

# Variation of size, numerical concentration and size distribution of free volume of heat shrink polyethylene prepared by electron irradiation cross-linkage with temperature probed by positron annihilation technique

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## Abstract

Variations of free volumes of cross-linked heat shrink low density polyethylene, prepared by the electron beam irradiation, in terms of temperature are studied through the analysis of positron annihilation parameters, such as  $S$  parameter, mean lifetime, lifetime and intensity of pick-off reaction of *ortho*-positronium (*o*-Ps), and a size distribution of free volume. Recognizable differences are observed for all parameters between the unirradiated and irradiation cross-linked polyethylene. Differences of parameters are also observed for the expanded polyethylene before and after the thermal treatments for shrinkage. Recognizable differences of free volumes as a function of temperature are not observed in all parameters between the calcium carbonate unfilled and filled heat shrink polyethylenes. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Heat shrink polymer; Low density polyethylene; Electron irradiated polyethylene

## 1. Introduction

The mechanical and thermal properties of polymers are sometimes well understood in terms of free volumes formed in an amorphous region. The elucidation of heat shrinkage phenomenon and macroscopic volume change of polymer films was anticipated to effectively interpreted in term of subnanoscopic free volume parameters, i.e. free volume size, numerical concentration and size distribution.

Heat shrink polymers are prepared by heating the moderately soft polymers to melting temperature, stretching them into two dimension until the area of the sheet in rubbery state polymers became several times bigger than their original area, and cooling down slowly to room temperature keeping them stretched. The drawn films are shrunk by annealing them above critical temperature.

The macroscopic volume change is interpreted to occur by the transformation of thermo-dynamically nonequilibrium to equilibrium states by heat shrink polymer on

annealing via dissipation of molecular motions and the microstructural changes in amorphous regions. It is of great interest to understand the heat shrink process by characterizing the microstructural state of these materials using size and numerical concentration of free volume as parameters.

In the present study, the authors choose a low density polyethylene, cross-linked by electron beam irradiation to make a heat shrink polymer, from an industrial importance. The preparation and heat shrink process of cross-linked low density polyethylene is illustrated in Fig. 1 [1].

The size, numerical concentration and size distribution of free volume are estimated by means of positron annihilation lifetime measurement, in which annihilations of positron and positronium (*o*-Ps) are specified. Ps is a coupled state of electron and positron and two different spin states are stable. Antiparallel spin state is *para*-positronium (*p*-Ps,  $\tau$ : ~125 ps) and parallel spin state is *ortho*-positronium (*o*-Ps,  $\tau$ : ~140 ns in vacuum). *o*-Ps has been proved to be an effective probe to estimate the free volume size and numerical concentration present in amorphous region of polymers as the lifetime and intensity of *o*-Ps are correlated well with the average size and numerical concentration of free volumes, respectively [2–6].

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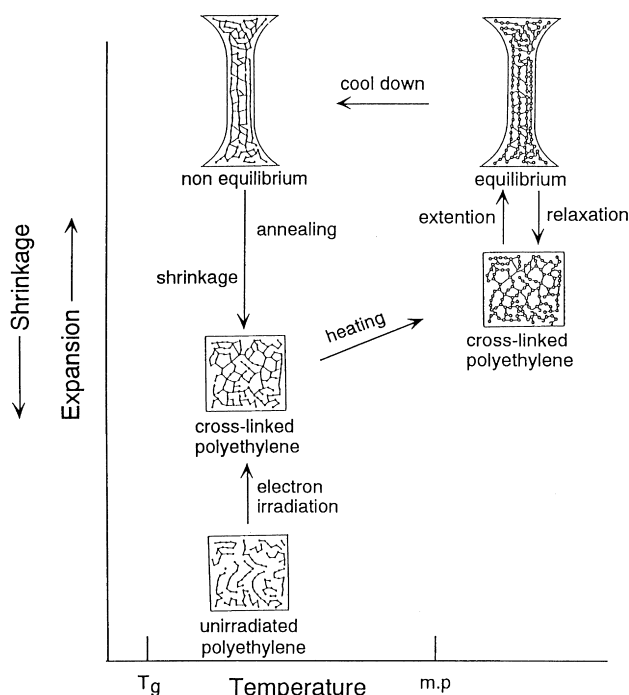


Fig. 1. Thermal process of heat shrink polyethylene.

In the present article, authors described the variation of free volume size and numerical concentration and free volume size distribution for electron irradiated low density polyethylene before and after the drawing, as well as before and after the heat shrinkage, upon temperature [7].

## 2. Experimental

### 2.1. Specimens

Heat shrink polymers used in the experiments are cross-linked low density polyethylene (Sumikasen C215, Sumitomo Chemical Industry Co. Ltd.) prepared by an electron beam irradiation in Tochigi Factory of Sumitomo Electric Industry Co. Ltd. The details are summarized in Table 1.

Irradiated polyethylene was heated to 423 K and expanded two dimensionally at the rate of 50 mm/s to make a sheet (0.5–1.0 mm in thickness) and cooled down

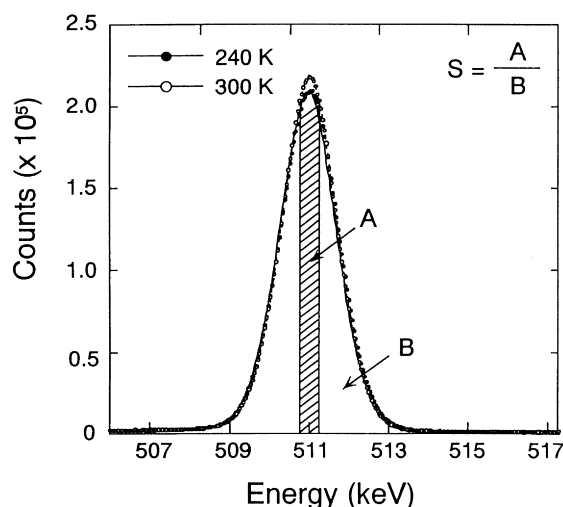


Fig. 2. Definition of  $S$  parameter.

to room temperature. The stack of sheets ( $1.0 \times 1.0 \text{ cm}^2$  and 1.0 mm in thickness) were used as specimen in a positron annihilation lifetime measurement. The penetration depth of 546 keV ( $E_{\text{max}}$ ) positrons emit from  $^{22}\text{Na}$  nuclei in the polymers is less than 1.0 mm.

### 2.2. Apparatus

Pure germanium semi-conductor detector (EG and G Ortec, GEM-13180-p, energy resolution at 514:1.1 keV) was used for the measurement of annihilation  $\gamma$  ray.

A high efficiency fast-fast coincidence lifetime measuring equipment with time resolution of  $\sim 220$  ps was used for the lifetime measurement. The details are described in the previous article's published [4,11].

The positron source was  $3.7 \times 10^5$  Bq  $^{22}\text{NaCl}$ , deposited on a  $10 \mu\text{m}$  Kapton foil and folded. The source was sandwiched between two identical specimens. The annihilation curves of positrons were measured in 20 h time intervals to collect approximately  $4 \times 10^6$  counts. The curves were analyzed by POSITRONFIT computer program.

The distribution of free volume size were obtained by an inverse Laplace transformation using CONTIN computer program compiled for a personal computer [8–10]. Details of Laplace inversion were described in the previous Refs. [11,12].

Table 1  
Specification for the preparation of heat shrink polyethylene

Sample	Electron beam	Irradiation dose (Gy)	Drawn speed (mm/s)	Filler <sup>a</sup>
A	Unirradiated	0	0	0
B	Irradiated	$2.4 \times 10^5$	0	0
C	Irradiated and drawn	$2.4 \times 10^5$	50	0
D	Irradiated, drawn and shrunk	$2.4 \times 10^5$	50	0
E	Unirradiated	0	0	20

<sup>a</sup>  $\text{CaCO}_3$  (Whiton SB, Shiraishi Calcium Co. Ltd).

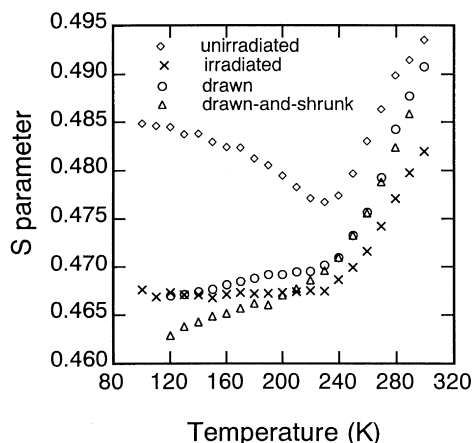


Fig. 3. Variation of  $S$  parameter for unirradiated, irradiated, drawn and drawn-and-shrunk heat shrink polyethylene by the elevation of temperature.

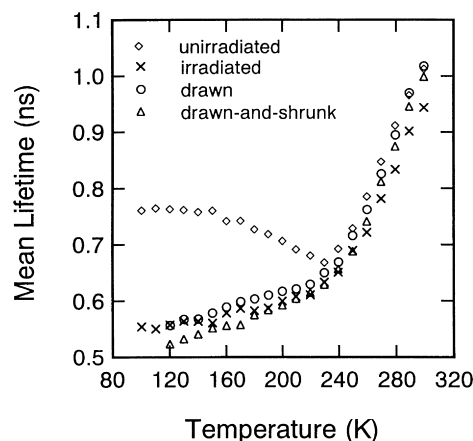


Fig. 5. Variation of mean lifetime for unirradiated, irradiated, drawn and drawn-and-shrunk heat shrink polyethylene by the elevation of temperature.

### 3. Results and discussion

#### 3.1. Temperature dependence of $S$ parameter

Definition of  $S$  parameter is illustrated in Fig. 2. As can be understood easily by the figure,  $S$  parameter is a measure to estimate sharpness of an annihilation peak of 511 keV. When positrons annihilate in vacancies or  $o$ -positronium annihilate in free volumes, positrons and  $o$ -positronium have higher probability to annihilate with electrons of outer orbitals of atoms, which have lower kinetic momentum, present at the wall of vacancies or free volumes in

an amorphous region of the sample and give smaller perturbation to energy of the annihilation  $\gamma$  ray to result the increases of  $S$  parameter.

However, the lack of vacancies and free volumes in a sample decreases the value of  $S$  parameter because annihilation of positrons with inner electrons of high kinetic momentum associated to lattice atoms increases and result in the perturbation of annihilation  $\gamma$  ray and increases the ratio of broadened peak. The increase of positronium formation probability also favors the sharpening of annihilation peak as self-annihilation of  $p$ -positronium yield very narrow annihilation peak.

Therefore, the increase of  $S$  parameter indicates the increase of size and/or numerical concentration of free volumes.

Variations of  $S$  parameters for unirradiated, irradiated, and irradiated and drawn, and drawn-and-shrunk heat shrink

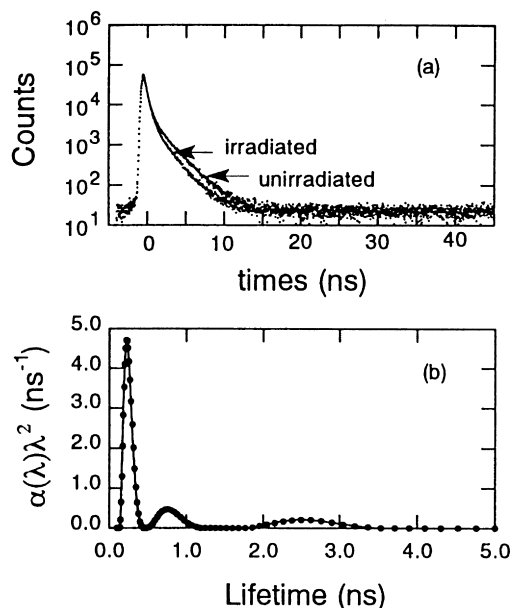


Fig. 4. Decay curve of positron annihilation for : (a) unirradiated and irradiated low density polyethylene; and (b) probability distribution function multiplied by square of annihilation rate ( $\lambda^2$ ) obtained by inverse Laplace transformation.

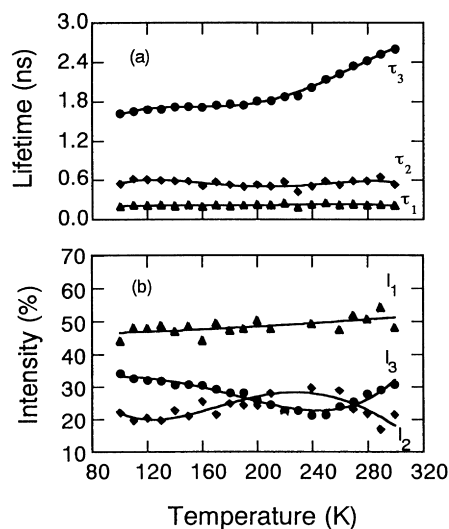


Fig. 6. (a) Variation of lifetime and (b) relative intensity by the elevation of temperature for unirradiated low density polyethylene.

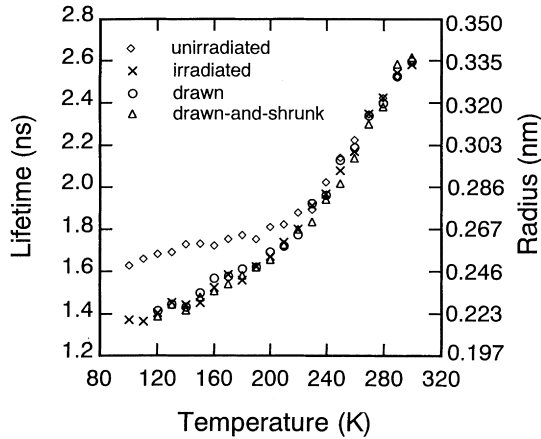


Fig. 7. Variation of *ortho*-positronium lifetime and the free volume radius by the elevation of temperature.

polyethylene were studied by elevating the temperature, and results obtained are shown in Fig. 3.

The decrease of *S* parameter by the electron beam irradiation to low density polyethylene in the wide temperature range suggests that the free volume shrinkage is realized by the strike cross-linkage of polyethylene through the generation of free radicals. This phenomenon coincides with the facts that density and rigidity of low-density polyethylene increase by the irradiation of electron beam.

The influence is exaggerated below glass transition temperature ( $T_g$ ). The increase of *S* parameter with the decrease of temperature in glass state for unirradiated sample was attributed to the increase of positronium formation probability as is confirmed by Fig. 8. The cause of probability increase of positronium formation with the decrease of temperature could not be clarified now. The electron beam irradiated polyethylene does not show this effect. *S* parameter is proved to work as a good over-all measure of corporate size and concentration of free volume of polymers.

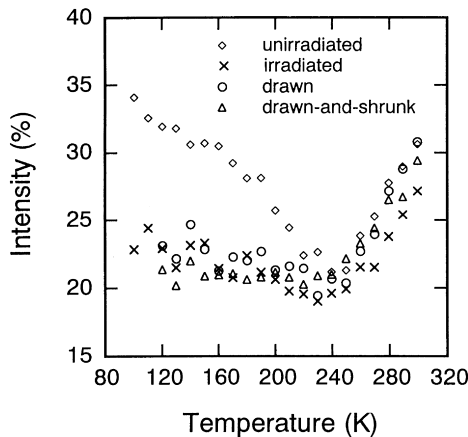


Fig. 8. Variation of relative intensity of pick-off annihilation by the elevation of temperature.

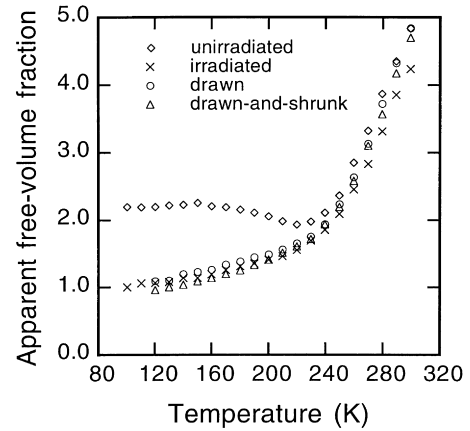


Fig. 9. Variation of free volume fraction by the elevation of temperature.

### 3.2. Temperature dependence of mean lifetime of heat shrink polyethylene

Positron annihilation curves of polymers are usually resolved into three or four lifetime components. The shortest components,  $\tau_1$ :  $\sim 150$  ps, is combined to self-annihilation of *p*-Ps and free annihilation of positron. The second shortest components,  $\tau_2$ :  $\sim 400$  ps, is attributed to annihilation of positrons trapped in various vacancies present in the crystalline region or at the interface between amorphous and crystalline regions and free volumes. The longest component,  $\tau_{3a}$ :  $\sim 1$  ns and its relative intensity  $I_{3a}$ , when resolved into three components, (or  $\tau_{3b}$ : 2–3.5 ns and its relative intensity  $I_{3b}$ , when resolved into four components), are associated to pick-off annihilations of *o*-Ps.

Decay curves of positron annihilation for unirradiated and irradiated heat shrink polyethylene, are shown in Fig. 4(a). After PATFIT analysis assuming three components of these decay curves, mean lifetime is calculated using the following Eq. [4].

$$\langle \tau \rangle = \tau_1 I_1 + \tau_2 I_2 + \tau_3 I_3, \quad (1)$$

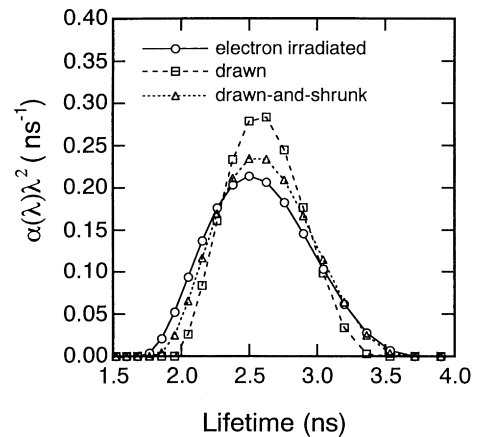


Fig. 10. Variation of lifetime distribution among electron irradiated, drawn and drawn-and-shrunk heat shrink polyethylene at room temperature.

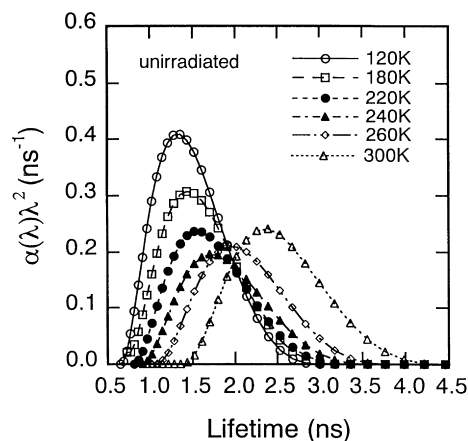


Fig. 11. Variation of lifetime distribution of electron unirradiated low density polyethylene by the elevation of temperature.

where  $I_1$ ,  $I_2$ , and  $I_3$  are intensity of  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  component, respectively.

The results obtained for unirradiated, irradiated, irradiated-and-drawn, and irradiated drawn-and-shrunk heat shrink polyethylenes are shown in Fig. 5. These results agree well with those obtained in terms of  $S$  parameter.

### 3.3. Temperature dependences of lifetime and numerical concentration of heat shrink polyethylene

Variations of life time parameters ( $\tau_1$ ,  $\tau_2$ ,  $\tau_3$ ) and intensities ( $I_1$ ,  $I_2$ ,  $I_3$ ) for unirradiated heat shrink polyethylene by temperature are shown in Figs. 6(a) and (b). The high yield of  $\tau_1$  component suggests the high formation probability of  $p$ -Ps in the low density polyethylene.

### 3.4. Temperature dependence of free volume size

Variation of free volume size for unirradiated, irradiated, and irradiated and drawn, and drawn and shrunk heat shrink polyethylene by temperature are shown in Fig. 7.

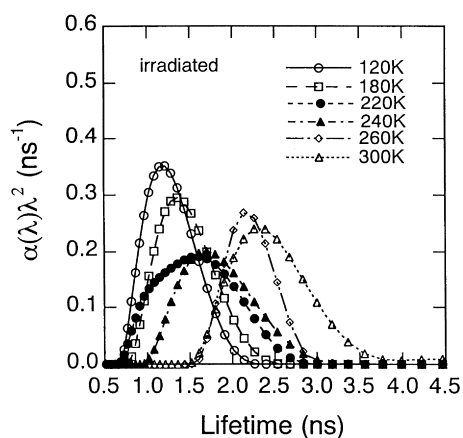


Fig. 12. Variation of lifetime distribution of electron irradiated low density polyethylene by the elevation of temperature.

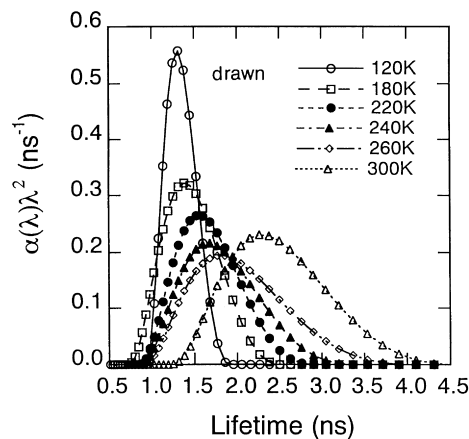


Fig. 13. Variation of lifetime distribution of drawn heat shrink polyethylene by the elevation of temperature.

Relationship between lifetime of pick-off reaction of  $o$ -positronium ( $\tau_3$ ) and free volume radius ( $R$ ) were proposed by Jean's group as follows [13].

$$\tau_3 = 0.5 \left[ 1 - \frac{R}{R + 0.166} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + 0.166}\right) \right]^{-1}, \quad (2)$$

where  $\tau_3$  and  $R$  are expressed in ns and nm, respectively.

Increase of free volume size with temperature is small in glassy state owing to the lack of backbone chain movement. Gradual increase of free volume size recognized is the result of the small increase of inter atomic distance due to thermal expansion and the movements of branch chains. The smaller free volume size for irradiated and cross-linked polyethylene is due to the strike cross-linkage of polyethylene. The free volume size of an irradiated sample is not changed by the drawing as is shown in Fig. 7. The increase of free volume size in rubbery state is about six times greater due to the movement of backbone chain. The free volume size in rubbery state is similar for unirradiated, irradiated, and irradiated-and-drawn heat shrink polyethylene.

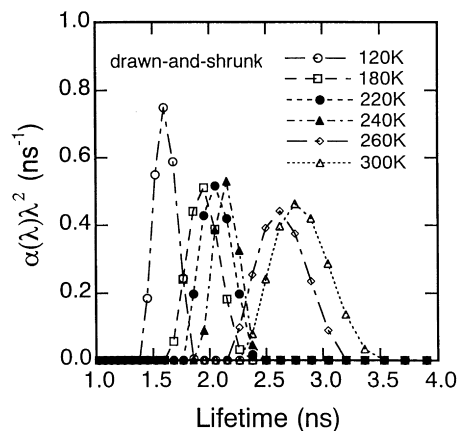


Fig. 14. Variation of lifetime distribution of drawn-and-shrunk heat shrink polyethylene by the elevation of temperature.

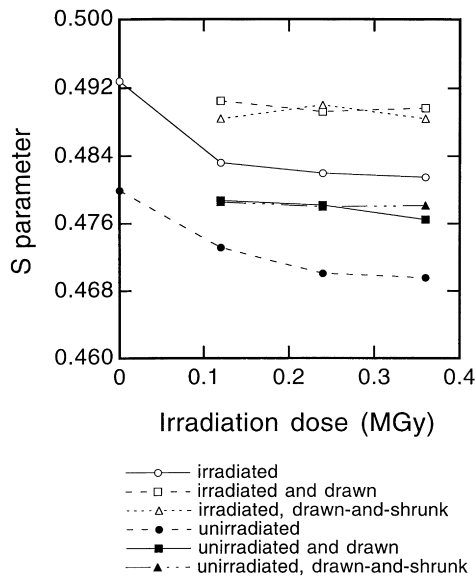


Fig. 15. Variation of  $S$  parameter by the irradiation dose of electron for electron irradiated, drawn and drawn-and-shrunk heat shrink polyethylenes (close: filled with calcium carbonate powders, open: unfilled).

### 3.5. Temperature dependence of numerical concentration of free volume

Temperature dependencies of numerical concentration of free volume for unirradiated, irradiated, and irradiated-and-drawn heat shrink polyethylene are shown in Fig. 8. The decrease of numbers of free volume with the elevation of temperature in glassy state suggests the decrease of the formation probability of positronium with the elevation of temperature, but the cause is not clarified in the study. Both size and numbers of free volume increased in rubbery state and reduction of free volume size in irradiated heat shrink polyethylene is restored by the drawing.

### 3.6. Variation of free volume fraction by the elevation of temperature

The free volume fraction ( $f$ ) in the polymer is defined from macroscopic consideration as

$$f = 0.025 + \alpha_f(T - T_g) - \beta P, \quad (3)$$

where,  $\alpha_f$  is the formal delation coefficient at a rubbery state and  $\beta$  the compressibility of free volume at given temperature [14]. Although  $f$  can be correlated microscopically to  $V_f(A \times I_3 + B)$ , obtaining  $V_f$  (free volume) by applying Eq. (2) [15], it is difficult to estimate  $A$  and  $B$  from conventional physical properties of the pertinent polymer, we calculate ( $V_f \times I_3$ ) as an alternate of free volume fraction, and define as an apparent free volume fraction.

Variations of apparent free volume fraction for unirradiated, irradiated, irradiated and drawn, and irradiated-drawn-and-shrunk heat shrink polyethylenes by the elevation of temperature are shown in Fig. 9, which shows

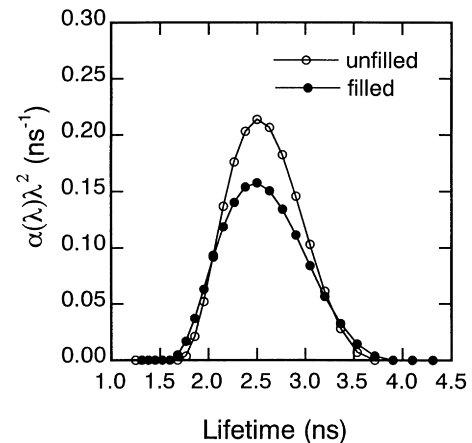


Fig. 16. Variation of lifetime distribution by the filling of calcium carbonate powder to heat shrink polyethylene.

similar behavior to  $S$  parameter and an average lifetime shown in Figs. 3 and 5, respectively.

### 3.7. Temperature dependence of distribution of free volume size

The typical result of inverse Laplace transformation of positron annihilation decay curve using CONTIN program is shown in Fig. 4(b).

The abscissa represents lifetime or free volume size and vertical axis expresses  $\lambda^2 \alpha(\lambda)$  in stead of  $\alpha(\lambda)$ , probability distribution function, to balance the intensities of  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  components. In Fig. 4(b),  $\tau_1$  and  $\tau_2$  components fused together owing to the lack of time resolution of the lifetime apparatus used, even though positron annihilation decay curve is resolved into two components by PATFIT.

Variations of size distribution of free volume of electron irradiated, irradiated and drawn, and irradiated-drawn-and-shrunk cross-linked polyethylenes by the elevation of temperature are shown in Fig. 10. The drawing of cross-linked polyethylene tends to uniform free volume sizes and annealing of the drawn polymer up to melting temperature diversifies free volume size.

Variations of size distribution of free volume of unirradiated low density polyethylene (A), electron irradiated and cross-linked polyethylene of sample A(B), drawn polyethylene of electron irradiated and cross-linked sample B(C), and drawn-and-shrunk heat shrink polyethylene of sample C(D) as a function of temperature are shown in Figs. 11–14, respectively. Both the average hole size and the distribution of free volume increased monotonously by the elevation of the temperature from 120 to 300 K showing fair uniformity and gradual dispersion to heterogeneous free volume size for thermally unstable irradiated, and irradiated and drawn samples by annealing, showing big and dispersed sizes distribution of free volume at 300 K for cross-linked polyethylene. The drawn-and-shrunk sample (D) shows different thermal behavior from those (sample A, B and C) shown in

Figs. 11–13. Fig. 14 shows that the size distribution of free volume of the sample increases successively as peaks shift parallel with the elevation of temperature and FWHM increases also by 2.5 times as the temperature elevates from 120 to 300 K.

### 3.8. Variation of positron annihilation parameters by the addition of filler

Temperature dependence of free volumes of heat shrink low density polyethylene with the addition of calcium carbonate powders as a filler are studied. A recognizable reduction in numerical concentration are observed for both  $S$  parameter and size distribution of free volume between the unfilled and filled heat shrink polyethylenes. As shown in Figs. 15 and 16, the filling of calcium carbonate powders into the polyethylene, causes a decrease in numbers of the free volume owing to the increase of positrons annihilates in calcium carbonate fillers.

## 4. Conclusion

1. Over-all information of the size and numerical concentration of free volume is reflected on  $S$  parameter.
2. Cross-linkage of low density polyethylene has a great influence to the free volume size.
3. Drawing of electron irradiated and cross-linked polyethylene gives a small effect on the free volume size and reduces numerical concentration of free volume.
4. Electron irradiation proceeds cross-linkage of low density polyethylene and reduces the numerical concentration of

free volume.

5. Size distribution of free volume gives clearer information to the variation of free volume in polymers by the thermal, polymerization and physical perturbation.
6. Numerical concentration of free volume of heat shrink polyethylene decreases by the filling of calcium carbonate powders, suggesting that some portion of positrons annihilates in calcium carbonate powders.

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