Free Volume Properties of Beta- Irradiated High Density Poly Ethylene (HDPE) Studied by Positron Method

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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 (^{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 (V_h) and free volume hole fraction (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 V_h and 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**.

Keywords: Positron, Free volume, Oxygen effect, Polymer

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 concentration of the free space hole. In 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 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. 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. 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].

K. Sato et. al. [4] have studied Positron (e+) and positronium (Ps) annihilation processes in polymers by positron age-momentum correlation spectroscopy, which can sensitively probe momentum distributions of e+, p-Ps, and o-Ps. For polyether sulfone and ethylene tetrafluoroethylene copolymer belonging to oxygen-containing polymers (O group) and fluorine-containing polymers (F group), respectively, significant effects of positron trapping by polar element are observed. The Doppler profile of o-Ps pick-off annihilation is strongly influenced by F atoms, giving rise to anomalous broadening. The results are discussed together with our previous data of the S¡I3 correlation in order to explore the feasibility of chemical analysis around the free volumes by age-momentum correlation spectroscopy

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

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 thermalized Ps is two to three order of magnitudes larger than the dimension of the free volume available in a typical molecular lattice.

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]

$$\gamma_p = \pi c r_o^2 \int_L \psi_L^*(r)\psi_{\beta+}^* \psi_{\beta+}(r)\psi_L(r)dr^3 \qquad (1)$$

where $\Psi_{\beta+}$ 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]:

$$\gamma_p = \pi c r_o^2 \rho_o \int_{V_o} \psi_{Ps}^*(r)\psi_{Ps}(r)dr^3 \qquad (2)$$

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

$$\gamma_P = \frac{\pi c r_o^2 \rho_O}{1+F(U_O,R_O,R_h)} \qquad (3)$$

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]:

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

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]:

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

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

$$V_h = \frac{4}{3}\pi R_h^3 \tag{6}$$

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:

$$F_h = A\ I_3 V_h \tag{7}$$

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 research, is an Ortec 807 [26] with an additional modification to perform the requirement of the study. The chamber is made from stainless steel and mounted on a varnished wood base, provided with moving cover which contains a vacuum gauge (maximum scale is 10^{-1} torr). This chamber coupled to mechanical vacuum pump by special valve, the vacuum pump and vent functions are combined in a single value. The investigated polymers {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.

Figure 2: A schematic diagram of the typical fast-slow coincidence circuit
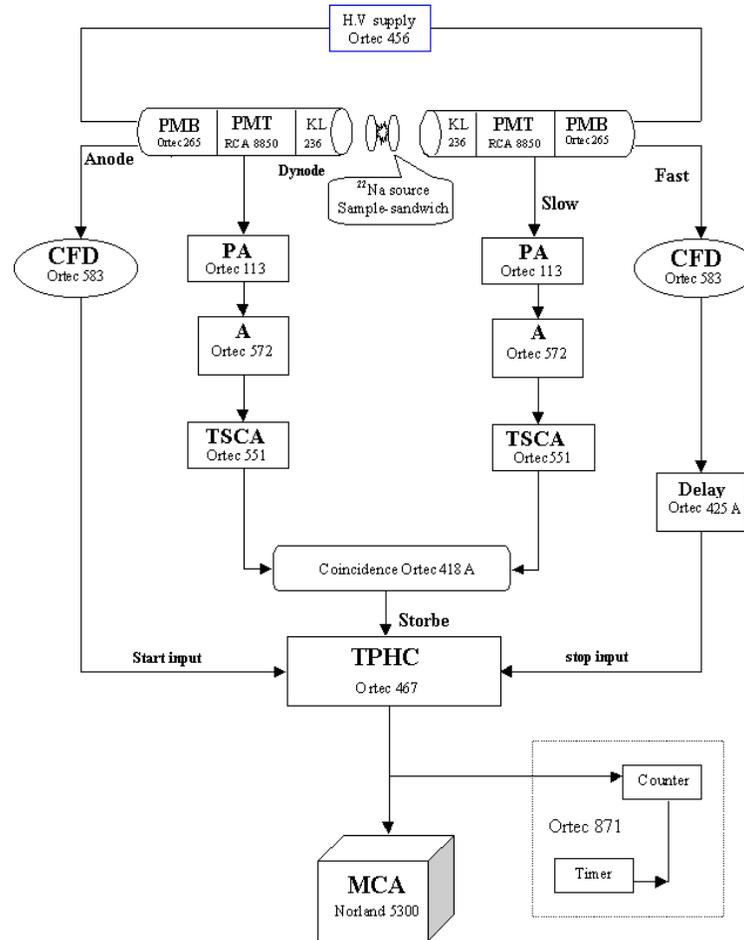
4. Results Discussion and Conclusions

High density polyethylene (HDPE) samples irradiated in the air and under vacuum at room temperature by different β-low doses up to a total dose of 12.3 Gy, with a dose rate of 3.6 Gy/h, were used to study the β-irradiation effect on positron lifetime and microstructural changes, and properties of this polymer

The value of τ_3 is found to be 1928 ps for unirrasiated samples, corresponding to an average V_h value of 0.0902 nm^3 and F_h value of 0.779 %. It is shown in figure (5), that the free volume hole size V_h value increases in presence air from 0.0902 nm^3 to 0.1149 nm^3, at a total β-dose of 1.2 Gy. This means an increment of 27.38 % in V_h value, corresponding to 13.59 % and 36.6 % increment in τ_3 and F_h values, respectively. These results indicating the predominant of degradation process of PE chains resulting in increasing of V_h values, and their density, I_3, as shown in figures (5) and (7), respectively, resulting in increasing of both τ_3 and F_h values, as showen in figures (4) and (6), respectively. As the β-irradiation dose increases above 1.2 Gy in air, the o-Ps lifetime and V_h decrease gradually down to minimum value at a total β-dose of 3.3 Gy. A reduction of 12.05 % in τ_3 value, corresponding to reduction of 21.7 % and 1.5 % in V_h and F_h values, respectively are observed, relative to their maximum values at total dose of 1.2 Gy. This suggests that the reaction of the effective free radicals which associated with an increase in crystallinity in the amorphous regions of HDPE, which reduces the free volume hole size, hence shortening of the o-Ps lifetime.

As β-total dose increases above 3.3 Gy, V_h value, hence τ_3 value increases with increasing β-dose up to a total dose of 8.7 Gy, an increment of 9.87 % and 4.98 % in V_h and τ_3 values are noticed and calculated. These results indicating that the degradation rate in PE chains increases with respect to

cross-linking and decreasing crystallinity rates. The final β-total dose induces a percentage reduction of 2.37 %, 4.54 % and 17.987 % in τ_3, V_h, and F_h values, relative to their values at β-total dose of 8.7 Gy, corresponding to a percentage increment of 4.49 and 4.88 in τ_3 and V_h value, respectively, with respect to their initial values. These results suggest the predominant of cross-linking and increasing crystallinity, in the amorphous regions of PE samples. The positronium formation probability is strongly affected by many factors, such as microstructure of polymer, crystallinity, and free radicals.

Irradiation of HDPE by β-rays produces free radicals by kicking H-atoms, resulting in different chemical reactions, such as recrystallization, creation of hydroperoxides, cross-linking and degradation. The atmospheric oxygen diffusion in HDPE sample during β-irradiation would form hydroperoxides at the polymer chains in the amorphous regions. By increasing the irradiation dose, cross-linking together with increasing of crystallinity in the amorphous regions is induced, and consequently the created hydroperoxides are predominant, resulting a reduction in the rate of degradation. That means degradation is the predominant process, in the irradiation dose range (0-1.5) Gy, whereas cross-linking and increasing crystillinity is the predominant within β-dose range (1.5-6.7) Gy. Above 6.7 Gy, degradation process predominant, later on increasing crystallinity and cross-linking increase resulting in reducing of degradation rate up to 12.3 Gy.

It is clear from the results for PE samples irradiated by β-dose in air and under vacuum, as shown in Figures (4), and (5) that the o-Ps lifetime, and V_h values for samples irradiated under vacuum are higher than those values for samples irradiated in air.

The average values of τ_3 and V_h for samples irradiated in air are less than their values for samples irradiated in vacuum by 80 ps, $0.0084 nm^3$ and 0.15 %, respectively. The reduction in their values is due to the effect of (oxidization process) hydroperoxides radicals, produce as a result of irradiation in the presence of atmospheric oxygen. Also β-irradiation in air causes a higher reduction in I_3 compared with irradiation in vacuum, as shown in Figure (4), this reduction is as a result of inhibition of o-Ps by peroxy radicals (carbonyl and hydroperoxides group), where the peroxy radicals have an electron affinity and may reduce *Ps* formation in PE samples.

Figure 4: Beta-ray irradiation effect on τ_3 in HDPE (in air & vacuum) The triangle simple represent the experimental data under vacuum, and the circule is represent the experimental data in air
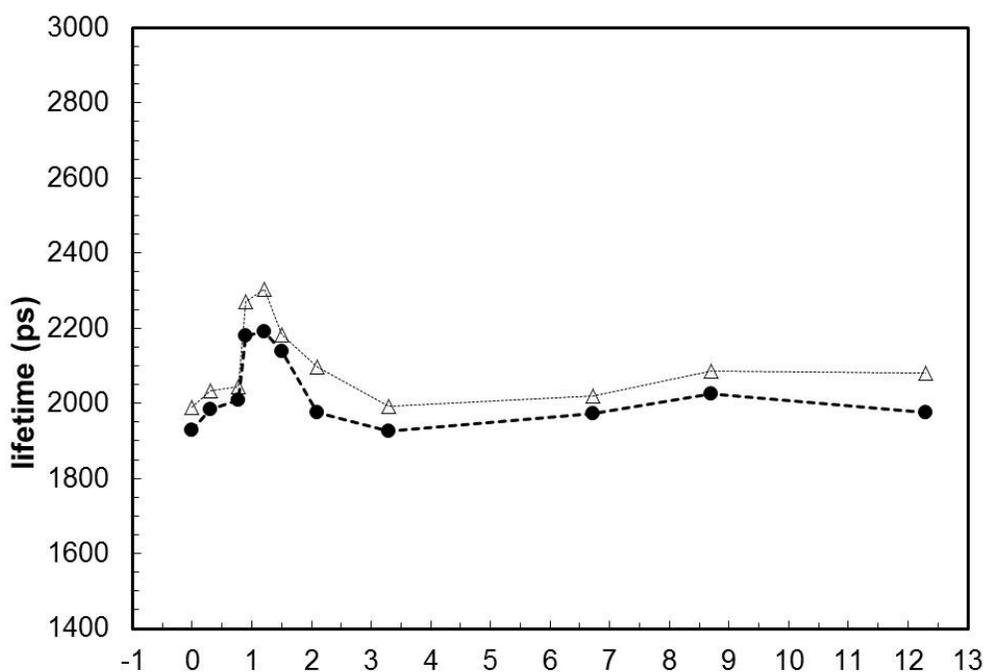
Figure 5: Beta-ray irradiation effect on V_h in HDPE (in air & vacuum)
The triangle simple represent the experimental data under vacuum, and the circle is represent the experimental data in air
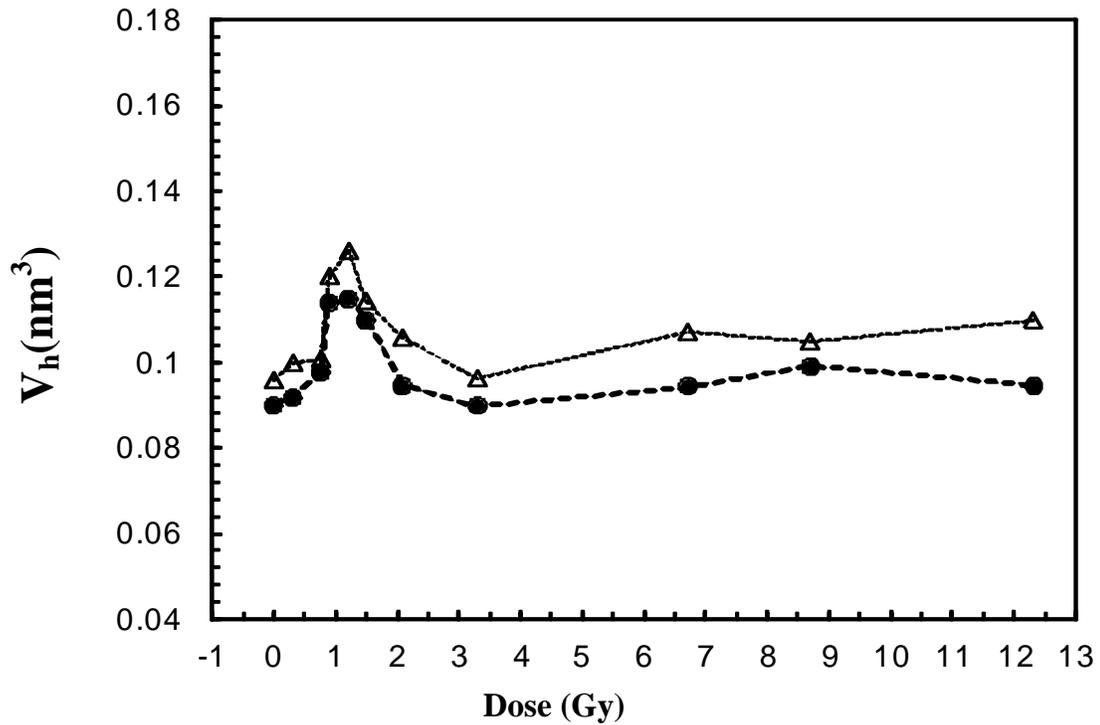
Figure 6: Beta-ray irradiation effect on I_3 in HDPE (in air & vacuum) The triangle simple represent the experimental data under vacuum, and the circle is represent the experimental data in air
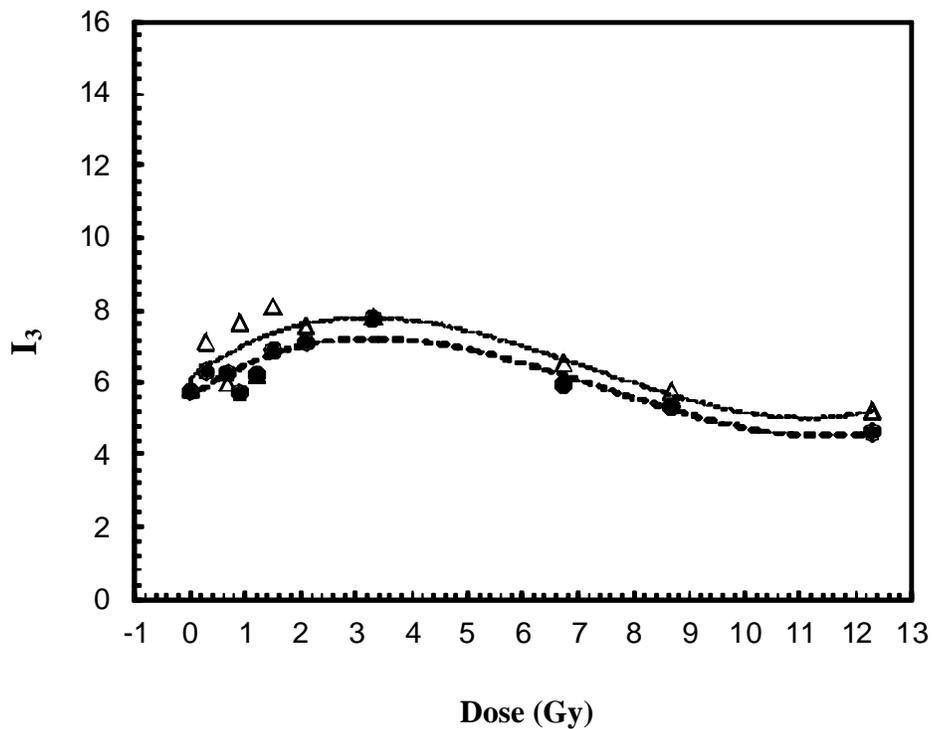
Figure 7: Beta-ray irradiation effect on F_h in HDPE (in air & vacuum) The triangle simple represent the experimental data under vacuum, and the circle is represent the experimental data in air
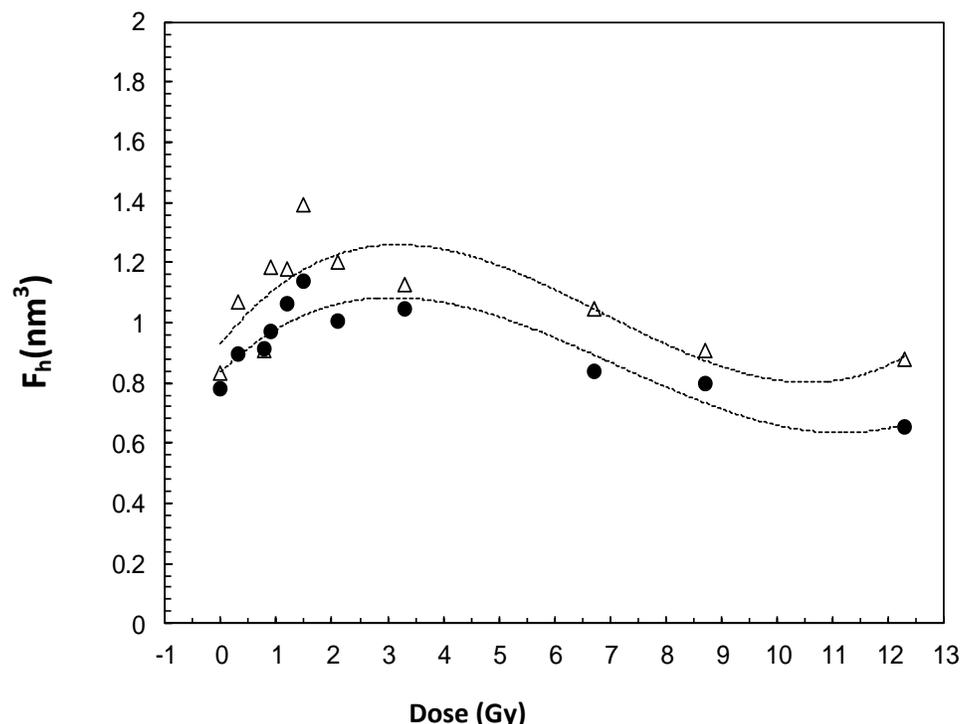
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