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Dielectric Relaxation Characteristics of Gamma-ray Irradiated Polyetheretherketone

Chung Lee [a], Ki-Yup Kim [a], Jae-Hee Kim [a], Boo-Hyung Ryu [b]
a Korea Atomic Energy Research Institute, 150 P.O.Box 105, Yuseong, Daejon, 305-353, clee@kaeri.re.kr
b Dept. of Safety Engg., Dongguk Univ. Seokjang, Kyungju, 780-350

1. Introduction

Polymeric insulating materials are widely used in a broad range of applications from the power supply industry to inner and outer space. However, the electrical performance of these materials could be compromised by their working environments and one of the most deleterious is nuclear radiation exposure such as a nuclear reactor and radiation facilities [1]. Poly- etheretherketone (PEEK) with low density, crystallisable thermoplastic and excellent heat and radiation resistance, is attracting attention as a next-generation electrical insulation. Even though radiation hardening materials such as PEEK are used in nuclear power plants, must have radiation and thermal resistance at the same time, however, only a few studies on both radiation and thermal degradation of the materials have been carried out.

In the present paper, molecular relaxation in radiation and thermal and thermal-radiation accelerated aged PEEK have been investigated using dielectric analyses.

2. Experimental

2.1 Sample preparation

The sample was PEEK films (300 μm thick, medium viscosity grade 450G; Victrex plc Inc.) cut into 250 by 250 mm squares for dielectric measurement.

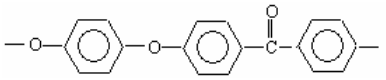

Figure 1. Repeating unit of PEEK

2.2 Thermal accelerated ageing

Calculation of the activation energy In this work, the thermal decomposing activation energy of PEEK was calculated for the prediction of the equivalent lifetime using thermal accelerated ageing. A TGA run and Flynn-Wall Ozawa equation were used to be obtained the activation energy of the thermal decomposition reaction [2]. The calculated activation energy was 241.87 kJ/mol.

$$\log F(\alpha) = \log \frac{AE_a}{R} - \log \beta - 2.315 - 0.4567 \frac{E_a}{RT} \qquad (1)$$

where A is the pre-exponential factor, β is the heating rate [K/min], R is the gas constant (=8.314 J·mol^{-1}K^{-1}), and E_a is the thermal decomposing activation energy [kJ/mol].

Thermal accelerated ageing using activation energy The thermal degradation was accelerated at 130ºC by the Arrhenius exploit method using the activation energy calculated by TGA.

Table 1. Equivalent lifetime and accelerated thermal ageing period of PEEK at T_1: 130°C, T_2: 90°C

Sample No.	Accelerated thermal ageing period, k_1 (hr)	Equivalent lifetime, k_2 (year)
PEEK$_0$	0	Virgin
PEEK$_{10}$	193	10
PEEK$_{30}$	579	30
PEEK$_{50}$	965	50

2.3 Radiation and thermal-radiation ageing

For the purpose of the dielectric relaxation properties with radiation degradation, the sample was irradiated with gamma 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 1000, 2000, 3000 kGy at a dose rate of 5 kGy/hr. For investigating the dielectric properties of the multi-aged PEEK, *i.e.* thermal ageing and radiation ageing, PEEK$_{10}$, PEEK$_{30}$, PEEK$_{50}$ were irradiated with a gamma ray of 400 kGy and 1000 kGy. The nomination of the aged samples was used with subscripts for thermal ageing and with superscripts for radiation ageing.

3. Results and discussion

3.1 Frequency dependency of ε_r' and ε_r"

Measured results of the temperature dependency of ε_r' is described first. At f = 1 kHz, ε_r' of the non-irradiated sample began increasing rapidly at 145°C but slowed above 150°C. Since this occurs above the glass transition temperature (T_g = 150°C), it is a principal dispersion (α dispersion) occurring by dipole orientation involving the main chain segment movement [3]. For a practical polymer, two kinds of dielectric absorption and dispersion of the temperature are above T_g, it is related with the frequency dependency at a constant frequency. In accordance with the previous research [4], PEEK has two kinds of absorption and dispersion at 150°C and 300°C. The temperature at which ε_r' begins to increased the shifted rapidly at higher temperatures is with thermal ageing and radiation dose. The variation in magnitude of the free volume caused by degradation such as electron beam irradiation was studied using positron annihilation [5]. S. Fujita et al. found that the magnitude of mean

free volume increases rapidly from T_g and this increase is suppressed by electron beam irradiation. It was found that 60 MGy of gamma ray irradiation causes cross-linking among the molecules in PEEK, especially above T_g [6]. It was also found that the C-C strength decreases with radiation dose whereas that of C-O and C=O increases for the oxidation using XPS [7]. From these reasons, radiation and thermal ageing disintegrates the molecules in PEEK, and promotes a cross-linking reaction at the same time, increasing the number of dipoles so that the aged samples showed a larger ε_r'. At a certain temperature, ε_r' increased with an increasing dose and thermal ageing time. It is interpreted that the orientation polarization increased due to the increasing number of dipoles with the radiation dose

3.2 Cole-Cole's circular arc

For many dielectric materials, the frequency properties of the complex relative permittivity (ε_r^*) agrees well with the Cole-Cole's circular arc law. Equation (2) corresponds to this arc [8].

$$\varepsilon_r^* = \varepsilon_{r\infty} + \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{1 + (j\omega\tau_0)^{\beta}} \quad (0 < \beta \leq 1) \qquad (2)$$

where ε_{rs} is the equilibrium permittivity, $\varepsilon_{r\infty}$ is the instantaneous permittivity, ω is the angular frequency, τ_0 is the mean relaxation time, and β is a parameter indicating the relaxation time distribution.
Relaxation intensity $\Delta\varepsilon_r$ is given by equation (3)

$$\Delta\varepsilon_r = \varepsilon_{r0} - \varepsilon_{r\infty} \qquad (3)$$

The circular arcs increased with an increasing radiation dose and thermal ageing time. The values of the relaxation intensity ($\Delta\varepsilon_r$) as a function of ageing are derived in Table 2. As shown in the table, the values of $\Delta\varepsilon_r$ increased with ageing.

The $\Delta\varepsilon_r$ value of $PEEK^{1000}$ (1000 kGy irradiated PEEK) rapidly increased compared with that of non-irradiated PEEK, and that of $PEEK^{2000}$ and $PEEK^{3000}$ was slightly increased. This indicates that radiation induced dipoles and impurities are produced abruptly at a 1000 kGy dose, thereafter, recombination and disintegration of the induced electric charges dominate above 1000 kGy.

As for the thermally aged PEEK, the $\Delta\varepsilon_r$ value of $PEEK_{10}$ increased gradually compared with $PEEK_0$, and that of $PEEK_{30}$ and $PEEK_{50}$ increased abruptly. It is considered that the generation and disintegration of the induced dipoles occurs competitively, and the space charge polarization increases by rapidly increasing the impurity ions more than $PEEK_{10}$.

As regards to the thermal-radiation aged PEEK, the magnitude of $\Delta\varepsilon_r$ is as follows; $PEEK_{10}^{400} > PEEK_{30}^{400} > PEEK_{50}^{400} > PEEK_{10}^{1000} > PEEK_{30}^{1000} > PEEK_{50}^{1000}$.

These results indicate that the degradation of PEEK depends mainly on radiation degradation, and is influenced by thermal ageing as well.

Table 2. Dielectric relaxation intensity of aged PEEK at 160°C

Sample		$\Delta\varepsilon_r$
Ageing	**No.**	
Virgin	$PEEK_0$	0.784
1000 kGy	$PEEK^{1000}$	0.9353
2000 kGy	$PEEK^{2000}$	0.9543
3000 kGy	$PEEK^{3000}$	1.0398
10 yr	$PEEK_{10}$	0.7983
30 yr	$PEEK_{30}$	0.9009
50 yr	$PEEK_{50}$	0.9828
10yr + 400kGy	$PEEK_{10}^{400}$	1.0713
10yr + 1000kGy	$PEEK_{10}^{1000}$	1.1466
30yr + 400kGy	$PEEK_{30}^{400}$	1.0578
30yr + 1000kGy	$PEEK_{30}^{1000}$	1.1853
50yr + 400kGy	$PEEK_{50}^{400}$	1.1035
50yr + 1000kGy	$PEEK_{50}^{1000}$	1.2017

4. Conclusion

Dielectric properties of gamma-ray irradiated PEEK, thermally aged PEEK, and irradiated PEEK after thermal ageing were measured with the following results:

Radiation induced electric charges were produced abruptly at 1000 kGy irradiated PEEK. Thereafter, recombination and disintegration of the induced electric charges occurred simultaneously above 1000 kGy.

The degradation level of thermal-radiation aged PEEK depended upon the radiation degradation.
The relaxation intensity values from the arcs can be useful for the evaluation of degradation level of PEEK.

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REFERENCES

[1] S.S. Bamji, *IEEE Trans. on EI.*, Vol. 27, No. 2, pp. 402-404, 1992.
[2] Annual book of ASTM standards, E1641, pp. 1041-1045, 1994.
[3] C.J. Pratt and M.J.A. Smith, *7th Int'l Conf. Dielectr. Materi. Measure. Applic.*, pp. 64-67, 1996.
[4] C. Lee *et al*, *Proc. of the KIEEME Annual Summer Conf. 2003*, Vol. 4, No. 1, pp. 485-488, 2004. (Korean)
[5] K. Shinyama, M. Baba and S. Fujita, *Proc. of 1998 Int'l Symp. on Electr. Insul.*, pp. 387-391, 1998.
[6] A.S. Vaughan and G.C. Stevens, *Polymer*, Vol. 36, No. 8, pp. 1531-1540, 1995.
[7] K. Shinyama, M. Baba and S. Fujita, *Prep. Int'l Conf. on Material Engg. for Resources*, pp. 55-56, 1998.
[8] S. Fujita, K. Shinyama and M. Baba, *10th Int'l Symp. on Electrets*, pp. 115-118, 1999.