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Evaluation of Irradiated Oxidation of XLPE Based on Thermal and IR Reflection Properties

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Abstract : For evaluating the radiation degradation of cross-linked polyethylene (XLPE) cable insulation due to the irradiated oxidation, XLPE was irradiated with γ-ray. For each irradiated samples, TGA, DSC, FT-IR, and tensile tests were carried out. Regarding radiation degradation, oxidative process was predominant. TGA, DSC and FT-IR can be useful tools for evaluating the radiation degradation due to the irradiated oxidation because these analyses need only small amount of samples. The results of TGA, DSC and FTIR analyses showed the similar tendency for irradiated degradation. They can be useful tools for evaluating the oxidation of insulating material by non-destructive testing.

Key words: cross-linked polyethylene (XLPE), γ-ray, TGA, DSC, FT-IR

1. Introduction

Polymeric materials are widely used for electrical insulation in a broad range of applications which cover the power supply industry to inner and outer space. However, the electrical performance of these materials could be compromised by their working environment and one of the most deleterious is that where nuclear radiation is present[1]. The important cause of degradation on the Cross-linked polyethylene(XLPE) used at the nuclear environment such as nuclear power plant etc. was related to the oxidation due to the irradiation. Accordingly, in this research, oxidation of XLPE cable insulation as result of the radiation degradation in nuclear power plant was evaluated. XLPE was irradiated with gamma ray(γ-ray) up to 2000kGy at a dose rate of 5kGy/hr in the presence of air at room temperature. Thermal analyses such as temperature at 5% weight loss and oxidative induction time using TGA and DSC were carried out for each irradiated specimens as well. Tensile properties and FT-IR analysis was investigated for each irradiated specimens.

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2. Experimental Procedures

2.1 Sample preparation

In this study, 22.9kV XLPE cable insulation was used as a control specimen. It was cut as a sheet type with a thickness of 0.2mm. For the purpose of evaluation the radiation degradation of XLPE, thermal analyses and tensile properties as radiation degradation carried out. The samples were irradiated with γ-rays in the presence of air at room temperature, in a ^{60}Co facility at the Korea Atomic Energy Research Institute. The overall doses were 400, 800, 1200, 1600, and 2000kGy at a dose rate of 5kGy/hr.

2.2 TGAs

Thermal gravimetric analysis was performed to confirm the co-relationship between mechanical properties and its probable rules. Thermal gravimetric analysis carried out with 10°C/min of increasing rate for measuring the temperature at 5% weight loss and 1, 2, 5 and 10°C/min of increasing rates for activation energy, at nitrogen atmosphere using Thermo gravimetric analyzer (TA Instrument, Model 2950).

The Kissinger method has been used in this study to determine the activation energy from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experi-

ments [2]. The activation energy can be determined by the Kissinger method without a precise knowledge of the reaction mechanism, using the following equation:

$$\ln\left(\frac{\beta}{T_{maz}^2}\right) = \left\{\ln\frac{AR}{E} + \ln[n(1-a_{\max})^{n-1}]\right\} - \frac{E}{RT_{\max}}$$

where β is the heating rate, T_{max} is the temperature corresponding to the inflection point of the thermal oxidative degradation curves which corresponding to the maximum reaction rate, A is the pre-exponential factor, α_{max} is the extent of conversion at T_{max}, and n is the reaction order. From a plot of $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$ and the fitting to a straight line, the activation energy E can be calculated from the slope. T_{max} was measured using differential thermogravimetry (DTG) curves at various heating rates.

2.3 DSC

The oxidative induction time (OIT) measurements were made in TA Q1000 differential scanning calorimeter at 180°C. Each irradiated sample was cut into small pieces, placed in an aluminum pan. The temperature was raised to 180°C at the rate of 10°C/min in nitrogen atmosphere and then the atmosphere was changed to oxygen and held at a constant temperature until the exothermic oxidation reaction was completed. The OIT was the intersection of the extrapolations of the DSC baseline and the tangent to the exotherm [3].

2.4 FT-IR

The radiation degradation of XLPE was investigated using infrared emission spectroscopy. FTIR-ATR (Fourier transform infrared attenuated total reflection) spectrometer was used to specify the structural changes as γ-ray irradiation.

2.5 Tensile Properties

The irradiated XLPE and the control were subject to tensile mechanical testing following ASTM standard D 638 [4]. The tensile properties of the sample at room temperature were evaluated using an Instron universal mechanical tester (Model 1130), after γ-ray irradiation during one week. A crosshead speed of 100 mm/min and a gauge length 50 mm were used. The specimen load was sensed by a 500 kg capacity Instron type-A load cell. This cell was mechanically calibrated by precision standard weights prior to the testing of each set of samples. From these experiments, elongation at break and tensile strength of all samples was obtained. An average of 5 specimens was tested. All tensile tests were run under time mode.

3. Results

3.1 TGA

TG thermograms of γ-ray irradiated XLPE under nitrogen gas are shown in Fig. 1. One stage weight loss was observed. The weight loss of the sample was almost stable below 150°C, but above 200°C the weight loss increased abruptly. As radiation dose increased, the thermograms shifted toward the left side and decomposing temperature decreased. Temperature at 5% weight loss and activation energy of γ-ray irradiated XLPE are shown in Fig. 2. In this figure, below 400kGy radiation dose, temperature at 5% weight loss ($T_{5\%}$) decreased as radiation doses abruptly and thereafter, $T_{5\%}$ decreased slightly.

Fig. 3 shows the DTG thermograms of 2000kGy irradiated XLPE at various heating rates. As the heating rate increased, the thermograms shifted toward the right. On the DTG curves, the most rapidly decomposing temperature of the curves (T_{max}) is clear and it increased with the increase of heating rate. These values at 1, 2, 5 and 10°C/min were 432.49, 442.30, 457.53 and 469.31°C, respectively. To esti-

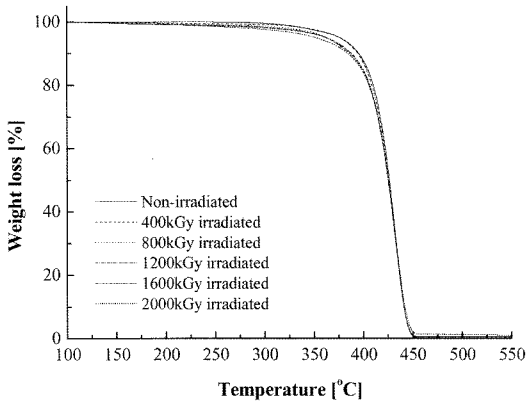

Fig. 1. TG thermograms of γ-ray irradiated XLPE

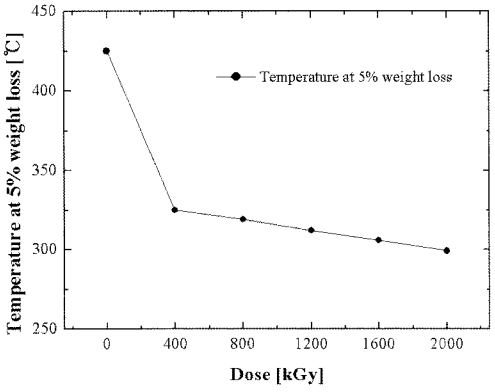

Fig. 2. Temperature at 5% weight loss of γ-ray irradiated XLPE

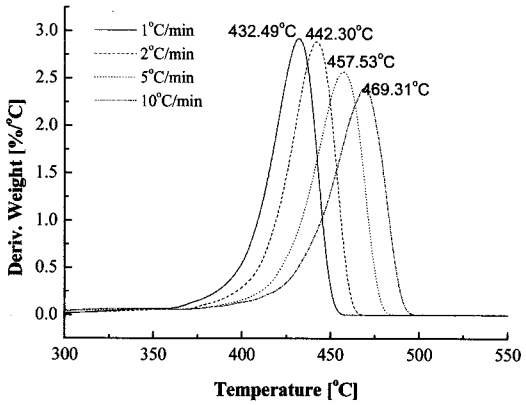

Fig. 3. DTG thermograms of 2000kGy irradiated XLPE at various heating rates

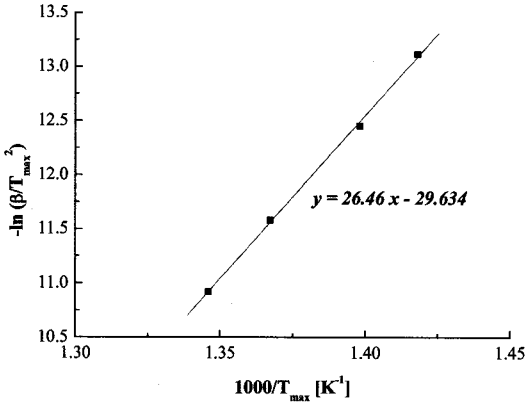

Fig. 4. The Kissinger plots of 2000kGy irradiated XLPE

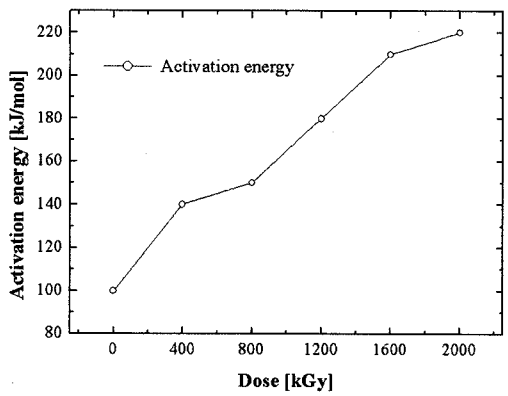

Fig. 5. Activation energy of γ-ray irradiated XLPE

mate the decomposition activation energy through the Kissinger equation as shown, the value T_{max} could be measured from DTG curves in Fig. 3 and the relationship between the two terms of the Kissinger equation such as $\ln(\beta/T_{max}^2)$ and $1/T_{max}$ are plotted in Fig. 4. Thermal decomposition activation energy were obtained from the slopes of the straight lines in the relation plot of $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$. Fig. 5 shows the calculated thermal decomposing activation energies of non-irradiated and γ-ray irradiated XLPE samples on 400, 800, 1200, 1600, 2000kGy were 95.9, 140.6, 152.7, 177.6, 213 and 219.3kJ/mol respectively. As radiation dose increased, thermal decomposing activation energy increased. From the test results, it is confirmed that the XLPE insulated electrical system can be evaluated by measuring the thermal decomposing activation energy against radiation degradation.

3.2 DSC

Fig. 6 shows the melting point of γ-ray irradiated XLPE. The melting point of the sample decreased as radiation dose increased. Below 800kGy it decreased abruptly, and thereafter decreased slightly. As radiation dose increased, the melting peaks shifted toward the left side. The measured values for oxidative induction time (OIT) and melting point as a

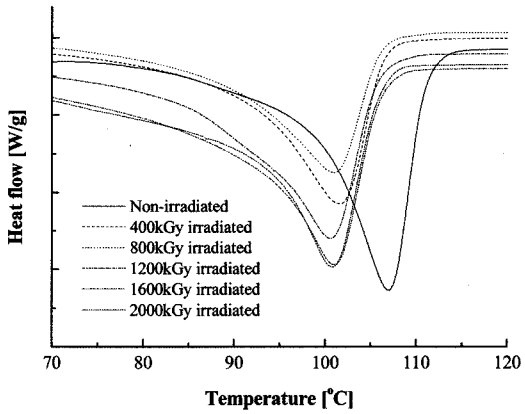

Fig. 6. DSC melting curves of γ-ray irradiated XLPE (heating rate; 10°C/min)

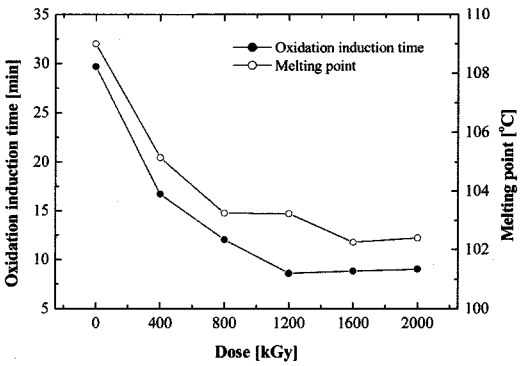

Fig. 7. Oxidative induction time and melting point of γ-ray irradiated XLPE

function of radiation dose are given in Fig. 7. The shape of the OIT curve is similar to the plots of melting point, elongation at break and tensile strength as a function of radiation dose (see Fig. 9), which is expected since OIT should also be a measure of degradation [5]. These results indicate that OIT can be used to measure aging approximately, or at least to assure that the aging is not excessive. An advantage of the use of OIT and TGA for assessment of aging effect of polymeric insulator is the very small amount of material needed for a measurement. Therefore, these thermal analyses such as TGA and DSC are non-destructive in the sense that minute samples which can be obtained from the insulation surface for analysis.

3.3 FT-IR

Fig. 8 shows the FT-IR spectra of γ-ray irradiated XLPE. Irradiation in the presence of air results in several changes in the polymer structure [6]. Compared with non-irradiated control sample, carbonyl (1715cm^{-1}) was formed in γ-ray irradiated sample, and the peaks became large as radiation doses increase. In 400kGy, 800kGy irradiated sample, hydroxyl peak (3200~3313cm^{-1}) occurred. At higher doses, a double bond (C=C, 1610 cm^{-1}) was observed as well as a loss of hydroxyl peak. These result in oxidation reaction due to irradiation of XLPE in the presence of air [7]. As radiation doses was increased, the concentration of carbonyl peaks were increased.

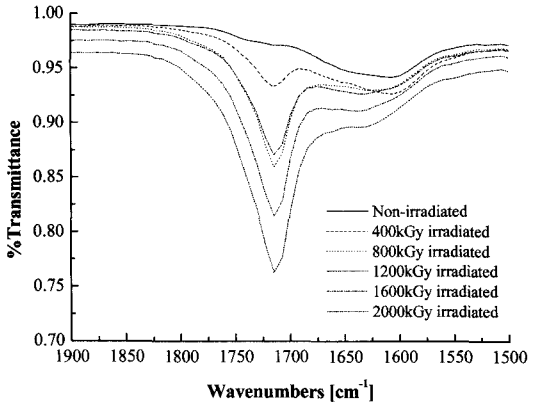

Fig. 8. FTIR-ATR spectra of γ-ray irradiated XLPE

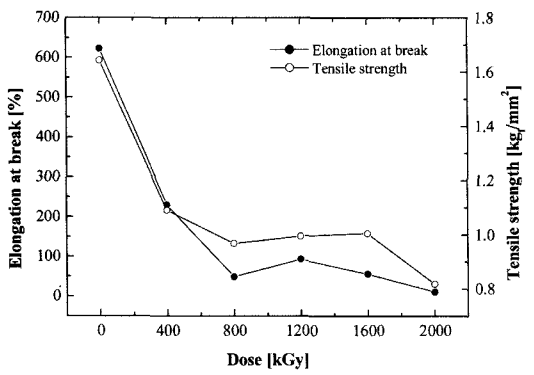

Fig. 9. Elongation at break and tensile strength of γ-ray irradiated XLPE

3.4 Tensile properties

Fig. 9 shows on elongation at the break and tensile strength of γ-ray irradiated XLPE. As radiation doses increased, elongation at breakdown decreased sharply below 800kGy dose and was saturated above 800kGy dose. Below 800kGy dose, decrease of elongation was considered due to loss of elasticity because predominant cross-linking reactions and recombination with side chains scission made structural changes from linear to network. Cross-linking reactions occurred competitively with oxidative reaction above 800kGy dose (see Fig. 8), even though radiation doses increased. On the whole, elongation at breakdown and tensile strength as a function of radiation doses was proportional to temperature at 5% weight loss, oxidative induction time, and melting point.

4. Conclusions

Temperature at 5% weight loss, thermal decomposing activation energy, melting point, oxidative induction time, FT-IR and tensile strength of γ-ray irradiated XLPE were measured for evaluating the radiation degradation of XLPE cable insulation. From the results, the following conclusions have been reached:

(1) The shapes of temperature at 5% weight loss, oxidative induction time, elongation at break as a function of radiation dose all showed simiilar tendency, all decreasing as the radiation dose is increased.

(2) Thermal decomposing activation energy increasaed as the radiation dose is increased.

(3) As radiation dose increased, it was confirmed by FTIR spectra of γ-ray irradiated XLPE that oxidative reactions have ocurred.

(4) The results showed the similar tendency for radiation degradation. TGA, DSC and FTIR analyses can be useful tools for evaluating the oxidation of insulating material by non-destructive testing method.

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