The Radiation Resistance Evaluation of Electrically Insulating Polymers

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Abstract - In this research, the radiation resistance of ethylene propylene rubber (EPR) and chlorosulfonated polyethylene (CSPE) which can be used as a insulating materials of for electrical cable in the nuclear power plant were investigated. EPR and CSPE were irradiated by γ-ray at various doses ranging from 50 to 500 kGy at room temperature in air. The irradiated EPR and CSPE was investigated in terms of activation energy, mechanical properties, and oxidation stability. The experimental results revealed that CSPE exhibited the higher radiation resistance in comparison to that of EPR.

Key words : Radiation resistance, Ethylene propylene rubber, Chlorosulfonated polyethylene

INTRODUCTION

Polymers have been widely used as insulating materials of electrical cables in nuclear power plants due to their outstanding mechanical and electrical properties (Kuriyama *et al*. 1979; Chen *et al*. 2009). However, these insulating polymers are generally exposed to high energy radiation. The physical and mechanical properties of the exposed polymers are deteriorated due to crosslinking, chain scission reaction and oxidative degradation caused by high energy radiation, thereby resulting in the remarkable reduction in the lifetime of the polymers (Du and Liu 2010; Seguchi *et al*. 2011). Thus, it is necessary to investigate the radiation resistance of these insulating polymers which is important to extend the service duration of the nuclear power plants.

Research on the investigation of radiation resistance of insulating polymers have been reported. Lee *et al* reported that evaluation of radiation resistance of ethylene propylene rubber (EPR) was investigated by using dielectric analysis and thermal gravimetric analysis (Lee and Kim 2008). The radiation resistance of EPR was studied by Seguchi *et al* in terms of tensile properties, gel fraction, swelling ratio, and chemical structure (Seguchi *et al*. 2011). Gillen *et al* reported to monitor the aging of the chlorosulfonated polyethylene (CSPE) insulating materials exposed to high-energy radiation conditions through cross-sectional modulus profiling, solvent uptake and swelling test (Gillen *et al*. 2005). The correlations between the mechanical properties and oxidation induction time of the EPR and CSPE were studied by Calmet *et al.* (Calmet *et al*. 2002). However, the multilateral study on radiation resistance of EPR and CSPE which are used as insulating materials of electrical cables has rarely been carried out.

In this study, the radiation resistance of commercially-available cable materials as EPR and CSPE was investigated. EPR and CSPE sheets were irradiated by γ-rays under various conditions and the irradiated sheets were then investigated in terms of activation energy, mechanical properties, and oxidation stability by using universal testing machine,

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differential scanning calorimeter, thermogravimetric analyzer, and chemiluminescence analyzer.

MATERIALS AND METHODS

Materials

Ethylene propylene rubber (EPR) and chlorosulfonated polyethylene (CSPE) supplied from Taihan Electric Wire Co., LTD and used as received.

γ-ray irradiation

The 500 μm thick EPR sheet and CSPE sheet (20 cm × 20 cm) was irradiated by γ-ray in the presence of air at room temperature in a ^{60}Co facility at the KAERI, Korea. The doses ranged from 50 to 500 kGy and the dose rate was 10 kGy hr^{-1}.

Characterizations

The thermal decomposition temperatures were carried out using thermogravimetric analyzer (TGA, Model 2950, TA Instrument, USA) between 50 and 600°C at heating rates of 1, 3, 5, 10, and 20°C min^{-1} under nitrogen atmosphere (Cho *et al*. 1998). The activation energy using the decomposition temperatures measured by TGA were calculated from the following Kissinger equation:

$$-\ln\left(\frac{\beta}{T_m^2}\right)=\frac{E_d}{RT_m}-\ln\left(\frac{AR}{E_d}\right),$$

where β is the heating rate (°C min^{-1}), T_m is the most rapidly decomposition temperature (K), E_d is the decomposing activation energy (kJ mol^{-1}), R is the gas constant, and A is the pre-exponential factor (Cho *et al*. 1998; Kim *et al*. 2000). The tensile strength and elongation-at-break were measured using a universal testing machine (UTM, Instron Model-4210, Instron Engineering Co., USA) according to the ASTM Standard D638. The oxidation induction temperature (OIT) was measured using differential scanning calorimetry (DSC, Q1000, TA Instrument, USA) between 0 and 200°C at a heating rate of 10°C min^{-1} under pure oxygen gas atmosphere. The OIT was determined as the onset of the decomposition (Schmid *et al*. 2006). Chemiluminescence analysis was performed using chemiluminescence analyzer (CLA, CLA-FSI, Tohoku Electronic Industrial. Co., Ltd, Japan) under the air atmosphere at 25°C for 20 min.

RESULTS AND DISCUSSION

In order to investigate the change in the activation energy with a dose, the thermal decomposition temperature of the irradiated EPR and CSPE at various doses were measured by TGA. The activation energy of the irradiated EPR and CSPE at various doses was calculated by Kissinger equation based on the obtained decomposition temperatures and the result is shown in Fig. 1. In the case of EPR, although all the irradiated EPR showed lower activation energy in comparison to that of the control with 278 kJ mol^{-1}, the activation energy was decreased up to 266 kJ mol^{-1} with an increasing dose to 100 kGy, above which it increased to 271 kJ

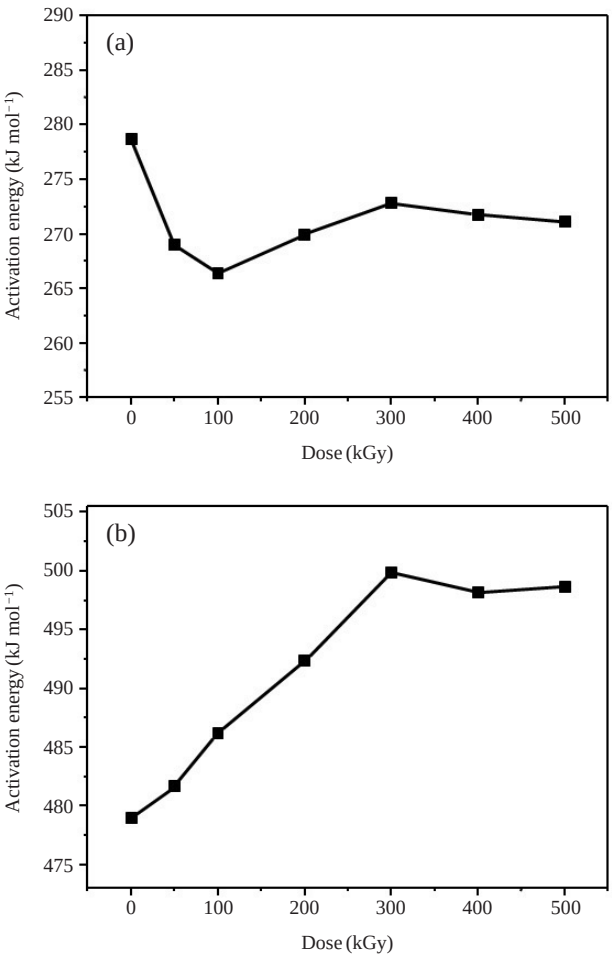

Fig. 1. Activation energy of EPR (a) and CSPE (b) as a function of dose.

mol^{-1}. This result could be mainly ascribed to the fact that, at the dose less than 200 kGy, the activation energy was decreased by the main occurrence of the chain scission during irradiation due to the presence of radiation-liable propylene structure in the polymer backbone, but, at the higher dose, the simultaneously proper occurrence of the crosslinking sightly increased the activation energy (Seo *et al*. 2010). On the other hand, all the irradiated CSPE exhibited higher activation energy in comparison to that of the control with 478 kJ mol^{-1}. The activation energy of the irradiated CSPE was increased up to 499 kJ mol^{-1} with a increasing dose to 300 kGy, above which it leveled off. Unlike the EPR, this increase could be attributed to the fact that the crosslinking reaction of CSPE prevailingly occurred during the irradiation, and therefore resulting in the improvement of the CSPE thermal stability (Pinel and Gueguen 1991; Tripathy *et al*. 2000).

Tensile properties of EPR and CSPE such as tensile strength and elongation-at-break as a function is presented in Figs. 2 and 3. As shown in Fig. 2(a) and (b), the tensile strengths of EPR were gradually decreased to 11.6 MPa with an increasing dose. However, the tensile strengths of the CSPE were increased up to 20.4 MPa with an increasing absorption at the lower dose 200 kGy, above which these were slightly increased up to 20.6 MPa. Furthermore, as shown in Fig. 3, the elongation-at-break of both EPR and CSPE was gradually reduced with an increasing dose. However, the extent of reduction for CSPE was much smaller than that of EPR, indicating that CSPE has higher radiation resistance than EPR does. These results could be attributed to the increase in the brittleness induced by mainly occurrence of chain scission in EPR and crosslinking in the CSPE during the irradiation (Kuriyama *et al*. 1979).

To estimate the relative extent of radiation-induced oxidative degradation which has a significant effect on the life-

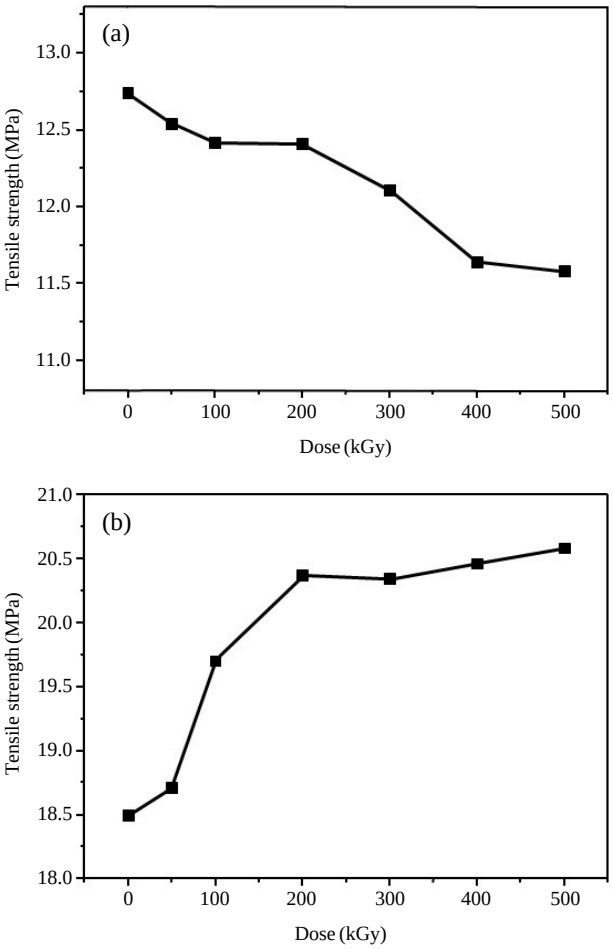

Fig. 2. Tensile strength of EPR (a) and CSPE (b) as a function of dose.

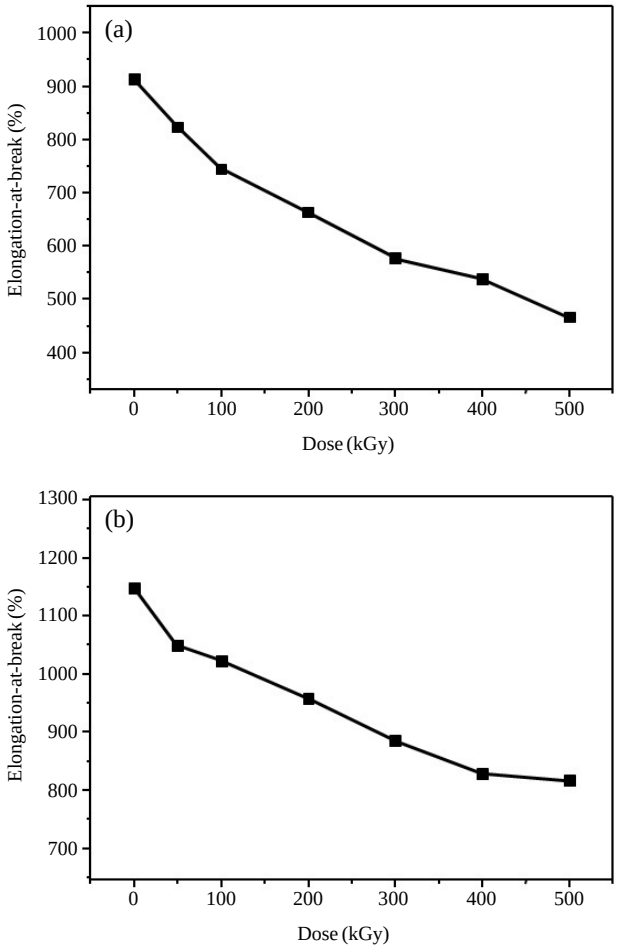

Fig. 3. Elongation-at-break of EPR (a) and CSPE (b) as a function of dose.

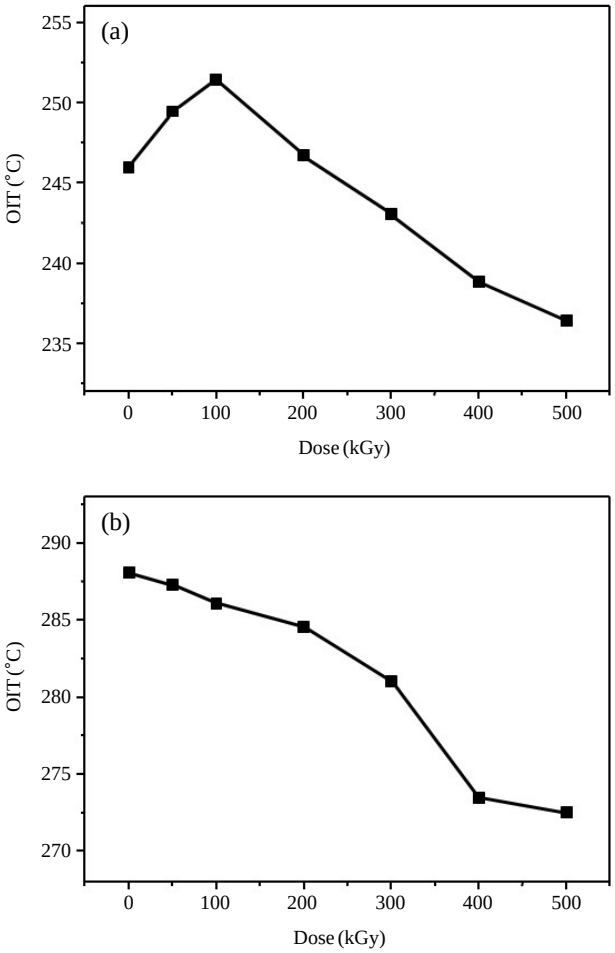

Fig. 4. Oxidation induction temperature of EPR (a) and CSPE (b) as a function of dose.

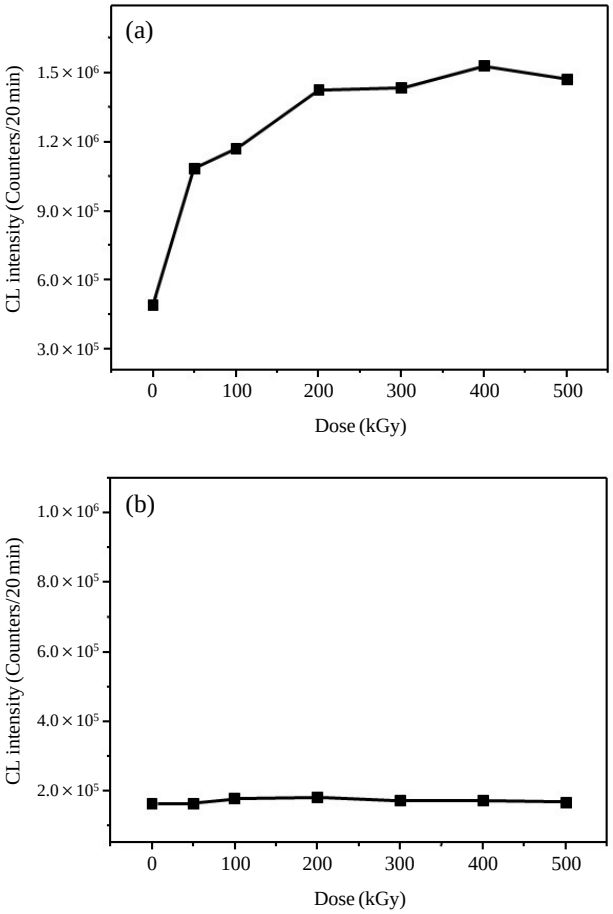

Fig. 5. Chemiluminescence analysis of EPR (a) and CSPE (b) as a function of dose.

time of insulating polymers, the oxidative stability of EPR and CSPE was investigated through measurement of oxidation induction temperature (OIT) using DSC (Ginic-Markovic *et al*. 1998; Calmet *et al*. 2002). Fig. 4 shows the changes in OIT as a function of dose. As shown in Fig. 4, in comparison to that of the control of EPR, 246˚C, the OIT of irradiated EPR was increased to 251˚C with an increasing dose up to 100 kGy, over which it was gradually decreased to 236˚C. On the other hand, the OIT of irradiated CSPE was gradually decreased to 272˚C with an increasing dose compared to that of the control, 288˚C. These results indicates that both EPR and CSPE underwent radiation-induced oxidative degradation and the extent of oxidative degradation was dependant on dose (Konar *et al*. 1994).

To further investigate the radiation-induced oxidative degradation, EPR and CSPE was investigated by chemiluminescence analysis which measured the relative chemiluminescence intensities of the oxidized species resulting from the radiation-induced oxidative degradation and the results are presented in Fig. 5 (Osawa *et al*. 1986; Setnescu *et al*. 2004). As shown in Fig. 5(a), the chemiluminescence intensity of the irradiated EPR was dramatically increased with an increasing dose in comparison to that of EPR, indicating that the EPR was liable to the oxidative degradation caused by the radiation due to the presence of radiation-liable propylene structure in the polymer backbone (Corrales *et al*. 2002; Zaharescu *et al*. 2010). On the other hand, as shown in Fig. 5(b), the chemiluminescence intensity of all the irradiated CSPE was similar to the control. This result means that the oxidative degradation of CSPE induced by radiation did not significantly occurred. Therefore, CSPE is more radiation-resistant than EPR (Allen *et al*. 2002). This result is different from that of the OIT measurement using DSC analysis under the oxygen atmosphere because the chemiluminence analysis measures the degree of the formed oxida-

tive species after the irradiation and oxidation induction temperature (OIT) measurement estimates the resistance of insulating polymers to oxidative thermal decomposition which is determined by the onset of exothermic oxidation in material at specified temperature under the oxygen atmosphere (Allen *et al*. 2002; Calmet *et al*. 2002).

CONCLUSION

In this study, the radiation resistance of EPR and CSPE as a commercially available cable material were investigated in terms of activation energy, mechanical properties, and oxidative stability. The results of activation energy measurement revealed that the activation energy of EPR was reduced with a dose, while that of CSPE was increased. On the basis of the results of tensile properties, the tensile strength of EPR was decreased with a dose but that of CSPE was increased. The elongation-at-break of EPR had more reduction with a dose in comparison to that of CSPE. The results of OIT measurement showed that the OIT of both EPR and CSPE was shifted to a lower temperature. The results of chemiluminescence analysis showed that the oxidized species formed by radiation-induced oxidative degradation was generated in EPR than in CSPE. These changes in the activation energy, mechanical properties, and oxidative stability could be ascribed to the predominance of chain scission in EPR and crosslinking in CSPE during irradiation in the air. Therefore, the radiation resistance of EPR was lower than that of CSPE due to the presence of radiation-liable propylene group in EPR backbone.

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REFERENCES

Allen NS, Rivalle G, Edge M, Corrales T and Catalina F. 2002. Chemiluminescence processes in thermal and photochemically oxidised poly(ethylene-co-1,4-cyclohexanedimethylene terephthalate (PECT): influence of stabilisers. *Polym. Degrad. Stab.* **75**:237-246.

Calmet JF, Carlin F, Nguyen TM, Bousquet S and Quinot P. 2002. Irradiation ageing of CSPE/EPR control command electric cables. Correlation between mechanical properties and oxidation. *Radiat. Phys. Chem.* **63**:235-239.

Chen J, Huang X, Jiang P and Wang G. 2009. Protection of SEBS/PS blends against gamma radiation by aromatic compounds. *J. Appl. Polym. Sci.* **112**:1076-1081

Cho YS, Shim MJ and Kim SW. 1998. Thermal degradation kinetics of PE by the Kissinger equation. *Mater. Chem. Phys.* **52**:94-97.

Corrales T, Catalina F, Peinado C, Allen NS and Fontan E. 2002. Photooxidative and thermal degradation of polyethylenes: interrelationship by chemiluminescence, thermal gravimetric analysis and FTIR data. *J. Photochem. Photobio. A: Chemistry* **147**:213-224.

Du BX and Liu HJ. 2010. Effects of atmospheric pressure on tracking failure of gamma-ray irradiated polymer insulating materials. *IEEE Trans. Dielectr. Electr. Insul.* **17**:541-547.

Gillen KT, Bernstein R and Celina M. 2005. Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials. *Polym. Degrad. Stab.* **87**:335-346.

Ginic-Markovic M, Choudhury NR, Dimopoulos M, Williams DRG and Matisons J. 1998. Characterization of elastomer compounds by thermal analysis. *Thermochimica Acta.* **316**: 87-95.

Kim WI, Kim SD, Lee SB and Hong IK. 2000. Kinetic characterization of thermal degradation process for commercial rubbers. *J. Ind. Eng. Chem.* **6**:348-355.

Konar J, Samanta G and Avasthi BN. 1994. Oxidative degradation of EPDM rubber using phase transferred permanganate as oxidant. *Polym. Degrad. Stab.* **43**:209-216.

Kuriyama I, Hayakawa N and Nakase Y. 1979. Effect of dose rate on degradation behaior of insulating polymer materials. *IEEE Trans. Dielectr. Electr. Insul.* EI-14:272-277.

Lee KY and Kim KY. 2008. ^{60}Co γ-ray irradiation effect and degradation behaviors of a carbon nanotube and poly(ethylene-*co*-vinyl acetate) nanocomposites. *Polym. Degrad. Stab.* **93**:1290-1299.

Osawa Z, Konoma F, Wu S and Cen J-F. 1986. Photo-oxidative degradation of polystyrene: comparison of chemiluminescence with other analytical methods. *Polym. Photochem.* **7**:337-347.

Pinel B and Gueguen V. 1991. Effects of irradiation dose rate and thermal aging on changes in the properties of elastomeric materials (EPR-CSPE) for cable insulation and sheating. *IEEE.* CH3029-6:944-949.

Schmid M, Ritter A and Affolter S. 2006. Determination of exidation induction time and temperature by DSC. *J. Ther-*

mal Analysis and Calorimetry **83**:367-371.

Seguchi T, Tamura K, Ohshima T, Shimada A and Kudoh H. 2011. Degradation mechanisms of cable insulation materials during radiation-thermal ageing in radiation environment. *Rad. Phys. Chem.* **80**:268-273.

Setnescu R, Kaci M, Jipa S, Setnescu T, Zaharescu T, Hebal G, Benhamida A and Djedjelli H. 2004. Chemiluminescence study on irradiatied low-density polyethylene containing various photo-stabilisers. *Polym. Degrad. Stab*. **84**:475-481.

Soe YD, Lee HS, Kim YS and Song C. 2010. A study on the aging degradation of ethylene-propylene-diene monomer (EPDM) under LOCA condition. *Nucl. Eng. Tech.* **43**:279-286.

Tripathy AR, Patra PK, Sinha JK and Banerji MS. 2000. Application of differential scanning calorimetry and differential thermogravimetric techniques to determine the ratio of blend components in reactive chlorinated elastomer blends. *J. Appl. Polym. Sci*. **83**:937-948.

Zaharescu T, Jipa S, Henderson D, Kappel W, Maris DA and Maris M. 2010. Thermal and radiation resistance of stabilized LDPE. *Radiat. Phys. Chem.* **79**:375-378.

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