

Fractional Free Volume Dependence of Neutron-Irradiated Polystyrene (PS) Measured by Positron Method

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Abstract

The fractional free volume (F_h) in polystyrene (PS) as a function of neutron-irradiation dose has been measured, using positron annihilation lifetime (PAL) method. The results show that F_h values decreased with increasing n-irradiation dose up to a total dose of 501.03×10^{-2} Gy.

A percentage reduction of 2.14 in F_h values is noticed after the initial n-dose corresponding to a percentage reduction of 42.14/Gy. The total n-dose induces a percentage reduction of 7.26, corresponding to a percentage reduction of 1.45 per Gy. These results indicate that cross-linking is the predominant process induced by n-irradiation.

The results suggest that n-irradiation induces structure changes in PS, causing cross-linking in PS chains, whereas the presence of oxygen during irradiation causes retardness of cross-linking yield, which consequently affects the values of the above mentioned parameter with respect to their values in case the irradiation is performed in vacuum.

الخلاصة

تم قياس الحجم الحر الجزئي للبولي ستايرين كدالة لجرعة التشعيع بالنيوترون باستخدام العمر الزمني لفناء البوزترون . أوضحت النتائج تناقص قيم الحجم الحر الجزئي بزيادة جرعة التشعيع ولغاية جرعة التشعيع الكلية 501.03×10^{-2} كراي. إن جرعة التشعيع الأبتدائية قد سببت نسبة اختزال مئوية في الحجم الحر الجزئي مقدارها 2.14 والمساوية لنسبة اختزال مئوية 42.14 لكل كراي.

لقد أحدثت جرعة التشعيع الكلية نسبة اختزال مئوية في الحجم الحر الجزئي مقدارها 7.26 والمساوية لنسبة اختزال مئوية 1.45 لكل كراي.

توضح النتائج بأن عملية التشابك هي العملية السائدة للبولي ستايرين نتيجة تشعيه بالنيوترون، كما وأن النتائج قد بينت بأن التشعيع قد أحدث تغيرات تركيبية في البوليمر والتي أدت إلى تشابك سلسله لكن ظهور الأوكسجين أثناء عملية التشعيع قد أدى إلى تراجع في نتائج عملية التشابك الكلي وهذا بدوره قد أثر على المعاملات اعلاه مقارنة بقيمها في حالة التشعيع بالفراغ.

Introduction

Positronium annihilation lifetime (PAL) has been used to determine the local free-volume hole properties (microstructure) in polymeric materials [1]. It has been recently used to determine the defect properties, at the atomic

level scale for polymer materials [2]. The sensitivity of PAL is due to the localization of positronium (Ps) atom (a bound atom consisting of an electron and a positron) in those holes ranging from 1Å^0 to 20Å^0 in size while most studies have been performed in the bulk. It has

been shown that PAL can be used to probe the surface properties [3,4]. In PAL technique [5], one employs the anti-electron, the positron as a probe. Because of the positively -charged nature of the positron, the positron and the Ps atom are attracted by the electrons of the polymers and trapped in open spaces like holes, voids or cavities.

The annihilation photons come mainly from these open spaces. Positrons are commonly produced by a positron-emitting radioactive isotope such as ^{22}Na or ^{64}Cu .

Ps atom formed can be in the Singlet State or the Triplet State. The Ps formed in singlet and triplet states are called para- positronium (p-Ps) and ortho-Positronium (o-Ps), respectively.

Their lifetimes in free space are 0.125 and 140 ns, respectively. In condensed medium the mean lifetime of (o-Ps) is considerably reduced due to its interaction with the surrounding molecules.

The positron in o-Ps may annihilate with an atomic or molecular electron of opposite spin, in which case, the mean life of (o-Ps) is reduced to a few nanosecond [6]. Results of PAL measurements as a function of temperature [7], pressure [8,9], time of aging [10] degree of crystallinity [11] and gamma irradiation [12] gave evidence that the positron and Ps atom are localized in these preexisting local holes and the free volume in polymers.

The o-Ps lifetime (τ_3) is related to the mean free-volume hole radius (R) according to the semi-empirical formula [13]:

$$\tau_{o-Ps} = 0.5 \left[1 - \frac{R}{R_o} + 0.159 \sin\left(\frac{2\pi R}{R_o}\right) \right]^{-1} \text{ (ns)} \quad (1)$$

where $R = R_o + \Delta R$, and ΔR is the electron layer thickness. The free-volume hole size (V_h) is:

$$V_h = \frac{4}{3} \pi R^3 \quad (2)$$

The fractional free volume, F_h (the ratio of the free volume to the total volume) is given by the empirical fitted formula [14]:

$$F_h = C V_h I_{o-Ps} \quad (3)$$

where C is a constant, its value is 1-2 nm^{-3} in polymers, V_h is the free volume hole size, and I_{o-Ps} is the intensity of (τ_{o-Ps}). The effects of irradiation on the microstructure of polymers

were reported [15, 19].

The aim of the present study is to investigate the effect of n-irradiation in the microstructure of PS, and thereby the changes in F_h as a function of n-irradiation dose.

Experimental Details and Data Analysis

The polystyrene (PS) samples were prepared in the laboratory, with a thickness of 2 mm and a diameter of 32 mm. The samples were irradiated in air with neutron-flux using a Am-Be neutrons source, with a dose rate of 19×10^{-4} Gy/h.

Total irradiation dose was 501.03×10^{-2} Gy. The positron lifetime measurements were performed using a fast-slow coincidence system with a time resolution of 340 ps. The positron source activity was 12 μCi .

The positron lifetime spectra were measured for each individual irradiation dose value with total integral counts of 2×10^6 . The peak-to-background ratio was better than 2300:1. The lifetime spectra were analyzed into three-lifetime components using PFPOFIT program [20]. The lifetime component, their relative intensities and the parameters of the prompt curve were simultaneously fitted. The free-volume hole size and the fractional free volume were calculated using Eqs.(1, 2, and 3), respectively.

Results and Discussion

Positron annihilation lifetime (PAL) technique was employed to study the microstructural changes in (PS) within low and limited n-doses. The results of analysis of n-irradiated PS lifetime spectra are listed in Table [1].

The o-Ps lifetime is found to be 2164 ps corresponding to fractional free volume of 1.3496% for unirradiated sample. The fractional free volume values are plotted as a function of n-irradiation dose in Fig [1]. As shown in Fig [1] the values of F_h decreases with increasing n-dose. A reduction of 2.135% in F_h value is measured after the initial n-irradiation dose, corresponding to a percentage reduction of 42.135 per Gy. The maximum reduction in fractional free volume is noticed at n-irradiation total dose of 108.79×10^{-2} Gy, where a percentage reduction of 22.91 in F_h value is taken place as a result of irradiation total dose, corresponding to a percent reduction of 21.1 per unit n-irradiation dose (per Gy). Increased cross-linking and attached carbonyl and hydroxyl group produced

as final products up-on the decay of the primary and oxygen-stabilized radicals, could be responsible for reduction in fractional free volume [21].

As the total n-irradiation dose increases, and reaches 501.03×10^{-2} Gy, the percentage reduction in F_h value is 7.26 corresponding to reduction of 1.45% per Gy. It is clear when the total irradiation dose increases 98.9 times greater than the initial n-dose, the percent reduction per unit dose (Gy) is reduced to a value of 0.0342 times less than the reduction value induced by the initial dose. That mean the initial dose is more effective dose, and its effect is 29.1 times greater than the total n-irradiation dose of 501.03×10^{-2} Gy. This is due to the influence of free radicals induced as a result of higher irradiation doses, which causes reduction in the predominant process (the cross-linking) induced by the initial dose.

The results indicate that n-irradiation dose induces cross-linking and degradation of the PS chains, but the former is the predominant process so the net process is the cross-linking in the amorphous regions of PS and increasing crystallinity in the amorphous regions. This causes reduction of amorphous regions, subsequently, reduction in fractional tree volume. As the total n-irradiation dose increases above 108.8×10^{-2} Gy the amount of the accumulated tree radicals induced by n-irradiation become predominant, resulting in increasing degradation rate in the presence of oxygen, so the resultant is a reduction in cross-linking rate subsequently slight increase in F_h values.

Although PS is normally cross-link under irradiation but it shows an oxygen effect. The cross-linking is retarded considerably by irradiation of PS in air [19, 22]

Since the o-Ps lifetime and the total positronium formation probability are the parameters, which vary as a function of the chemical microstructure of the polymer. It is expected that Ps irradiated by n-doses undergo structural changes, due to cross-linking and degradation, but cross-linking is the predominant process. The cross-linking seems to be significant for increasing crystallinity in the amorphous regions, hence reducing F_h in these regions.

Table (1). τ_3 , I_3 , V_h and F_h values in Ps as a function of n-dose.

Dose ($\times 10^{-2}$ Gy)	τ_3 (ps)	I_3 (%)	V_h (nm^3)	F_h (%)
0	2164	8.0025	0.1124 ± 0.002	1.3496 ± 0.04
5.07	2136 ± 53	8.025 ± 0.27	0.1097 ± 0.003	1.3207 ± 0.05
13.39	2111 ± 55	8.4 ± 0.243	0.1073 ± 0.003	1.3522 ± 0.04
22.83	2200 ± 70	7.642 ± 0.27	0.1159 ± 0.004	1.3290 ± 0.048
36.39	2106 ± 59	7.845 ± 0.235	0.1068 ± 0.003	1.2572 ± 0.038
59.28	2035 ± 58	7.98 ± 0.333	0.1000 ± 0.003	1.1981 ± 0.04
76.84	2109 ± 55	7.82 ± 0.274	0.1071 ± 0.003	1.2567 ± 0.04
108.79	2124 ± 68	6.389 ± 0.252	0.1085 ± 0.004	1.0404 ± 0.04
154.39	2179 ± 57	7.7036 ± 0.2096	0.1138 ± 0.003	1.3160 ± 0.036
210.21	2141 ± 61	7.7205 ± 0.246	0.1102 ± 0.003	1.2765 ± 0.039
296.21	2147 ± 62	8.027 ± 0.33	0.1107 ± 0.003	1.3339 ± 0.046
501.03	2102 ± 99	7.8383 ± 0.205	0.1064 ± 0.005	1.2516 ± 0.05

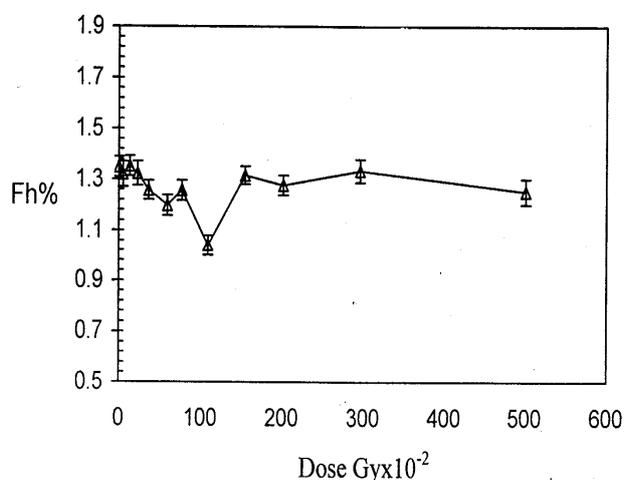


Fig.(1). F_h (%) for PS as a function of n-dose.

Conclusions

Although the neutron doses were relatively small, but they induce significant effects on PS structure which is accurately determined by position measurements. An extension of this work will be carried out to study the effect of high n-doses on the behavior of positronium annihilation lifetime parameters.

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