Radiation Effects on Dielectric Relaxation of Poly(vinylidene fluoride)

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1. Introduction

Fluoropolymers are well known for their excellent thermal and chemical stability as well as mechanical properties. Among them, Poly (vinylidene fluoride) (PVDF) has attracted considerable attention in many areas of research and industrial use [1]. This is due to its electrical properties, resistance to weathering, durability, biocompatibility, and processibility. Also, its lightweight conformal properties, low cost, availability in large-area sheets, and broad-band acoustic performance have made PVDF an effective piezoelectric material for a variety of invasive medical imaging transducers, ultrasonic transducers and PVDF cables [2-4]. The application of piezoelectric materials for an ultrasonic transducer can be used for the diagnoses of nuclear fuel assembly in nuclear power plants as well as industrial facilities [5]. Even though piezoelectric materials such as PVDF used for non-destructive test in nuclear power plants, must have radiation resistance, only a few studies, however, on radiation degradation of the materials have been carried out.

In the present paper, molecular relaxation in radiation accelerated aged PVDF have been investigated using dielectric analysis.

2. Experimental

2.1 Sample preparation

The PVDF films were supplied by Goodfellow Cambridge (England). The film has a thickness of 0.08 mm and density of 1.76 gm/cm^3. The PVDF films were irradiated with γ-rays on the presence of air at room temperature, in a ^{60}Co facility at the Korea Atomic Energy Research Institute. The total doses were 200, 400, 600, 800, 1000 kGy at a dose rate of 5 kGy per hour.

2.2 Measurement of Dielectric Properties

In the dielectric analysis, the PVDF 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 agreement for monitoring the bulk properties of PVDF is the ceramic parallel plate sensor. The parallel plate sensor consists of a lower and upper electrode. The lower electrode is the excitation electrode and contains a resistance temperature detector (RTD) to accurately monitor the sample temperature. The upper electrode is the response electrode and contains a guard ring to prevent from the fringing effects.

A sample of PVDF film 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 newtons of force on the sample. Data was acquired while heating at a rate of 2.5°C/min from -50 to 150°C and a multiplexing frequency (1, 2, 4, 6, 10, 20, 40, 60, 100, 200, 400, 600 Hz and 1, 2, 4, 6, 10, 20, 40, 60, 100 kHz.).

3. Results

3.1 Frequency dependency of ε_r' and ε_r"

Figure 1 shows the frequency dependency of ε_r' and ε_r" used as the parameters at -30°C. In both cases of the non-irradiated and irradiated PVDF, ε_r' decreased with an increasing frequency. ε_r" peaked from -20 to 0°C, so called, absorption. These phenomena are explained by using dipoles orientation with segment movements of the main chains. In figure 1, ε_r' decreased with an increasing radiation dose at a certain frequency, this is

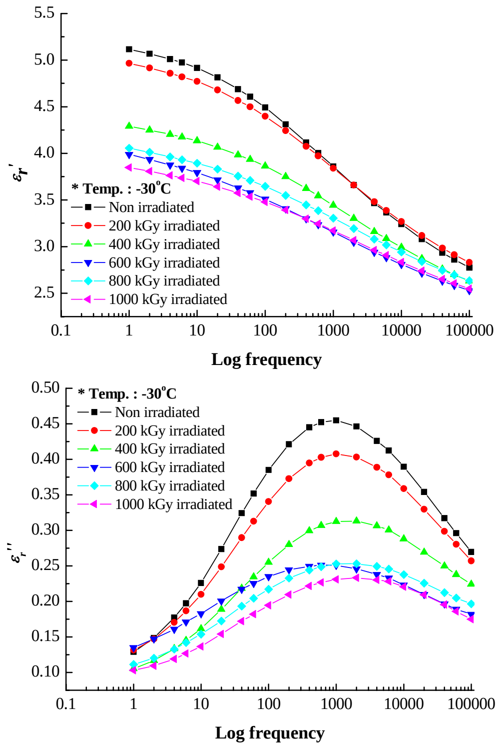

Figure 1. Frequency dependency of ε_r' and εr" of irradiated PVDF.

due to the structural changes in PVDF with ageing as described for the temperature dependency of ε_r' and ε_r'' [9]. The decrease of ε_r' and the peaks of ε_r'' with an increasing frequency is due to the extermination of the atomic, electronics polarization that appears at a low frequency. It is considered that ε_r' and ε_r'' decrease at a certain frequency because of the structural changes of irradiated PVDF, which is contrary to the Debye equation [10].

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 (1) corresponds to this arc [11].

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

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 (2)

$$\Delta\varepsilon_r = \varepsilon_{r0} - \varepsilon_{r\infty} \qquad (2)$$

Cole-Cole's circular arcs of irradiated PVDF are plotted for the frequency dependency of ε_r' and ε_r'' in figure 2. The radii of the circular arcs decreased with an increasing radiation dose. As regards the values of the relaxation intensity ($\Delta\varepsilon_r$) as a function of radiation dose, the values of $\Delta\varepsilon_r$ decreased with radiation dose. A.M Jeffery and D.H. Damon interpreted that these dielectric relaxation characteristics are due to the ionic conduction with ethylene propylene rubber [12], it seems to be contrary to the case of PVDF.

The $\Delta\varepsilon_r$ of 600, 800, and 1000 kGy irradiated PVDF rapidly decreased compared with that of non-irradiated and 200 kGy irradiated PVDF. This indicates that radiation induced dipoles and impurities are extinct abruptly at a 600 kGy dose, thereafter, recombination and disintegration of the induced electric charges dominate above 600 kGy. It is also considered that the generation and disintegration of the induced dipoles occurs competitively, and the recombined molecules of irradiated PVDF are more stable than non-irradiated PVDF.

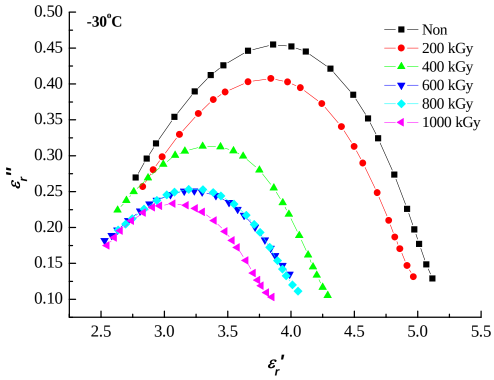

Figure 2. Cole-Cole's circular arc plots of irradiated PVDF at -30ºC.

4. Conclusion

Dielectric properties of gamma ray irradiated PVDF were measured with the following results.

The dielectric relaxation intensity of irradiated PVDF decreased with increasing radiation dose due to the recombination of radiation induced charges and recombined molecules. The dielectric relaxation intensity from the circular arc model can be useful for the evaluation of degradation level of PVDF.

Acknowledgments

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