Iraqi Journal of Physics, 2009 *Vol-7, No-10, pp. 35-39*

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

A. A. Al-Bayati

Dept. of Physics, College of Science, University of Baghdad, Baghdad, Iraq

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 in the free volume equal to 42.14/Gy.

The total n-dose induces a percentage reduction of 7.26, corresponding to a percentage reduction of 1.45/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 طريقة العمر الزمني لفناء البوزترون. أوضحت النتائج تناقص قيم الحجم الحر الجزئي بزيادة جرعة التشعيع ولغاية جرعة التشعيع الكلية $501.03x10^{-2}$ كراي. إن جرعة التشعيع الإبتدائية قد سببت نسبة اختزال مئوية بالحجم الحر الجزئي مقدارها 2.14 والماوية لنسبة اختزال مئوية 42.14لكل كراي .

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

توضح النتائج بأن عملية التشابك هي العملية السائدة للبولي ستايرين نتيجة تشعيعه بالنيوترون، كما وأن النتائج قد بينت بأن التشعيع قد أحدث تغيرات تركيبية في البولي ستايرين والتي أدت إلى تشابك سلاسله لكن ظهور الأوكسجين أثناء عملية التشعيع قد أدى إلى تراجع في ناتج عملية التشابك الكلي وهذا بدوره قد أثر على المعاملات أعلاه مقارنةً بقيمها في حالة التشعيع بالفراغ .

INTRODUCTION:

Positronium annihilation lifetime (PAL) method 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 method is due to the localization of positronium (Ps) atom (a bound atom consisting of an electron and a positron) in those holes ranging from $1A^o$ to $20A^o$ 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, ^{64}Cu.

The Ps atom formed can be in the Singlet State or the Triplet State. The Ps atoms 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 meanlife 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]:

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

Where $R=R_0+\Delta R$, ΔR is the electron layer thickness.

The free-volume hole size (V_h) is:

$$V_h = \frac{4}{3}\pi R^3 \ldots \qquad ....(2)$$

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

$$F_h = CV_h I_{o-Ps} \qquad .... (3)$$

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 present study is to investigate the effect of n-irradiation on 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 2mm and a diameter of 32 mm. The samples were irradiated in air with neutron-flux using an Am-Be neutron source, with a dose rate of 19×10^{-4} Gy/h.

The 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 (Na-22) activity was $12^{\mu Ci}$.

The positron lifetime spectra were measured for each individual irradiation dose value with a 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 PFPOSFIT program [20].

The lifetime components, 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 Equs. 1, 2, and 3.

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 τ_3 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 decrease 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 /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 groups produced as final products upon the decay of the primary and oxygen- stabilized radicals, could be responsible for the 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 a reduction of 1.45%/Gy. It is clear that 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. This means that the initial dose is a 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 a 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, which causes reduction of amorphous regions and subsequently a reduction in fractional free volume.

As the total n-irradiation dose increases above 108.8×10^{-2} Gy the amount of the accumulated free radicals induced by n-irradiation becomes predominant, resulting in increasing degradation rate in the presence of oxygen, so the result is a reduction in cross-linking rate and subsequently slight increase in F_h values.

Although PS is normally cross-linked under irradiation but it shows an oxygen content dependency (i.e.; photo-oxidization) 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.

CONCLUSION:

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.

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

Dose ($Gy\times10^{-2}$)	**τ_3 (ps)**	**I_3**	**V_h (nm^3)**	**F_h (%)**
0	2164 42	8.0025 0.26	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

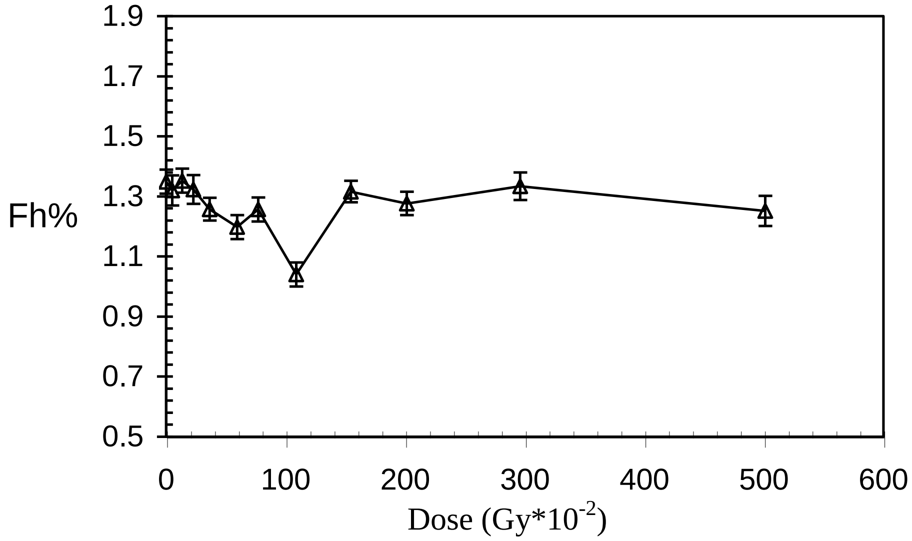

Fig. (1) Fractional free volume in PS as a function of N-Dose.

REFERENCES:

[1] Jean, Y. C., and Schreader, D. M., "Positron and Positronium Chemistry" Elsevier Eds., Amesterdam (1988).

[2] Kansy, J., Consolati, G., and Dauwe, C. "Positronium trapping in Free Volume of Polymers" Radiat. Phys. Chem. 58 (2000) 427.

[3] Mogenson, O. E., "Positron Annihilation in Chemistry" Berlin, Springer (1995).

[4] Borek, J., and Osoba, W., "Free Volume in Selected Vinyl Polymers" J. Nukleonika, 42 No.1 (1997) 2732.

[5] Schrader, D. M., and Jean, Y. C., "Positron and Positronium Chemistry", Eds. Elsevier, Amsterdam (1998).

[6] Tao, S. J., "The Formation of Positronium in Molecular Substances" Appl. Phys. 10 (1976) 67.

[7] Hirade, T., Frans, H. T., Maurer, M., and Eldrup, M., "Positronium Formation at Low Temperature" Radiat. Phys. Chem., 58 (2000) 465.

[8] Deng, Q., Jean, Y. C., "Free Volume Distribution of an Epoxy Polymer probrd by Positron Annihilation: Pressure Dependence"; Macromolecules, 26 (1993) 30.

[9] Elias, M. M., and Al-Bayati, A. A., "Pressure Dependence of Free Volume Hole Properties in PE probed by Positron Lifetime Technique" Dirasat, Pure Science, 26 No.1 (1999) 120.

[10] Saleem, H., "Study of the Characteristics of Positron Lifetime Spectra in Epoxy Resin" M. Sc., Thesis, Univ. Baghdad, (2001).

[11] Liu, J., and Jean, Y. C., "Free-volume Distribution of PS probed by Positron Annihilation" Macromolecules, 26 (1993) 7149.

[12] Al-Bayati, A. A., "Investigation of Positron and Positronium Formation in Solid Polymers" Ph. D. Thesis,

[13] Univ. of Baghdad, (1998).

[14] Nakanishi, H., Wang, S. J., and Jean, Y. C., "Positron Annihilation Studies of Fluids" Sharma, S. C. Eds., World Scientific, Singapore (1998).

[15] Jean, Y. C., "Positron Spectroscopy of Solids", Eds., Dupasquier, A. and Mills, A. P., JR, ISO, Pub., Amsterdam (1995).

[16] Hsu, F.H., and Hadley, H., JR, "Positron Annihilation in irradiated PS and PE" Positronium Muonium Chemistry American, Society, Washington, D. C., (1979).

[17] Kindl, P., Puff, W., and Sormann, H., "A Free Four-term Analysis of Positron Lifetime Spectra of Irradiated Teflon" Phys. Stat. Sol (a) 58 (1980) 489.

[18] Suzuk, T., Miura, T., Oki, Y., Numajiri, M., Kondo, K., and Ito, Y., "Positron Irradiation Effect on PP and PE Studied by Positron Annihilation" Radiat. Phys. Chem. 45 No.4 (1995) 657.

[19] Kudoh, H., Sasuga, T., and Seguchi, T., "High Energy Ion Irradiation Effect on Polymer Materials" Radiat. Phys. Chem. 50 No.3 (1997) 299.

[20] El-Sayed, A. M. A., "Positron Annihilation Study of Neutron Irradiated PE" Materials, Sci. Forum, 363-365 (2001) 272.

[21] Puff, W., "PFPOSFIT: A new Version of a Program for Analyzing Positron Lifetime Spectra with Non-Gausian Prompt Curve" Comput. Phys. Commun., 30(1983) 359.

[22] Hsu, F. H., and Hadley, J. H., "Positron Annihilation in Irradiated Polystyrene and Polyethylene" Phys. Lett. A, 34(1971) 39.

[23] Al-Jumaili, K. S., "Study of the Oxygen Effects on the Positron Lifetime in Some Solid Polymers" M. Sc. Thesis Univ. Baghdad, (2002).