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Radiation Effects on γ-Ray Irradiated Ethylene Propylene Rubber using Dielectric Analysis

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Abstract - To evaluate the radiation degradation of ethylene propylene rubber (EPR), radiation effects on EPR were investigated by using dielectric analysis and thermal-gravimetric analysis. Permittivity, loss factor, tanδ, and thermal decomposition temperature were observed for γ-ray irradiated EPR. As the radiation dose was increased, the peak temperature of the loss factor and tanδ of EPR were increased and loss factor and tanδ at peak temperature were decreased. Activation energies were calculated using loss factor and thermal decomposition for γ-ray irradiated EPR as well. The trends of both calculated activation energies showed the same tendencies as radiation dose was increased.

Keywords: EPR, radiation effects, dielectric analysis, activation energy

1. Introduction

The electrical properties of polymeric insulating materials could be compromised by their working environments, one of the most deleterious of which is that exposed to nuclear radiation [1]. Particularly, the electrical failure induced from the breakdown of insulation materials is important in nuclear power generating stations. Therefore, excellent radiation resistance characteristics as well as electrical and mechanical properties must be considered for these materials so that serious accidents can be avoided.

Radiation and thermal degradation under the normal and accident operations of a reactor in the nuclear power generating stations can be deleterious degradation factors. IEEE quality standards regulate that class 1E electric cable, field splices, and connections can endure ^{60}Co to a dosage of 0.5 [MGy] under normal conditions, even 1.5 [MGy] for loss of coolant accident (LOCA) conditions [2].

In particular, dielectric tanδ is widely used for the evaluation of insulation degradation with electrical insulating resistance. In case of an increasing leakage current through the insulation materials, increased dielectric tanδ would be accompanied, then the temperature inside the materials would be increased as increased applied voltage. Consequently, breakdown strength would be degraded. Because of these phenomena, dielectric tanδ can cause long-term breakdown in the insulating materials and increase abruptly by absorption of the moisture. Therefore, diagnosis of dielectric properties is determined by evaluating the degradation of the insulating materials [3].

In this study, dielectric permittivity, loss factor, and tanδ were measured to develop the evaluation technique on the radiation degradation of EPR because dielectric characteristics are related to molecular interaction and these affect its mechanical properties. The thermal gravimetric analysis and mechanical properties were also measured.

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2. Experimental

2.1 Sample Preparation

In this study, EPR was used as a control specimen. EPR was made of a 50:50 [mol%] composition ratio of ethylene to propylene and provided by JINRO Industries (Korea).

For the purpose of comparing the dielectric, thermal analyses, and mechanical properties as radiation degradation occurs, 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 total doses were 400, 800, 1200, 1600, and 2000 [kGy] at a dose rate of 5 [kGy/hr].

2.2 Dielectric Properties Measurement

In the dielectric analysis, the sample is placed in direct contact with the sensor. The electrodes transmit an applied oscillating voltage to the sample and sense the response of the sample from the applied voltage. The optimum sensor arrangement for monitoring the bulk properties of the EPR sheet is the ceramic parallel plate sensor. The parallel plate

sensor consists of lower and upper electrodes. The lower electrode is the excitation electrode and contains a resistance temperature detector (RTD) to accurately monitor sample temperature. The upper electrode is the response electrode and contains a guard ring to prevent fringing effects. Fig. 1 shows a measurement system to measure dielectric permittivity, loss factor, and tanδ.

Dielectric properties were investigated using a Dielectric Analyzer (TA instrument, Model 2970). A sample EPR sheet (0.2 mm thick) was placed on the ceramic parallel plate sensor, and after purging for 3 minutes with dry nitrogen gas, the upper ram was lowered to exert 300 [N] of force on the sample. Data was acquired while heating at a rate of 3°C/min from -150°C to 50°C and multiplexing frequency (1, 3, 10, 30, 100, and 300 Hz and 1, 3, 10, 30, and 100 kHz) at a constant voltage of 1 [V].

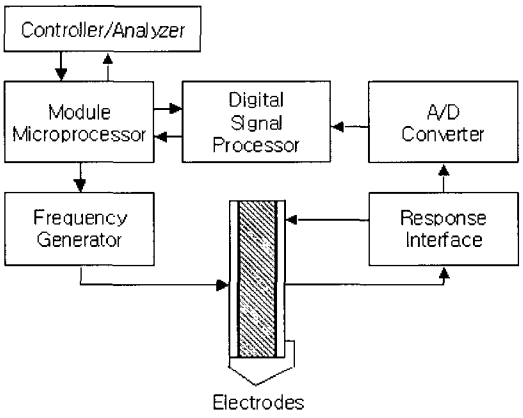


Fig. 1 Block diagram of dielectric parameters measurement system

Dielectric analysis offers high sensitivity, a wide frequency range, and the ability to accommodate a wide variety of samples. These qualities permit the characterization of subtle molecular transitions that are not easily distinguishable by other thermal analysis techniques. The energy of activation can be obtained by performing a linear least squares analysis on the plot of ln(frequency) versus $1/T_{max}$ where T_{max} is the temperature that corresponds to the loss factor peak maximum at a certain test frequency. The slope of the resultant plot when multiplied by the gas constant R (8.314 J/mole) will reveal the energy of activation.

2.3 Thermal Gravimetric Analysis

Thermal gravimetric analysis was performed to confirm the co-relationship between dielectric properties and mechanical properties. Thermal gravimetric analysis was carried out with 10°C/min increased rate for measuring the temperature at 5% weight loss and 10, 25, 50, 75, and 100°C/min increased rates for thermal decomposition activation energy measurement in a nitrogen atmosphere using a 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 experiments [4]. The activation energy can be determined by the Kissinger method, without precise knowledge of the reaction mechanism, using (1).

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

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

2.4 Mechanical Properties

The control and the irradiated EPR samples were subject to mechanical tensile testing following the ASTM standard D638 [5]. The tensile properties of the sample at room temperature were evaluated using an Instron universal mechanical tester (Model 1130) after γ-irradiation. A crosshead speed of 100 mm/min and a gauge length of 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 testing each set of samples. From these experiments, elongation at break of all samples was obtained. Five specimens were tested and the average values were obtained. All tensile tests were run under time mode.

$$\varepsilon=\frac{L-L_0}{L_0}\times 100$$

where ε is elongation at break, L is the length at break, and L_0 is initial length of the specimen.

3. Results and Discussion

3.1 Dielectric Properties

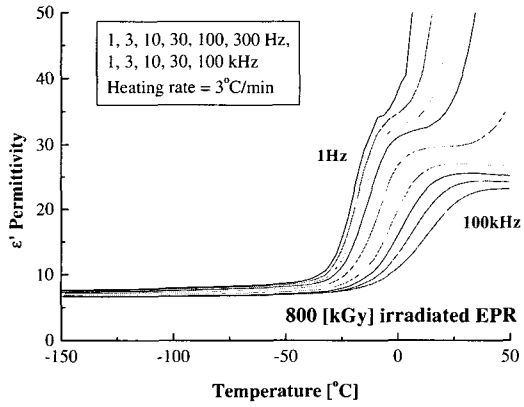
In general, dielectric permittivity and loss factor of the

insulating materials depend upon the applied voltage, frequency, and temperature [6]. In this research, the permittivity, loss factor, and tanδ measurements were carried out for non-irradiated and 400, 800, 1200, 1600, and 2000 [kGy] irradiated EPR at various frequencies from -150°C to 50°C of temperature ranges. The dielectric properties' tendencies of each irradiation dose of EPR was shown to be similar. On behalf of all data, frequency dependency of permittivity, loss factor, and tanδ on 800 [kGy] irradiated EPR are shown in Fig. 2. As applied frequency increased, permittivity, loss factor, and tanδ decreased. This can be explained using the Debye equation about permittivity and loss factor, as shown in (2) and (3) [7].

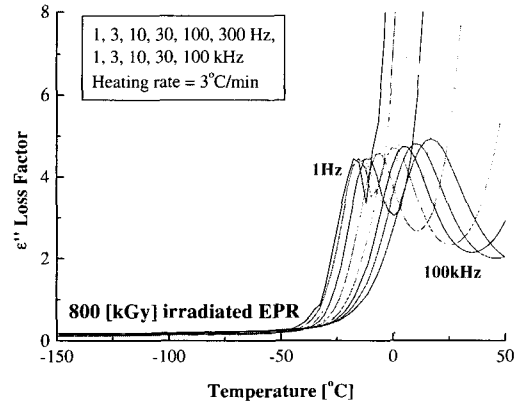
$$\varepsilon' = \frac{(\varepsilon_r - \varepsilon_u)}{1+(\omega\tau)^2} \tag{2}$$

$$\varepsilon'' = \frac{(\varepsilon_r - \varepsilon_u)\omega\tau}{1+(\omega\tau)^2} + \frac{\sigma}{\omega\varepsilon_0} \tag{3}$$

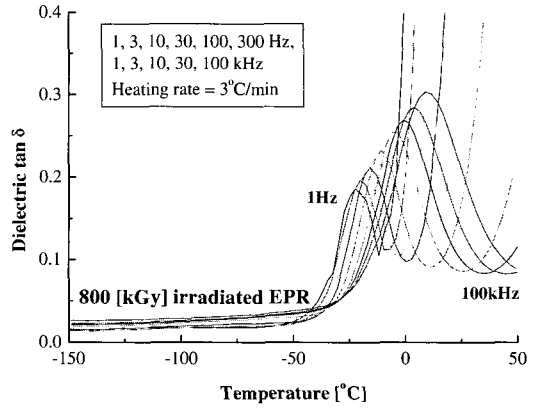
where $\varepsilon'$is dielectric permittivity, $\varepsilon''$is the dielectric loss factor, ε_u is unrelaxed permittivity, ε_r is relaxed permittivity, τ is relaxation time (sec), and σ is ionic conductivity (1/ohm· m).



(a) Permittivity



(b) Loss factor

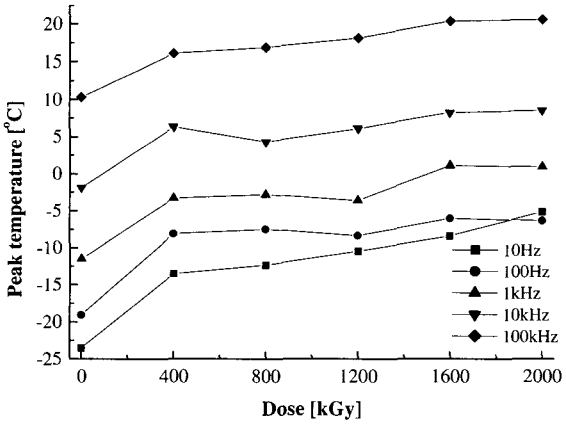


(c) Tanδ

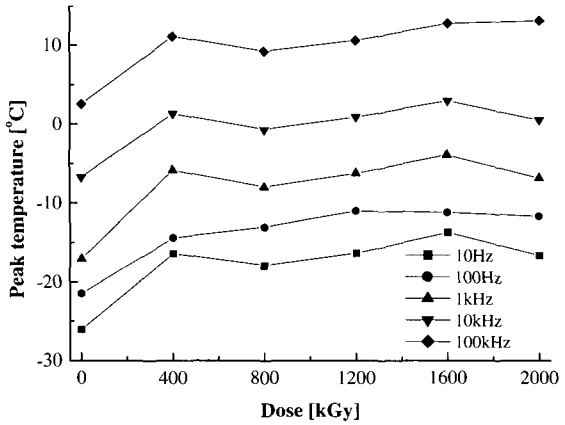
Fig. 2 Frequency dependency of permittivity, loss factor, and tanδ on 800 [kGy] irradiated EPR (applied voltage: 1V)

The dielectric data reveals one relaxative frequency-dependent transition. The alpha transition or glass transition is seen starting in the temperature region of -25°C. The alpha transition is due to large scale rotational motion of dipoles in the amorphous phase [8].

Temperature at peak in the loss factor and tanδ curves of EPR as a function of γ-ray irradiation are shown in Fig. 3. Both loss factor and tanδ, the values of peak temperature showed increasing tendency as irradiation doses were increased in each measured frequency. The EPR sample seems to be deteriorated by γ-ray irradiation, and the peak temperature shifts toward a higher temperature by the decomposition of the crystalline portion [9, 10]. With a high dose, the irradiated EPR crystalline portion is decreased by the oxidation reaction compared with non-irradiated and low dose samples, and it agrees well with previous research [11]. Above the temperature that starts at the transition peak of each frequency, i.e., the region of -25°C at 1 Hz, the values of loss factor and tanδ at a constant temperature show no regular tendency versus radiation doses.



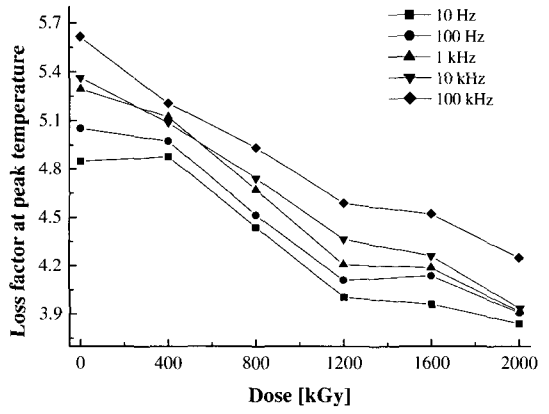
(a) Loss factor



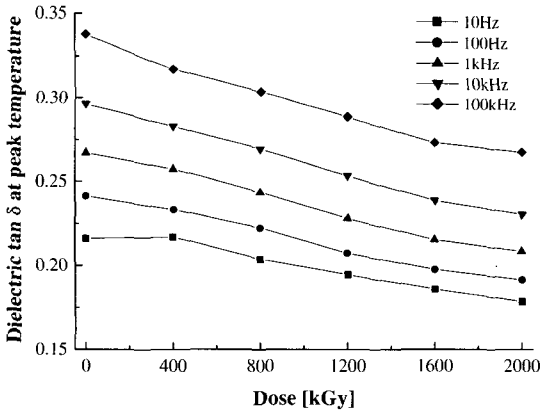
(b) Tanδ

Fig. 3 Temperature at peak in loss factor and tanδ curves of EPR as a function of γ-ray irradiation (applied voltage: 1V)

Loss factor and tanδ of EPR at a transition temperature as a function of γ-ray irradiation are shown in Fig. 4 the values of loss factor and tanδ decreased as applied frequencies were increased. As applied frequencies increased,



(a) Loss factor



(b) Tanδ

Fig. 4 Loss factor and dielectric tanδ of EPR at a transition temperature as a function of γ-ray irradiation (applied voltage: 1V)

dielectric loss factor decreased abruptly and dielectric tanδ was proportional to the loss factor. This tendency is well explained by the Debye equation about the loss factor. The denominator of the first term was increased abruptly and ionic conductivity was also increased in (3) as applied frequencies increased. In Fig. 4, the values of loss factor and tanδ at a transition temperature decreased linearly as radiation doses increased, and these tendencies can be a useful tool for evaluating the radiation degradation of EPR.

Fig. 5 shows the values of the loss factor and tanδ of γ-ray irradiated EPR at 40°C of measuring temperature, which is similar to the temperature of real cable situations in the nuclear power plant. Both the loss factor and tanδ increased as radiation dose was increased. The increase of the loss factor is due to the oxidation reaction during the EPR's exposure to γ-ray. Dielectric loss analysis and FTIR spectroscopy are very convenient methods for detecting the early stages of degradation, mainly oxidation [12]. M. Giurginca et al. confirmed that oxygenated functional groups accumulated as radiation dose was increased using the FT-IR spectrum of γ-ray irradiated EPR [13]. The increase of tanδ on the irradiated sample is interpreted as due to cracks and micro-voids inside the polymer that were created with irradiation and then discharge inside the cracks and voids result in heating loss [14].

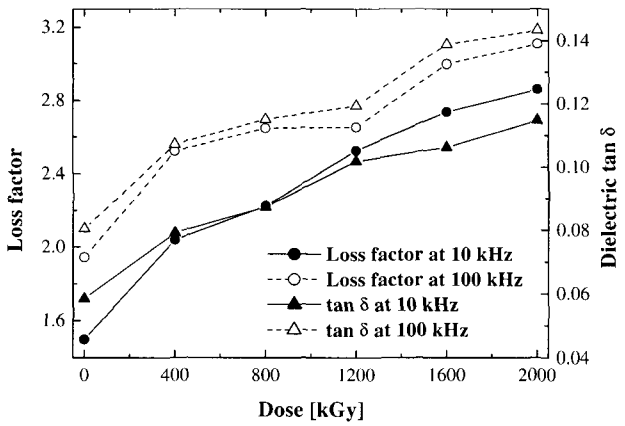


Fig. 5 Loss factor and dielectric tanδ of EPR at 40°C as a function of γ-ray irradiation (applied voltage: 1V)

3.2 Thermal Gravimetric Analysis and Mechanical Properties

Fig. 6 shows weight versus temperature of γ-ray irradiated EPR. A similar tendency of weight loss was observed for non-irradiated and γ-irradiated EPR. For non-irradiated EPR, residual weight above 500°C is around 35%. However, residual weight above 500°C is about 42% for all irradiated samples regardless of the irradiated dose. The decomposing temperature decreased as the irradiation doses were increased. The 5% decomposing temperature of

non-irradiated EPR was about 353.18°C, and that of 2000 [kGy] irradiated EPR was 345.2°C. Under irradiation as well as high temperature in the presence of oxygen, the degradation of the polymeric insulation became severe due to the oxidation reaction in which the main polymeric chains are broken down and the weight of the decomposition by-products is lighter and volatile enough [4].

For a lot of polymeric materials used in electrical insulation applications, the damaging effects of radiation interaction will be evident in the mechanical properties, and loss in tensile strength or elongation will be the failure criteria rather than the change in electrical properties [15].

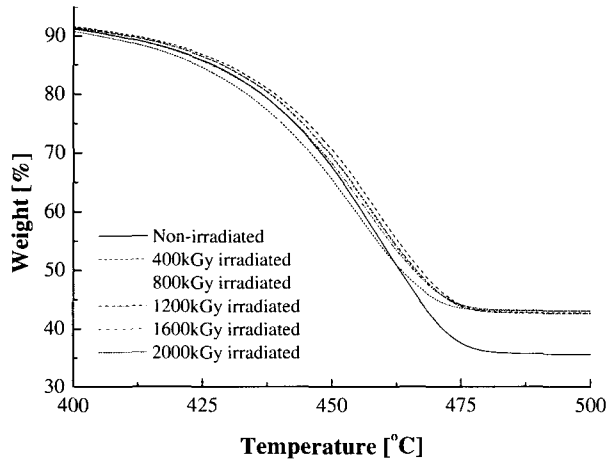


Fig. 6 TG thermograms of EPR as a function of γ-ray irradiation (heating rate: 10°C/min)

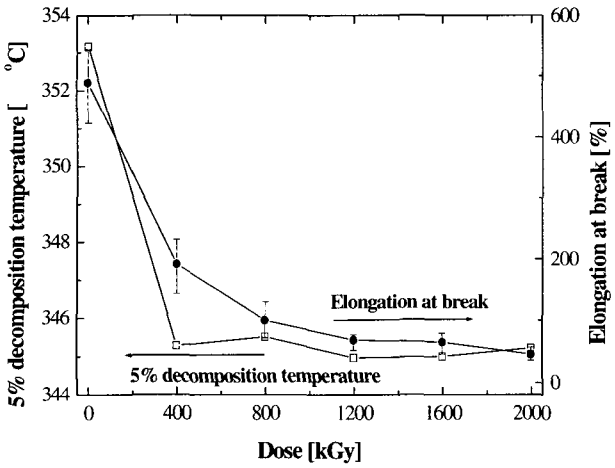


Fig. 7 5% decomposition temperature and elongation at break of EPR as a function of γ-ray irradiation

For many polymers, oxidation is the dominant ageing mechanism. The result of oxidation is brittle polymeric materials, and consequently, the elongation at break of the materials is an indicator of the state of degradation. Conventionally, the reduction in elongation at break to 50% absolute value is taken as the failure criterion for the insulation materials [16]. Fig. 7 shows the 5% weight loss temperature and elongation at break of the γ-ray irradiated EPR as a function of radiation dose. The tendencies of both 5% weight loss temperature and elongation properties agree well with increasing irradiation doses. Below 400 [kGy] of irradiation, the values of both properties decreased abruptly and both showed saturated tendencies above 400 [kGy] irradiation.

3.3 Activation Energy using Dielectric Loss Factor and Thermal Decomposition

Arrhenius plot was constructed for transition of loss factor curves of irradiated EPR by plotting ln(frequency) versus $1/T_{max}$. Activation energies determined from the slope of these plots are 74.5, 87.7, 94, 87.4, 84.3, and 79 kJ/mole for non-irradiated and 400, 800, 1200, 1600, and 2000 [kGy] for irradiated EPR.

To estimate the thermal decomposition activation energy through the Kissinger equation, the value of T_{inf} could be measured from the DTG curves. In general, the Arrhenius equation for using thermal decomposition activation energy is widely used as a physical model for lifetime prediction during thermal aging [7, 8]. Thermal decomposing activation energies were obtained from the slopes of the straight lines in the relation plot of $-\ln(\beta/T_{inf}^2)$ versus $1000/T_{inf}$. The calculated thermal decomposing activation energies as a function of radiation dose are shown in Figure 8.

The trend of the calculated activation energies from dielectric loss factor and thermal decomposition agreed well with each other for increasing radiation doses. For low irradiation dose, below 800 [kGy], both calculated activation energies from dielectric loss factor and thermal decomposition increased abruptly. Some weak portion is considered to be volatile and the binding energy, if residues are high enough, is due to γ-ray irradiation. On the other hand, the calculated activation energies were decreased for high irradiation above 800 [kGy]. Above an 800 [kGy] irradiation dose, the decreasing of activation energies are assumed because the main chains were decomposed.

The calculated activation energies of γ-ray irradiated EPR are not in accordance with the results from the mechanical properties and 5% weight loss temperature from TGA. In a high dose region, mechanical test and 5% weight loss temperature show no remarkable differences as irradiation doses were increased. However, the oxidation reaction still occurred at a high dose region, and this can be evaluated by the results of the calculated activation energies. It is possible to detect the degradation characteristics of high dose irradiated EPR by using activation energies calculated from dielectric loss factor and thermal decomposition.

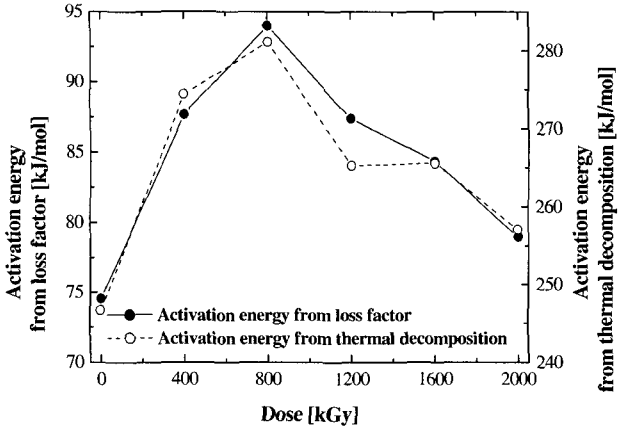


Fig. 8 Activation energies of γ-ray irradiated EPR using loss factor and thermal decomposition

4. Conclusions

To study the radiation degradation of EPR using dielectric analysis, dielectric loss factor and tanδ were compared with the results of TGA and mechanical tests.

From the results, the following conclusions were obtained for irradiation doses.

1. As irradiation dose increased, the values of dielectric loss factor and tanδ were increased due to the radiation-induced oxidation reaction.

2. The values of thermal decomposition temperature and elongation at break, which is an indicator of the state of degradation, were constant above 800 [kGy] irradiation dose, but the values of dielectric loss factor were increased.

3. The values of activation energies calculated from dielectric loss factor and thermal decomposition showed similar tendencies, and showed that the oxidation of EPR occurs at a high dose of irradiation.

Acknowledgements

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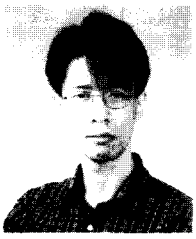

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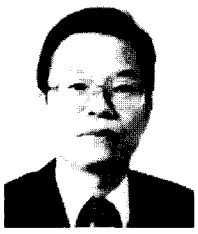

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