

Investigation of Proton-Irradiation-Induced Free-Volume Changes in Cyanate Ester Resin

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1. Introduction

Cyanate ester (CE) resins are used as matrix materials for fiber-reinforced plastic (FRP) truss structures in low Earth orbit (LEO) satellites because of their excellent dimensional stability, low dielectric loss, and high thermal stability. In the LEO environment, these externally exposed structures are continuously subjected to radiation from trapped electrons and protons as well as solar energetic particles (SEPs), resulting in accumulated radiation doses [1]. Free volume in polymers is closely associated with molecular mobility, small-molecule diffusion, and physical aging, making it an important microstructural parameter for understanding the long-term radiation durability of CE resins. Positron annihilation lifetime spectroscopy (PALS) is a widely used nondestructive technique for characterizing defects and free-volume properties at the atomic and molecular scales [2]. In particular, the lifetime and intensity of ortho-positronium (*o*-Ps) formed in polymers provide information on the size and relative changes of free-volume holes [3]. In this study, PALS was employed to investigate changes in the free-volume characteristics of CE resin induced by proton irradiation and to evaluate its microstructural stability against proton irradiation from a free-volume perspective.

2. Materials and Methods

The CE resin was cured at 180 °C for 2 h and subsequently machined into rectangular specimens with dimensions of 10 mm × 10 mm × 1.23 mm. Proton irradiation was performed using a 100 MeV proton beam at the TR103 target room of the Korea Multi-purpose Accelerator Complex (KOMAC) (Fig. 1). The absorbed doses were 0, 10, 20, 100, and 200 kGy, with the 0 kGy specimen serving as the non-irradiated reference.

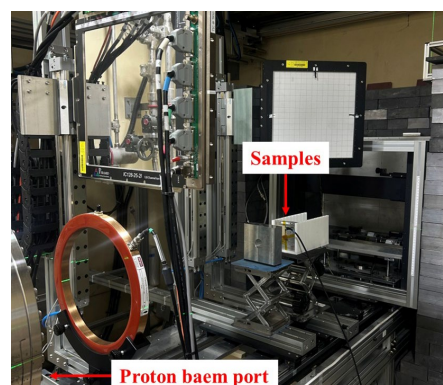


Fig. 1. TR103 target room for proton irradiation.

PALS measurements were performed using a conventional fast-fast coincidence system equipped with plastic scintillators (BC422, Saint-Gobain) and standard electronic modules. The positron source was prepared by depositing a ²²NaCl solution (30 μCi) onto a polyimide foil (10 mm × 10 mm × 7.6 μm), followed by drying and folding the foil in half. For each measurement, the positron source was sandwiched between two identical specimens. The positron lifetime spectra were analyzed using *PALSfit3* software [4]. The source correction was performed using the empirical method proposed by Djourellov and Misheva [5]. The positron annihilation lifetime spectra were analyzed using a three-component lifetime model. Figure 2 shows a representative positron lifetime spectrum of the non-irradiated CE specimen and the corresponding three-component fit. The measured lifetime spectrum was decomposed into three lifetime components, τ_1 , τ_2 , and τ_3 .

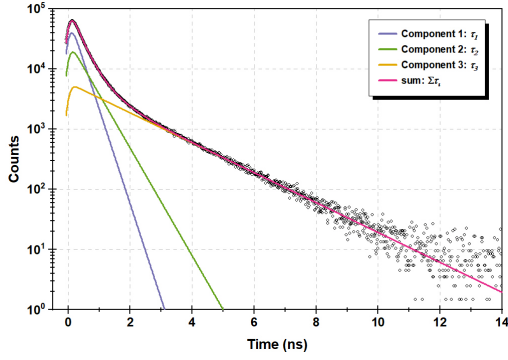


Fig. 2. Positron annihilation lifetime spectrum of the non-irradiated CE resin and its three-component fit consisting of τ_1 , τ_2 , and τ_3 lifetime components.

The free-volume hole radius (R) was determined from the o -Ps lifetime component (τ_3) using the Tao–Eldrup model with an empirical parameter of $\Delta R = 0.166$ nm [3]. The relationship between τ_3 and R is given by

$$\frac{1}{\tau_3} = 0.5 \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]$$

The free-volume hole volume (V_f) and fractional free volume (FFV) were calculated using the following equations:

$$V_f = 4/3 \pi R^3$$

$$\text{FFV} = CI_3 V_f$$

where I_3 is the o -Ps intensity, and C is an empirical scaling constant that accounts for the probability of o -Ps formation. In this study, $C = 0.0018$ was used [3].

3. Results and Discussion

The variations in τ_1 , I_1 , τ_2 , and I_2 as a function of proton absorbed dose are summarized in Table I. Both τ_1 and τ_2 varied with proton irradiation. The maximum changes in τ_1 and τ_2 relative to the non-irradiated specimen were approximately 20.3% and 12.5%, respectively. The corresponding intensities (I_1 and I_2) also varied with absorbed dose. The maximum changes in I_1 and I_2 were approximately 37.0% and 54.6%, respectively. These variations in τ_1 , τ_2 , I_1 , and I_2 suggest that proton irradiation altered the positron annihilation environment within the CE resin and may be associated with irradiation-induced changes in its molecular structure. However, the variations in τ_1 and τ_2 alone are insufficient to identify specific changes in molecular structure or determine the dominant irradiation-induced mechanism.

The variations in the free-volume characteristics of the CE resin, including τ_3 , R , I_3 , and FFV, as a function of proton absorbed dose are shown in Fig. 3. Figure 3(a) shows the variations in τ_3 and R calculated using the Tao–Eldrup model. Both τ_3 and R exhibited similar dose-dependent behavior, increasing with absorbed dose up to

100 kGy and subsequently decreasing at 200 kGy. Compared with the non-irradiated specimen, the maximum increases in τ_3 and R were approximately 4.3% and 2.9%, respectively, at 100 kGy. These results indicate a non-monotonic dose dependence of the mean free-volume hole radius in the CE resin, with an increase up to 100 kGy followed by a partial decrease at 200 kGy.

Table I: Positron lifetime components (τ_1 and τ_2) and their corresponding intensities (I_1 and I_2) of CE resin as a function of proton absorbed dose.

Absorbed Dose (kGy)	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
0	275.5 ± 7.2	46.0 ± 3.9	485.7 ± 20.5	31.3 ± 3.7
10	275.9 ± 7.8	47.2 ± 4.2	488.7 ± 22.7	30.1 ± 3.9
20	279.1 ± 6.0	49.6 ± 3.2	512.2 ± 21.9	27.8 ± 3.0
100	297.8 ± 6.7	55.0 ± 3.6	546.4 ± 32.5	22.4 ± 3.4
200	219.7 ± 7.1	29.0 ± 2.4	428.3 ± 8.2	48.5 ± 2.3

Figure 3(b) shows the variations in I_3 and FFV as a function of proton absorbed dose. The I_3 values remained nearly constant over the entire dose range, ranging from 22.54% to 22.73%, with a maximum change of approximately 0.5% relative to the non-irradiated specimen. This variation was relatively small compared with the maximum changes of approximately 4.3% and 2.9% observed for τ_3 and R , respectively. Thus, while the mean free-volume hole size exhibited some variation with proton irradiation, the o -Ps intensity remained relatively stable over the investigated dose range.

FFV exhibited a dose dependence similar to that of τ_3 and R , increasing up to 100 kGy and subsequently decreasing at 200 kGy. At 100 kGy, FFV increased by approximately 8.7% relative to the non-irradiated specimen. Although FFV decreased at 200 kGy, it remained higher than that of the non-irradiated specimen. Overall, the free-volume characteristics of the CE resin exhibited a non-monotonic dose dependence, with an increase up to 100 kGy followed by a partial decrease at 200 kGy. Despite these dose-dependent variations, the overall changes in the free-volume characteristics remained limited over the investigated dose range.

Ionizing radiation can induce various processes in polymeric materials, including chain scission, crosslink scission, radical formation and recombination, additional crosslinking, and rearrangement of the polymer network. Therefore, the observed increase in the free-volume hole radius and FFV, followed by their partial decrease at the

highest dose, may result from multiple proton-irradiation-induced processes occurring concurrently or from changes in their relative contributions with increasing absorbed dose. However, because PALS primarily provides information on free-volume size and related characteristics, the present results alone cannot unambiguously identify specific molecular-level structural changes or the dominant irradiation-induced mechanism. Further chemical and mechanical characterization is therefore required to clarify the structural modification mechanisms of the CE resin under proton irradiation.

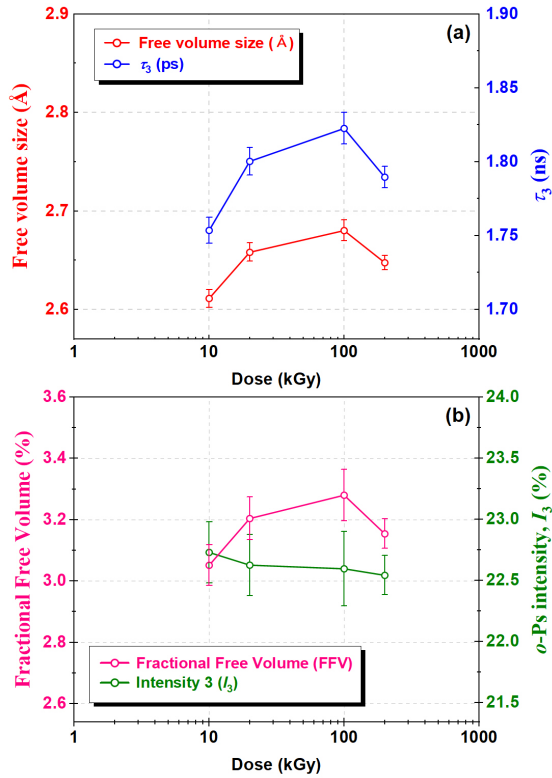


Fig. 3. Free-volume characteristics of CE resin as a function of proton absorbed dose: (a) *o*-Ps lifetime (τ_3) and free-volume hole radius (R); (b) *o*-Ps intensity (I_3) and fractional free volume (FFV). Error bars represent the standard deviations.

4. Conclusions

In this study, PALS was used to evaluate changes in the free-volume characteristics of CE resin induced by proton irradiation. Although the free-volume characteristics exhibited dose-dependent variations, the overall changes remained limited over the investigated dose range up to 200 kGy. In particular, the mean free-volume hole radius showed some variation with absorbed dose, whereas the *o*-Ps intensity remained nearly constant over the entire dose range. These results suggest that the free-volume structure of the CE resin was largely preserved under the present irradiation conditions. The present findings provide experimental baseline data for understanding the radiation response of CE resins used in LEO structural applications.

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