

Neutron-Induced Free Volume Evolution in Cyanate Ester Resin Characterized by Positron Annihilation Lifetime Spectroscopy

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1. Introduction

Cyanate esters (CEs) are well-established high-performance thermosetting resins that have been widely employed as matrix materials for aircraft composites and other aerospace structural applications owing to their high thermal stability and low dielectric loss [1]. The cyclotrimerization of cyanate ester monomers produces highly crosslinked polycyanurate networks containing bulky triazine structures, which result in increased free volume with increasing crosslink density and relatively low moisture absorption [2]. As free volume plays a crucial role in controlling molecular mobility, diffusion behavior, dielectric response, and radiation resistance in high-performance polymer systems, understanding its evolution under irradiation is of significant importance. In aerospace and space environments, CE resins used as matrix materials in advanced structural composites may be subjected to neutron irradiation. Because the polymer matrix constitutes the continuous phase responsible for load transfer and environmental stability, radiation-induced microstructural changes such as chain scission, crosslink rearrangement, and defect formation can directly influence the integrity of the composite system. Positron annihilation lifetime spectroscopy (PALS) is a well-established and sensitive technique for probing sub-nanometer free volume holes in polymers [3]. In this study, neutron-induced variations in the free volume of cyanate ester resin were systematically characterized using PALS to elucidate irradiation-driven microstructural evolution.

2. Materials and Methods

A cyanate ester resin supplied by the Department of Organic and Nano Engineering, Hanyang University, was used in this study. The resin was cured at 180 °C for 2 h. The cured specimens were machined into rectangular samples (10 mm × 10 mm × 1.23 mm). Neutron irradiation was conducted at the Pneumatic Transfer System (PTS) of the HANARO research reactor operated by the Korea Atomic Energy Research Institute (KAERI), Republic of Korea. The thermal neutron flux at the irradiation position was approximately 2.4×10^{13} n cm⁻² s⁻¹. Samples were irradiated for 0, 1, 2, and 4 h, with the 0 h specimen serving as the non-irradiated reference (Fig. 1).

PALS measurements were performed using a conventional fast-fast coincidence system equipped with plastic scintillators (BC422) and standard electronic modules. The positron source was prepared by depositing ²²NaCl solution onto a polyimide foil (10 mm × 20 mm × 7.6 μm), followed by drying and folding; the source was sandwiched between two identical samples during measurements. Lifetime spectra were analyzed using *PALSfit3* software [4], and source correction was applied according to Djourelov and Misheva [5].

The o-Ps lifetime component (τ_3) was analyzed using the Tao-Eldrup model [3] with an empirical parameter (ΔR) of 1.66 Å to obtain the free volume hole radius (R). The hole volume (V_f) and fraction of free volume (FFV) were calculated as follows:

$$V_f = 4/3 \pi R^3 \quad (1)$$

$$\text{FFV} = 0.0018 \times I_3 \times V_f \quad (2)$$

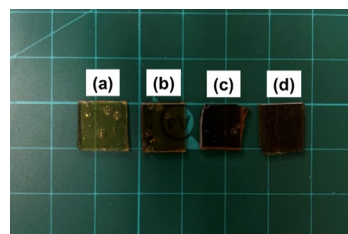


Fig. 1. Cyanate ester resin samples irradiated for different durations: (a) 0 h, (b) 1 h, (c) 2 h, and (d) 4 h.

3. Results and Discussion

The PAL spectra were analyzed using a three-component lifetime model. The free volume-related parameters derived from the o-Ps component (τ_3 , I_3 , R , and FFV) are summarized in Table 1 as a function of neutron irradiation time. The short-lifetime components (τ_1 and τ_2) exhibited irradiation-dependent variations. The τ_1 value decreased from 0.219 ± 0.006 ns at 0 h to 0.209 ± 0.006 ns at 1 h, followed by an increase to 0.270 ± 0.006 ns at 2 h, and remained relatively high at 0.264 ± 0.006 ns at 4 h. Similarly, τ_2 decreased from 0.439 ± 0.008 ns at 0 h to 0.427 ± 0.007 ns at 1 h, then increased to 0.502 ± 0.016 ns at 2 h before decreasing to 0.483 ± 0.015 ns at 4 h. The corresponding intensities also exhibited irradiation-dependent variations. I_1 increased from $30.88 \pm 2.11\%$ at 0 h to $47.01 \pm 2.82\%$ at 2 h, while I_2 decreased from $46.49 \pm 1.99\%$ to $32.92 \pm 2.66\%$ over the same period, with partial recovery at 4 h.

The o-Ps lifetime (τ_3) increased with irradiation up to 2 h, indicating an enlargement of sub-nanometer free volume holes. Consistently, the calculated hole radius showed a corresponding increase, as summarized in Table I. In contrast, the o-Ps intensity (I_3) decreased with irradiation suggesting a reduction in the relative concentration of such holes. Taken together, these trends indicate that neutron irradiation may modify the distribution of free volume.

Table I: Free volume parameters derived from PALS as a function of neutron irradiation time.

Time ^a (h)	τ_3 (ns)	I_3 (%)	R (Å)	FFV (%)
0	1.747	22.63	2.605	3.02
	±	±	±	±
	0.007	0.17	0.007	0.05
1	1.799	21.84	2.657	3.09
	±	±	±	±
	0.007	0.15	0.007	0.04
2	1.805	20.07	2.663	2.86
	±	±	±	±
	0.009	0.21	0.009	0.06
4	1.786	19.62	2.644	2.73
	±	±	±	±
	0.009	0.20	0.009	0.06

a: irradiation time

The FFV (Fig. 2) did not increase proportionally with τ_3 ; although a slight increase was observed at 1 h, prolonged irradiation resulted in an overall reduction compared to the non-irradiated specimen. The FFV did not increase proportionally with τ_3 ; although a slight increase was observed at 1 h, prolonged irradiation resulted in an overall reduction compared to the non-irradiated specimen. These trends suggest possible irradiation-induced modification of the network structure.

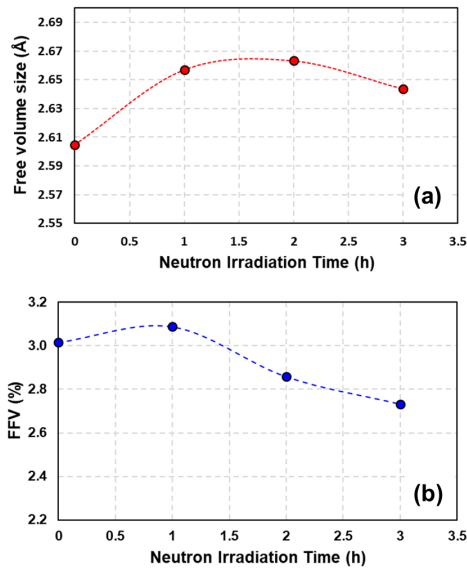


Fig. 2. Variation of (a) free volume hole size (R) and (b) fraction of free volume (FFV) as a function of neutron irradiation time. Dashed lines are guides to the eye. Error bars are smaller than the symbols and thus not clearly visible.

Crosslink scission is one possible consequence of neutron exposure and may contribute to local structural relaxation. However, competing processes (including radical recombination, additional crosslink formation, and network rearrangement) could also be involved. The observed free volume changes are consistent with the possibility of concurrent irradiation-induced processes. However, because PALS primarily provides information on free volume characteristics rather than detailed chemical structure, additional analyses would be necessary to clarify the dominant irradiation mechanism. Such complementary approaches may include measurements of the glass transition temperature, gel fraction determination, and mechanical testing.

3. Conclusions

Neutron-induced microstructural evolution in cyanate ester resin relevant to aerospace applications was investigated through free volume characterization using PALS. The initial enlargement of the free volume hole radius up to 2 h may be tentatively associated with irradiation-induced crosslink scission and local structural relaxation within the polycyanurate network, whereas the subsequent decrease at 4 h suggests the involvement of additional competing reactions. Overall, the results demonstrate that neutron irradiation modifies the sub-nanometer free volume structure of cyanate ester resin in a time-dependent manner, providing quantitative insight into radiation-induced changes in high-performance polymer matrices used in advanced structural composites.

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