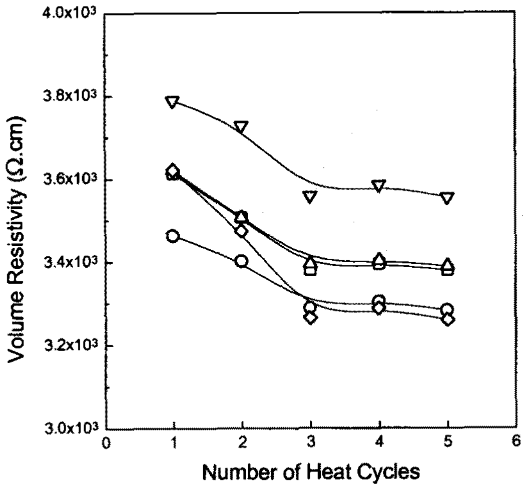

Fig.7. The volume resistivity as a function of heat cycle at 85℃ for carbon black filled HDPE/EEA composites with different crosslinking process and its density (gel%):
(□) radiation crosslinked (70),
(○) silane crosslinked (50),
(△) silane crosslinked (56),
(▽) silane crosslinked (63) and
(◇) non-crosslinked

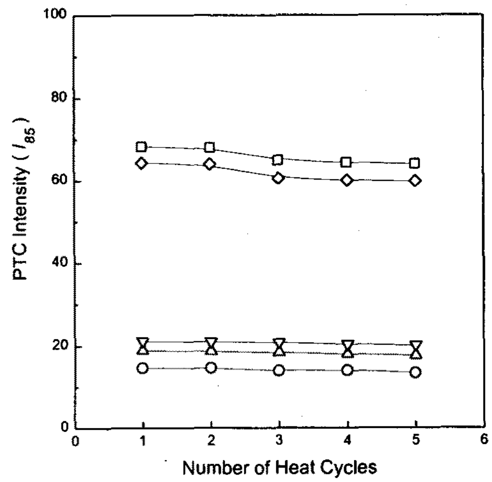

Fig.8. The PTC intsnsity(I_{85}) as a function of heat cycle at 85℃ for carbon black filled HDPE/EEA composites with different crosslinking process and its density (gel%):
(□) radiation crosslinked (70),
(○) silane crosslinked (50),
(△) silane crosslinked (56),
(▽) silane crosslinked (63) and
(◇) non-crosslinked

resistivity for all samples do not changed. In this experiment, there can not be found a difference between radiation and silane crosslinked samples.

Fig.8 shows the PTC intensity (I_{85}) as a function of heat cycle at 85℃ for the composites. While the values of I_{85} for silane crosslinked samples are not changed, the values of I_{85} for radiation crosslinked and non crosslinked samples slightly decrease after second cycle and are not changed more up to five cycles. As a result, as far as considering that the limiting temperature of self regulating heater is 85℃, both radiation and silane crossslinked samples show stable results with heat cycles. And it seems that as the sample is subjected to over melting temperatrue (140℃), silane crosslinked samples are more stable than radiation crosslinked one.

4. Conclusion

Effect of irradiation and annealing on PTC characteristic in carbon black filled HDPE/EEA composite was studied. Three kinds of samples, which include non-irradiated, irradiated, and annealed after irradiation were compared in terms of temperature dependence of volume resistivity. The resistivity at room temperature of the composite slightly decreased after irradiation. It is assumed that the relaxation of molecules, involving residual stress caused by rapid cooling in extrusion process, leads carbon particles to rearrange, resulting in decrease of resistivity. As irradiated samples were subjected to annealing, the resistivity and PTC intensity were increased. It is likely due to the decrease of crystallinity after annealing caused by heterogeneous distribution of crosslink junctions in the composite. In order to apply for silane crosslinking process to PTC products, silane crosslinked samples were compared with radiation crosslinked samples in terms of PTC characteristic and PTC stability. Silane crosslinked samples have lower PTC intensity (I_{85}) than radiation crosslinked sample. It can be explained that multiple networks restrict the movement of molecules in the composite. As s result of heat cycles at 140℃, the changes of resistivity and I_{85} for silane crosslinked samples were lower than those of radiation crosslinked sample. Whereas, in the case of test at 85℃, which is limiting temperature for self regulating heater, both silane and radiation crosslinked samples show stable results without pronounce changes of resistivity up to five cycles.

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