Fractional Free-Volume dependence of Oxygen in Beta-Irradiated Polystyrene Probed by Positron life time

[1]Khalid Salih J. **[2]Bahaa. H. R** **[3]Ehsan. D. J**

[1,2,3] Department of Physics, College of Education, University of Babylon, Babel, Iraq

[1]E-mail: Khalid_ik74@yahoo.com

Abstract:

Positron Annihilation Lifetime (**PAL**) technique has been employed to investigate the effect of low doses of β-irradiation (in air and vacuum) on the type of polymers namely: polystyrene (**PS**). A conventional fast-slow coincidence system was used for measuring the positron lifetime spectra. The time resolution of the system was 422±20 ps (the full width at half maximum (FWHM)) at ^{22}Na energy window. The lifetime spectra were resolved into three components by using PFPOSFIT program. The irradiation performed in air (in the presence of oxygen) and under vacuum with β^--rays by using ($\mathbf{^{90}Sr/^{90}Y}$) source at room temperature for ten different total dose, ranging from (0.3-12.3) Gy . The o-Ps lifetime parameters were used to determine the microstructure properties, namely: free volume hole size ($\mathbf{V_h}$) and free volume hole fraction ($\mathbf{F_h}$). The parameters were measured as a function of β-irradiation dose. The results of β-irradiation show that, the influence of β-irradiation on o-Ps lifetime, hence the $\mathbf{V_h}$ and $\mathbf{F_h}$ values for samples irradiated in air are less than their values for samples irradiated under vacuum, due to the effect of peroxy and hydroperoxide radicals formed in the presence of oxygen. The results show that cross-linking process is the predominant process as a result of β-irradiation **PS**.

تأثير الاوكسجين على الحجم الحر الجزئي مع تشعيع بيتا للبولي ستايرين بواسطة زمن عمر البوزترون

الخلاصة

استخدمت تقنية مطيافية زمن عمر فناء البوزترون (PALS) لدراسة تأثيرات جرع واطئة من دقائق بيتا السالبة (في الهواء و الفراغ) البولي ستايرين (PS). حيث استخدمت منظومة تطابق بطيئة-سريعة بميز زمني أمثل مقداره (422 ±22) بيكو ثانيه عند نافذة الصوديوم-22. وقد شععت مجموعتان من النماذج البوليمرية (وبنفس المقادير الوزنية) المستخدمة للدراسة، بمصدر السترونتيوم-90 (^{90}Sr/^{90}Y) الباعث لجسيمات بيتا. شععت المجموعة الأولى في الهواء عند درجة حرارة الغرفة بينما شععت المجموعة الثانية بالفراغ ولمدى من الجرع مقداره 0.3 كراي إلى 12,3 كراي وبمعدل 3.6 كراي/ ساعة، حللت النتائج إلى مركبات زمنية بوساطة برنامج PFPOSFIT. حددت الخصائص البنيوية الدقيقة للبوليمرات المتمثلة بالحجم الحر(V_h) والحجم الحر الجزئي (F_h) من خلال قياس زمن عمر فناء الاورثوبوزترونيوم (τ_3) ووجدت العلاقة بينهما وبين الجرع الإشعاعية المستخدمة. بينت النتائج التي حصل عليها، وبعد إجراء مقارنه بين الحالتين (في الهواء وفي الفراغ)، إن قيم زمن المركبة الثالثة (τ_3) وكذلك بالنسبة للحجم الحر والحجم الحر الجزئي للنماذج المشععة في الهواء هي اقل من تلك المشععة في الفراغ، ويعود ذلك إلى تأثير جذور البيروكسي والهايدروبيروكسي المتكونة نتيجة لتفاعل الجذور الحرة المتولدة بسبب تأثير دقائق بيتا مع الأوكسجين. التي تؤدي إلى اختزال الحجم الحر والحجم الحر الجزئي نتيجة لزيادة المناطق البلورية، بالتالي تناقص (τ_3). أوضحت النتائج أن عمليات التشابك في الأواصر البوليمرية لعينة البولي ستايرين هي العمليات السائدة. أكدت هذه الدراسة أن تقنية زمن عمر فناء البوزترون تعد تقنية ذات كفاءة عالية لدراسة خصائص الحجم الحر ولدراسة خصائص التركيب المجهري الدقيق لمتعددات الجزيئات بقياس النانومتر ودون النانومتر وبدقة قياس حوالي 7 بيكومترمكعب (pm^3).

1- Introduction:

Positron Annihilation Spectroscopy (**PAS**) is a useful tool to investigate the structure of the influence of radiation damage to the structure of polymeric materials. In this technique, the lifetime of positron and positronium are considered as non-destructive probe to study the characteristics parameters of these materials. Because of the relatively small size of the Ps probe (1.06A^o) compared to other probes, PAS is particularly sensitive to small hole and a free volume of angstroms in size and at a time of molecular motion from 10^{-10} s and longer [1]. Positron annihilation lifetimes are usually determined by detecting the prompt γ-ray (1.28MeV) from the nuclear decay that accompanies the emission of a positron from ^{22}Na radioisotope and the annihilation γ-rays (0.511MeV). The application of this technique is to study the microscopic properties of the matter, e.g., the effect of irradiation. The PAL spectra of most polymers have a long-lived component, which is attributed to *pick-off* annihilation of ortho-positronium (o-Ps) formed in amorphous region, the lifetime of the long-lived component (τ_3) is a measure of the size of interstitial space among polymer chain, which as referred to as "***free space hole***". The intensities of this component (I_3) is considered to contain information about the In concentration of the free space hole. conventional positron annihilation experiment, the positrons are injected into a solid with a mean energy of 200 keV [2]. They slow down to thermal energies within (1-10 ps) [2] by ionization and excitation reaction in the solid. During this time they penetrate a distance of (10 –1000) μm depending on the density of the solid (the penetration depth is roughly inversely proportional to the density). To understand the mechanism of positrons and positronium interactions with materials and also of positronium formation one has to deal with the models so far suggested for that: such as the "***Ore gap***" model, the "***Spur***" model, the "***Free volume***" model… etc. In this work the free volume model is mainly to be used. Oxygen during irradiation combine with active sites on the polymer chain to form peroxide links to reduce the net scission rate [3]. In PE and PS, cross-linking is the most important result of ionizing radiation, and the free radicals are the intermediate processes. If oxygen admitted to an irradiated polymer, the radicals are converted to peroxy radicals. The peroxy radicals are unstable so they form carbonyl (C=O) and hydroxyl (OH) groups, where, the oxygen destroyed the primary free radicals and peroxy intermediate is formed [4]. PE and PS, show oxygen effects that are dependent on sample thickness, dose rate and also the chemical structure, which is an important factor in oxidative scission [4]. In both polymers (PE and PS) irradiation with oxygen gives a much large scission to cross-linking ratio, although cross-linking predominates in vacuum irradiation in PE and PS. [3].

Al-Bayati [5] employed PALS to investigate γ-irradiation effect on polystyrene (PS) and polymethylmethacrylate (PMMA) in air at room temperature with dose up to 1340 kGy. It was found that the initial irradiation dose induced percentage increases in free volume and free volume fraction. These low doses induce degradation in the polymer chain except for PS, in which an opposite effects, the cross-linking, are dominant. Suzuki et.al., [6] studied the radiation effect on positronium formation in low temperature PE. In the case of non irradiated PE samples, they found at low temperature below the glass-transition temperature, the intensity of the long-lived component of positronium, I_3, increased due to an increase in the concentration of trapped electron. However, the increase in I_3 obtained in a few MGy γ-irradiated samples became very small due to the effect of induced radicals. Also, they have observed that the trapped electrons were affected by the intensity of the positron source used for a PALS experiment. Several other works of polymers have been studied by using PALS technique to study the irradiation effects such as: u.v-irradiation of acrylonitrile-butadiene-styrene (ABS) and polycarbnate (PC) [7], β-irradiated of (PP) and (ABS) [5], γ-irradiated of Teflon [8], γ-irradiated of epoxy [5,9] and γ-irradiated tissue [10]. As explained in the literature review, it is noticed that the effects of the low β-dose rang (0.3-12.3)Gy have not been studied for polymers by means of PALS teqnique and most works published used high β-doses (Mrad), in spite of the fact that β-rays is ionizing particles and have mass, therefore, the low doses effects are also important. In the present study the polymer; namely PS are studied in the presence of air and in vacuum to explain the oxygen effect during β-irradiation on the o-Ps lifetime. To the best of our knowledge β-irradiation effect under vacuum for the investigated samples in this work are not studied before.

2- Theory

2-1 The Free Volume Model

Brandt [14] proposed this model for positronium formation, which is an important model to explain the increment of the o-Ps lifetime in some molecular solids and polymers.

Molecular solids always contain a large fraction of imperfect sites, such as defect, voids, impurities, etc. These sites serve as free volumes for Ps formation. Ps atom is formed only if the free volume is equal to the volume of Ps atom or larger than a certain critical value [15]. It is termed as free volume model.

The de Broglie wavelength of the thermelized Ps is two to three order of magnitudes larger than the dimension of the free volume available in a typical molecular lattice. The Ps wave function may be considered to be deloclized as illustrated in Figure (1).

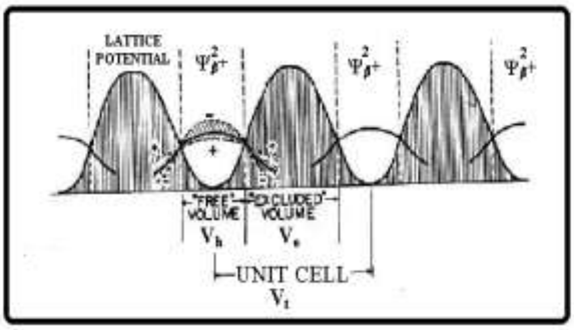

Fig. (1): Schematic plot of positronium wave functions according the free volume model [14].

In a lattice L of electron density distribution $|\Psi_L(r)|^2$ composed of neutral atoms or molecules with closed shells, i.e., in the absence of paramagnetic impurities, the electron pick up rate, γ_p of o-Ps in the lattice L is: [14]

$$\gamma_p = \pi c r_o^2 \int_L \psi_L^*(r)\psi^*_{\beta^+}\psi_{\beta^+}(r)\psi_L(r)dr^3$$

-------------------------------------(1)

where Ψ_{β^+} is the wave function of the positron in the field of the electron to which it is bound as o-Ps and the field of the lattice, r_o is the classical electron radius and c is the velocity of light. Brandt et al., [14] solved equation (2) by using the following assumptions:

1- The mutual Ps and the lattice polarization is neglected.
2- The lattice could be described as a square well potential of a height U_o and a radius R_o with an electron density ρ_o, or correspondingly by an "exclude volume" V_o, each centered in a cell volume V_t of radius R_t. In the region $R_o<R<R_t$, $U_t=0$ and $\rho_t=0$ representing a "free volume of the cell" $V_h=V_t-V_o$, and $V^*=V_t / V_o$ the "reduced cell volume", as represented in Figure (1).
3- The Ps atom is assumed to be thermalized.

By neglecting the internal structure of Ps and approximating the lattice interaction by a square well potential and considering the electron density (ρ_o) as a constant between the walls, equation (1) becomes [14]:

$$\gamma_P = \pi c r_o^2 \rho_o \int_{v_o} \psi^*_{Ps}(r)\psi_{Ps}(r)dr^3$$

....(2)

By using Wigner-seitz approximating [14] to evaluate Eq (2) for plane, spherical and cylindrical geometry, the solution is given as:

$$\gamma_P = \frac{\pi c r_o^2 \rho_o}{1 + F(U_o, R_o, R_h)}$$

……….(3)

where $F(U_o, R_o, R_h)$ is a function that depends upon the lattice geometry as a function of the scattering parameter.

Tao [16] and Eldrup et al. [17] suggest a relation between the annihilation rate γ_P and the hole size by using a spherical potential well of radius R_o with an a virtual electron layer with thickness ΔR. The pick-off annihilation rate in the unit ns^{-1} is given by [18]:

$$\gamma_p = 2\left[1-\frac{R_h}{R_o}+\frac{1}{2\pi}\sin\left(\frac{2\pi R_h}{R_o}\right)\right]$$
……………………………………………………………(4)

Where $R_o=R_h+\Delta R$ and $\Delta R = 0.166$ nm is in excellent agreement with observation in solid and liquids [19]. Equation (4) can be written as [19]:

$$\tau_3(ns)=\frac{1}{\gamma_p}=\frac{1}{2}\left[1-\frac{R_h}{R_0}+\frac{1}{2\pi}\sin\left(\frac{2\pi R_h}{Ro}\right)\right]^{-1}$$
…………………….(5)

and the free volume is given in the spherical geometry approximation as:

$$V_h = \frac{4}{3}\pi R_h^3$$
…………………………… (6)

In general, the simplest expression of free-volume (V_h) can be defined as the difference between the total volume and the occupied volume ($V_h = V_t - V_o$), where the free volume [20,21] is an open space that is freely moving in media

Kobayshi et.al., [22] proposed a semiemperical relation which may be used to evaluate the fractional free volume F_h given by:

$F_h=AI_3V_h$……………..(7)

Where **A** is normalization constant, its value is (1-2) nm^3 for polymers [23], I_3 is the intensity of τ_3, given in a percentage form and V_h is given in nm^3.

3-Experimental Details

The timing measurement refers to the determination of the time interval for the arrival of two pulses. Timing methods are characterized as "***slow***" or "***fast***" depending on the way the signals are derived. Slow timing signals are generated by an integral discriminator, whereas fast timing signals are based on the unshaped pulse at the output of the detector or a signal shaped specifically for timing. In either cases, timing is obtained by using a shaped signal at the output of the detector or a signal shaped at the output of the amplifier. A schematic diagram of the typical fast-slow coincidence circuit is illustrated in figure (2) which is used in the present work to measure the positron lifetime. The positron annihilation lifetime spectroscopy (PALS) is a microprobe technique, which is used to study the microstructure properties of matter. The system, which is used with (PAL), must have both a high pulsing efficiency and a good timing resolution. The full width at half maximum (FWHM) of the time distribution is often used as a measure of the overall timing uncertainty in the measurement system, represents the timing resolution, which should be narrow in order to distinguish between two closely spaced events.

The vacuum chamber used in this with an research, is an Ortec 807 [26] additional modification to perform the requirement of the study. The chamber from stainless steel and is made varnished wood base, mounted on a provided with moving cover which vacuum gauge (maximum contains a $^{-1}$ torr). This chamber is 10 scale pump coupled to mechanical vacuum by special valve, the vacuum pump and vent functions are combined in a single gated polymers value. The investi {high-density polyethylene (HDPE) and polystyrene (PS)} samples are prepared in the laboratory, the sample preparation system is described in reference [2]. The samples are manufactured by keeping 1.5 gm of polymer grains in the sample preparation system under a pressure of 200 bar during a period of 3 minutes at a temperature (T_m +25 C^o), where T_m is the melting temperature. The diameter of the samples is 32 mm with a thickness of 2 mm. The studied samples are irradiated in air and in vacuum with beta rays by using ^{90}Sr/ ^{90}Y beta source with activity of 3 mCi. The β-irradiation dose rate was 3.6 Gy/hr. The samples are irradiated up to a total dose of 12.3 Gy. The ^{22}Na positron source used in this work because of its convenient half-life, high positron fraction yield, there in wide separation in energy of emitted gamma (1.27 MeV) and the annihilation gamma (0.511 MeV) which provides easy discrimination between them [24], and low cost. The decay scheme of ^{22}Na is shown in Figure (3), which decays under emission of a positron to the excited state of ^{22}Ne [25], where ^{22}Na emits about 90% positron with maximum energy of 0.545 MeV.

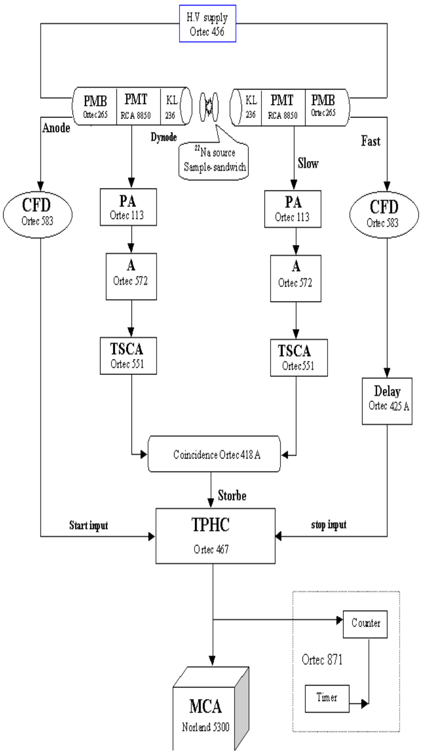

Figure (2) :A schematic diagram of the typical fast-slow coincidence circuit.

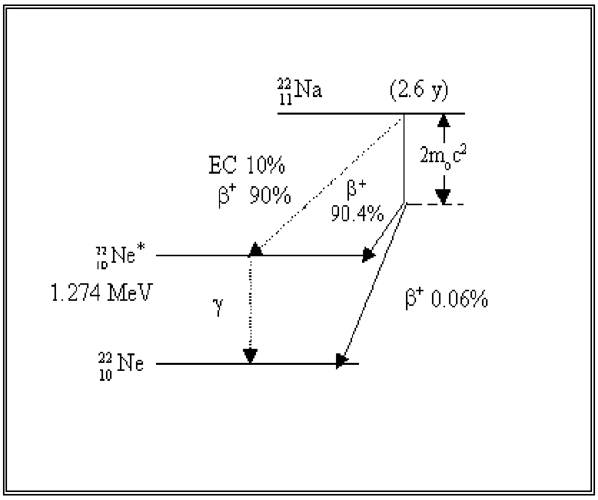

Fig.(2). Decay scheme of ^{22}Na

1- Results and discussion

Polystyrene (PS)

In this work, the analyses are carried out with three discrete lifetime component by using PFPOSFIT program attributed to various states of positron annihilation. The shortest lifetime component $\tau_1 \sim (100\text{-}200)$ ps, is attributed to free annihilation of the positrons with a contribution from the decay of p-Ps. The second lifetime component $\tau_2 \sim (300\text{-}400)$ ps is considered to be due to the annihilation of free positron and the annihilation of positrons trapped at the defects present in the crystalline region (with out forming Ps). The longest lifetime component $\tau_3 \sim (1000\text{-}3000)$ ps is attributed to the pick-off annihilation of the o-Ps in the free volume sites present mainly in the amorphous regions of the polymer matrix [20]. It is this third component which is important in understanding the polymer properties through the free volume model.

The lifetime spectra were analyzed τ_1 fixed at the theoretical value, with **125 ps**. The free volume holes radius, $\mathbf{R_h}$ and the free volume hole size, $\mathbf{V_h}$ are calculated by using formula (5) and (6), respectively; and the free volume hole fraction $\mathbf{F_h}$ is calculated by using formula (7).

It is clear from the results plotted in Figures (5), (6) and (7), that the o-Ps lifetime, thereby V_h, and F_h values for samples irradiated in vacuum are higher than their values for samples irradiated in air. This is due to the effect of peroxy radical formed as a result of the reaction between the effective free radicals and the atmospheric oxygen. The difference between τ_3 values, hence V_h values for samples irradiated in air and those values for samples irradiated in vacuum indicated that the cross-linking rate in the presence of atmospheric oxygen is less than the cross-linking rate in the absence of oxygen. That means the presence of oxygen during β-irradiation causes the increasing of the crystillanity in the amorphous region, and the cross-linking rate is higher than the degradation rate. Oxygen diffusion in the sample during irradiation is retarding the cross-linking rate. The fitted curves as shown in Figures (5), (6), and (7) represent a polynomial fitting of degree three of the points corresponding to various doses, which is given by:

$$P = a_o + a_1 D + a_2 D^2 + a_3 D^3 \qquad (8)$$

Where D is the various doses of β-irradiation and (a_o, a_1, a_2 and a_3) are coefficients to be determined.

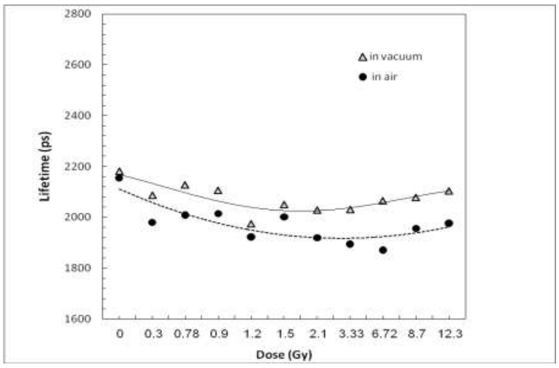

Fig (5). Beta-ray irradiation effect on τ_3 in PS (In Air & vacuum)

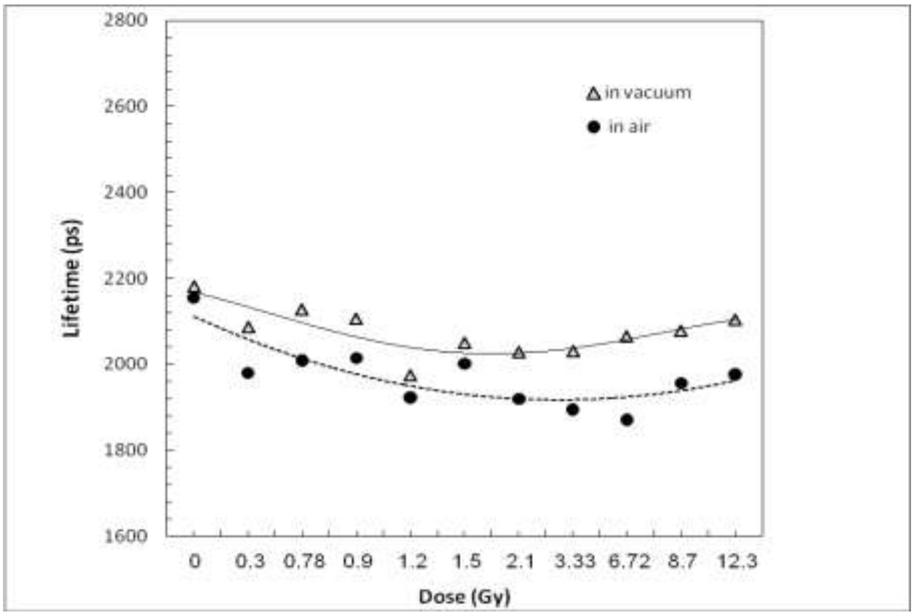

Fig (5). Beta-ray irradiation effect on τ_3 in PS (In Air & vacuum)

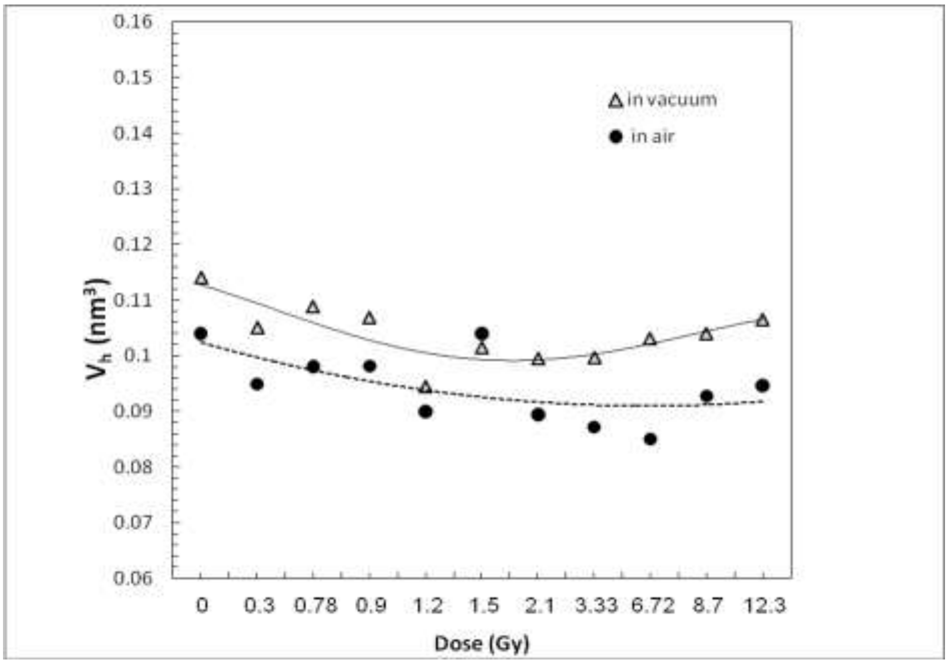

Fig. (6). Beta-ray irradiation effect on V_h in PS (in air & vacuum)

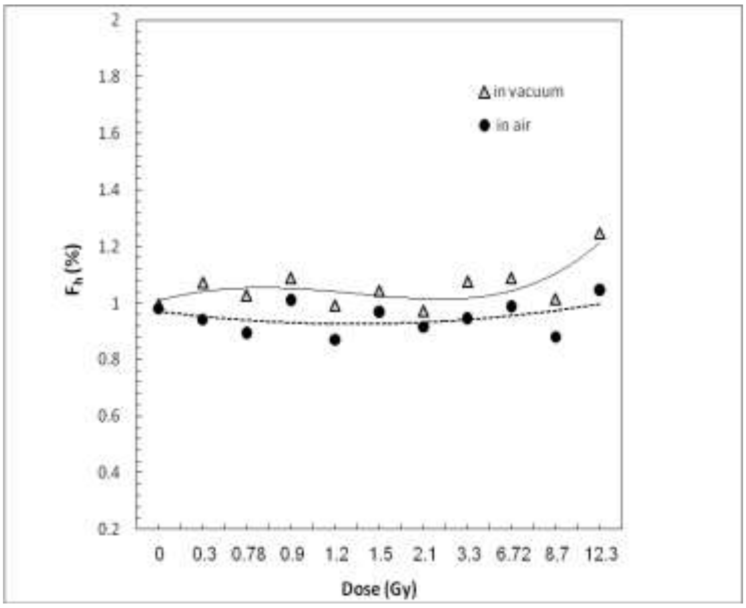

Fig. (7). Beta-ray irradiation effect on F_h in PS (in air & vacuum)

5 Conclusions

The main conclusions of this work can be summarized as follows:

1- Irradiation samples of polymer with and without the presence of atmospheric oxygen causes different structural changes depending on the chemical structure of the investigated polymer and the type of radicals formed.

2- The o-Ps lifetime parameter values for samples irradiated in vacuum are higher than those values for samples irradiated in air due to the effective radicals formed in the presence of oxygen.

3- The initial β-irradiation dose induces significant structural changes in PS, although it is known as radiation resistant.

4- The initial β-irradiation dose induces significant structural changes in PS, although it is known as radiation resistant.

Reference

1- J.Liu, Q.Deng and Y.C.Jean ؛ Macromolecules, 26(1993) 7149.
2- D.M.Schrader & Y.C.Jean; in "Positron and Positronium Chemistry"; D.M.Schrader & Y.C.Jean Eds., Elsevier Sci. Pub.,(1988),P.27.
3- M.H.Cohen and D.Turnbull; J.Chem. Phys., 31 (1959)1164.
4- H.J.Ache; in "Positronium and Muonium Chemistry", H.J.Ache Eds., American Chemical Society, (1979)
5- A.A.Al-Bayati; Ph.D. Thesis, University of Baghdad (1998).
6- T.Suzuki. Y.Ito, K.Kondo and E.Hamada Radit. Phys.Chem., 58 (2000) 485.
7- R.Ramani and C.Ranganathaiah; Polymer degradation and stability,69(2000) 354.
8- P.Kindl, W.puff and H.Sormann; Phys.Stat.Sol. (a), 58(1980) 347.
9- A.A.Al-Bayati, A.A.Abdulah & M.M.Elias ؛The Forth Arab Conference on the Peaceful uses of Atomic Energy), Tunis 1998,Rep.No. 1266.
10- A.H.Al-Mashhadani; Ph.D.Thesis, University of Baghdad, (1998).
11- G.F.Knoll ؛ "Radiation Detection and Measurements", John Wiley & Sons Eds.
12- EG & G; Ortec Catalog (1978).
13- M.Dole, C.D.Keeling and G.Rose; 76(1954) 4304.
14- W.Brandt, S.Berko & W.W.Walker; Phys.Rev., 120(1960) 1289.
15- W.Brandt & J.Wilkenfeld ؛ Phys.Rev., B12 (1975) 2579.
16- S.J.Tao; J.Phys.Chem., 56 (1972) 5499.
17- M.Eldrup, D.Lightbody & J.N.Sherwood; Chem.Phys., 63(1981) 51.
18- H.Nakanishi & Y.C.Jean;P.159 of ref.5.
19- A.P.Mills, Jr.;Phys.Rev.Lett. , 46(1981)717.
20- M.H.Cohen and D.Turnbull; J.Chem. Phys.,31 (1959)1164.
21- G.S.Grest and M.H.Cohen; Adv.Chem.Phys.,48 (1981) 455.
22- Y.Kobayashi, W.Zheng, E.F.Meyer, J.D.McGrvey, A.M.Jamieson & R.Simha; Macromolecules, 22 (1989) 2302.
23- J.Liu, Q.Deng & Y.C.Jean ؛ Macromolecules, 26(1993) 7149.
24- J.Pirenne, Arch. Sci. Phys.Nat .,28 (1949) 273.
25- R.Paulin; "Positron Solid-State Physics", W.Brandt & A.Depasquier Eds., North Holland Pub., Co. Amsterdam (1983), P.1.
26- J.A.Wheeler and N.Y .Ann ؛ Acad, Sci., 46 (1946) 219.