Investigation of Beta - irradiation effects on the microstructure of Low Density Polyethylene (LDPE) using (PALT)

A. A. Abdullah, A. A. Al-Bayati and A.A. Selman
Department of Physics, College of Science, University of Baghdad. Baghdad-Iraq.

Abstract

Beta-irradiation effects on the microstructure of LDPE samples have been investigated using Positron Annihilation Lifetime Technique (PALT). These effects on the ortho-positronium (o-Ps) Lifetime τ_3, the free positron annihilation lifetime τ_2 , the free-volume hole size (V_h) and the free volume fraction (f_h) were measured as functions of Beta irradiation - dose up to a total dose of 30.28 kGy.

The results show that the values of τ_3, V_h and f_h increase gradually with increasing Beta dose up to a total dose of 1.289 kGy, and reach a maximum increment of 17.4%, 32.8% and 5.86%, respectively, while τ_2 reachs maximum increment of 211.9% at a total dose of 1.59 kGy. Above these doses, the values show nonlinear changes up to a maximum dose of 30.28 kGy.

The results are discussed in the view point that Beta - irradiation may induce degradation, cross-linking and increasing of crystallinity in the amorphous regions of LDPE.

فحص تأثيرات أشعة بيتا على التركيب الدقيق للبولي أثلين ذي الكثافة المنخفضة بأستخدام (PALT)

علي عطية عبد الله , عبد الحسين عبد الأمير البياتي, أحمد عبد الرزاق سلمان

جامعة بغداد - كلية العلوم – قسم الفيزياء – الجادرية – بغداد - العراق

الخلاصة

فحصت تاثيرات التشعيع ببيتا على البنية الدقيقة لمادة البولي اثلين المنخفضة الكثافة باستخدام تقنية زمن عمر فناء البوزترون ، حيث لوحظت تلك التاثيرات على زمن عمر الاورثو - بوزترونيوم τ_3 وزمن عمر فناء البوزترون الحر τ_2 والحجم الحر للثقب(V_h) وجزء الحجم الحر (f_h) وقد قيست تلك المعلمات كدوال لجرع بيتا حتى الجرعة الكلية البالغة 30.28 كيلو كري ، توضح النتائج ان قيم τ_2 و V_h و f_h تزداد بدريجياً مع زيادة جرعة بيتا حتى الجرعة الكلية 1.289 كيلو كري محققة زيادات قصوى تصل الى 17.4% و 32.8 % و5.86% على التوالي ، بينما تحقق قيمة τ_2 زيادة قصوى بحدود211.9% عند الجرعة الكلية 1.59 كيلوكري. بعد تلك الجرع تظهر هذه القيم تغيرات غير خطية حتى الجرعة القصوى 30.28 كيلوكري، وقد نوقشت تلك النتائج في ضوء وجهة النظر أن التشعيع ببيتا قد يؤدي الى انحطاط وترابط تقاطعي وزيادة في التبلور وذلك في المناطق العشوائية لمادة البولي اثلين المنخفضة الكثافة.

Introduction

When positrons from a radioactive source (energy of few hundreds of keV) penetrate a solid they slow down to thermal energies by inelastic collisions within a psec(10^{-12}s). In molecular solids (e.g polymers) a high fraction of positrons forms positronium (Ps), the formation probability and annihilation characteristics of Ps in these solids depend on their chemical and physical properties. Due to

the ability of the positron to form a variety of electronic states in molecular solids (free positron and Ps, positron and Ps bound to vacancies and voids), positron annihilation lifetime yields a unique information regarding the polymer properties under study. The unique aspect is derived from the fact that the positron electron annihilation process produces photons, which contain information on both electron density and electron momentum, which is a characteristic of annihilation. There exsist many physical probes for characterizing the structure and properties of polymer (1,2,3). However, only a limited number of probes are available for characterizing the free-volume properties, due to the very small size and the dynamical nature of the free volume (4).

In Positron Annihilation Lifetime Technique (PALT) the positron is considered as a nuclear probe. Because of its positive charge it is repelled by the core ions and preferentially localized in the atomic-size free-volume holes (V_h) of polymeric material. The positron and positronium annihilation are therefore ascribed mainly to the free-volume holes in the polymer. The ortho-positronium (o-ps) lifetime (τ_3) is related to the free-volume hole radius R (5) as:

$$\tau_3(ns) = 0.5[1 - \frac{R}{Ro} + 0.159\sin\frac{2\pi R}{Ro}]^{-1} ns \quad (1)$$

where R = Ro + ΔR , and ΔR = 0.1656 nm which is the electron layer thickness. Ro is the radius of the spherical potential well.

The free volume fraction (f_h) is given by the following empirical formula (6) :

$$f_h = AV_hI_3 \quad (2)$$

Where V_h (in nm^3) is the free-volume hole size to be calculated using the spherical radius (R) from equation (1), I_3 is the intensity of τ_3 which is a percentage quantity and A is a constant, its value is empirically determined to be (1-2) (nm^{-3}) in solid polymers.

During the last decade, PALT has been considered as a useful technique to investigate the free-volume changes under irradiation effects with the order of nanometers (7, 8, 9,).

Hsu and Hidly (10) studied polyethylene (PE) which was irradiated by γ- irradiation in vacuum and in air, investigating the effect of annealing, the free radical reactions and cross-linking by different arrangements of irradiation. Brouer et al (11) were able to resolve four lifetime components in the lifetime spectra for γ-irradiated PE samples, whereas Serna et al., (12) measured the free-volume hole size and the density, they also studied the o-Ps life time relation to the (PE) polymer crystallinity. Many types of PE irradiated by γ-rays were studied by Suzuki et al. (13,14), such as Ultrahigh Molecular Weight PE (UHMWPE), high density PE (HDPE) and low density PE (LDPE). They performed the irradiation in air at room temp. They found that HDPE showed large changes in the o-Ps intensity, whereas (LDPE) did not show such effects.

Positron irradiation effects on many types of PEs using ^{22}Na source of 30 μci activity have been studied by Suzuki et al. (13). They found that the highly crystalline PEs were more affected by positron irradiation than the low crystallinity PEs which was ascribed to a cross-linking. An important conclusion they have made is that: for a practical Positron Annihilation Lifetime Spectroscopy (PALS) experiments, the positron of the source irradiation effects on PEs are negligible.

Brauer et al. (15) reported an investigation of High Density Polyethylene (HDPE) irradiated by γ-rays with doses up to 1460 kGy. They showed that there is a correlation between the polymer density changes, due to the irradiation, and the longest lifetime component intensity.

γ-irradiation effects on HDPE using Positron Annihilation Lifetime Spectroscopy (PALS), were studied by Al-

Bayati et al. (16,17), they found that a crystallinity was induced, due to the irradiation, in the amorphous regions of PE and can be detected.

Also, PALS techniques were used by Wang et al., (18) to study the microstructural changes of LDPE films before and after irradiation by 12 MeV electron with a total dose of 280 kGy in air at room temp., they found that the intensity (I_3) of, the o-Ps lifetime, decreased with only 3% as the dose increased up to 80 kGy. Further increase in the dose did not significantly changes I_3, They ascribe this as, due to cross-linking at dose ≥ 80 kGy, which reduces the available free volume causing high probability for o-Ps annihilation. The aim of the present work is to investigate the effects of β-irradiation in the regions of low doses on the microstructure of LDPE.

Experimental and Data Analysis

The PE samples were prepared in the laboratory using commertial (LDPE) grains (16) with a diameter of 32 mm and thickness of 1.5 mm. Some physical properties of (LDPE) is given in table (1).

These samples were irradiated in air at room temperature. Beta-radiation source was $^{90}Sr/^{90}Y$ of 1 Ci activity ($E_{(\beta)max.}$= 2.28 MeV). The dose rate was 0.302 kGy/h. The irradiation was performed up to a total dose of 30.28 kGy. The positron lifetime measurements were performed using a conventional fast-slow coincidence system (16) Fig. (E) with time resolution of 400 ps.

Table (1): Some physical properities of (LDPE).

Density (gm/c^3)	Crystallinity	I (eV)	Z eff	A eff
0.945	65 %	52.25	4.75	6.565

The positron source used is ^{22}Na with activity of 2.14 μci, and the fraction of positrons absorbed in the source was found to be 8% and corrected for it. The lifetime spectra were measured for each individual dose value with total integral counts of 0.5 x 10^6. The peak - to- background ratio was better than 2200: 1. The lifetime spectra were analyzed in three-lifetime components with χ, the reliability indicator, is in the interval (0.9-1.25). The average value of τ_1 (para-Ps annihilation lifetime) was found out of several measurements and fixed at 183ps where the reliability was found as $\chi \leq 1.25$ which gives the best results for three components analysis where the best variance ratio and reasonable deviation. The PFPOSFIT program (19) was used. The lifetime components, their relative intensities and the parameters of the prompt curve, were simultaneously fitted. The free-volume hole size (V_h) and the free volume fraction (f_h), were calculated using eqs. (1) and (2), respectively. The effect of irradiation by β was taken as a total one, neglecting the small possible effect of bremstrunhling radiation which might induced by β interaction with sample material (20). Referring to eqs. (1 and 2) it is clear that the values of τ_3 , I_3, V_h and f_h give an indication that the microstructure of LDPE has been affected.

Results and Discussion

The results of the analysis of the lifetime, the intensity, the free volume hole size and the free volume hole size fraction are given in Table (2). Each value of τ_3, I_3, τ_2 and I_2 are plotted as function of the absorbed dose in Figures (1-a), (1-b), (2-a) and (2-b), respectively. The free volume hole size, V_h and the free volume hole size fraction f_h are plotted against the doses in Figures (3-a) and (3-b), respectively.

Table (2) : The results of the Parameters analysis for β-Irradiated LDPE (τ_1 fixed at 183 ps)

Dose (kGy)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	V_h (nm^3)	f_h (%)
0	295±8	63.80±4.20	2050±18	8.90±0.20	0.1022±0.0034	1.364
0.075	462±17	16.64±1.00	2254±29	8.76±0.10	0.1226±0.0054	1.610
0.151	727±72	5.40±0.40	2407±42	6.94±0.20	0.1375±0.0085	1.432
0.227	575±178	6.35±0.90	2219±46	7.00±0.48	0.1186±0.0091	1.245
0.504	601±77	13.30±5.20	2388±48	8.05±0.30	0.1356±0.0097	1.637
0.604	574±100	13.40±5.00	2347±51	8.07±0.30	0.1314±0.01	1.591
0.768	704±124	6.80±2.20	2343±54	8.17±0.40	0.1310±0.108	1.605
0.840	357±180	17.20±9.40	2162±31	8.04±0.30	0.1130±0.006	1.362
1.060	714±190	8.90±2.40	2246±61	7.36±0.40	0.1214±0.012	1.337
1.289	764±140	7.17±2.10	2407±68	7.00±0.50	0.1375±0.013	1.444
1.590	920±215	7.10±0.90	2186±99	6.28±0.87	0.1153±0.019	1.086
3.100	778±140	5.10±2.50	2376±82	5.66±2.17	0.1344±0.017	1.141
4.000	818±190	6.04±2.70	2227±86	6.40±2.01	0.1194±0.017	1.148
5.820	643±116	8.70±3.10	2126±55	6.52±1.70	0.1095±0.011	1.071
10.65	650±120	7.20±2.10	2150±42	6.63±1.10	0.1118±0.008	1.112
15.18	629±100	7.40±2.40	2240±51	6.54±0.91	0.1206±0.01	1.185
30.28	570±98	6.80±3.10	2332±30	6.42±0.71	0.1299±0.006	1.251

As shown in Figures (1-a and b), a small dose of β-irradiation of 75 Gy induces an increment of about 10% in τ_3. The corresponding increment in V_h and f_h are about 19.9% and 18% respectively. At doses of 0.151 kGy and 1.284 kGy the value of τ_3 reachs a maximum value of 2407 ps, which is 7.4% higher than the initial value where no irradiation, and it is corresponding to 34.6% and 4.9% increment in V_h and in f_h respectively. After that τ_3 decreases to 2126 ps at β-dose of 5.82 kGy, corresponding to an increment of 3.71% with respect to the initial value (2050ps). This is corresponding to an increment of 7.1% in V_h and 21.5% in f_h.

These changes in the value of τ_3 may be interpreted as a result of the high destruction of the polymer bonds by such doses, where a larger free volume size is created. At higher doses the efficient free radicals formation causes a reduction in the o-Ps lifetime due to the quenching processes, as shown in Figure (1 -a). The degradation effects are outweighed by the free radicals effect in the dose range from 0.151 kGy to 1.06 kGy, where the value of τ_3 is decreasing continuously. The higher efficiency of the degradation of LDPE polymers chain is developing for the dose range from 5.82 kGy to the maximum β-dose, which causes τ_3 value increases as shown in Figures (1-a) and (3-a).

In general the value of I_3 shown in Figure (1-b) are not systematically increasing or decreasing, and this may indicate the quite complicated reactions between the o-Ps and the free radicals and the peroxy groups. The reduction of I_3 indicates that the probability of Ps formation is decreasing. Fitting the values of I_3 in table (2) to the formula $I_3 = I_{03} e^{\phi (Gy)^{-1} D(Gy)}$ (15), one can get the following empirical formula :

$$I_3 = 8.914 e^{-7.865\times10^{-5}(Gy)^{-1}D(Gy)} \quad (3)$$

which relates I_3 exponentially to the dose (D) where I_{03} is I_3 at D=0, and ϕ is a coefficient to be found, its unit is $(Gy)^{-1}$. Sompe researchers uses $I_3 = I_{03} + I' e^{-\phi (Gy)^{-1} D(GY)}$, but

our results have a high standard deviation because the doses are very low, so equation (3) is still convenient. Moreover, it is valid only for this (LDPE) samples under investigation, because it is well known that the structure of solid polymers can vary from one sample to another (21).
Beside the o-Ps reactions with the free radicals, and the peroxy groups, ionization mode reactions and oxidation mode reactions might partially take place affecting the Ps formation and its lifetime τ_3 and the intensity I_3 too. These reactions can be represented as:

1- Ionization Mode (IM) :

$$e^+ + e^- + R^{*(n)} \rightarrow e^+ + R^{*(n-1)} \quad (4\text{-a})$$

$$Ps + R^{*(n)} \rightarrow e^+ + R^{*(n-1)} \quad (4\text{-b})$$

$$Ps + R^{*(n)} \rightarrow [Ps - R^{*(n)}]^* \rightarrow e^+ + R^{*(n-1)} \quad (4\text{-c})$$

2- Oxidation Mode (OM) :

$$e^+ + e^- + R^{*(n)} \rightarrow e^- e^+ e^- + R^{*(n+1)} \quad (5\text{-a})$$

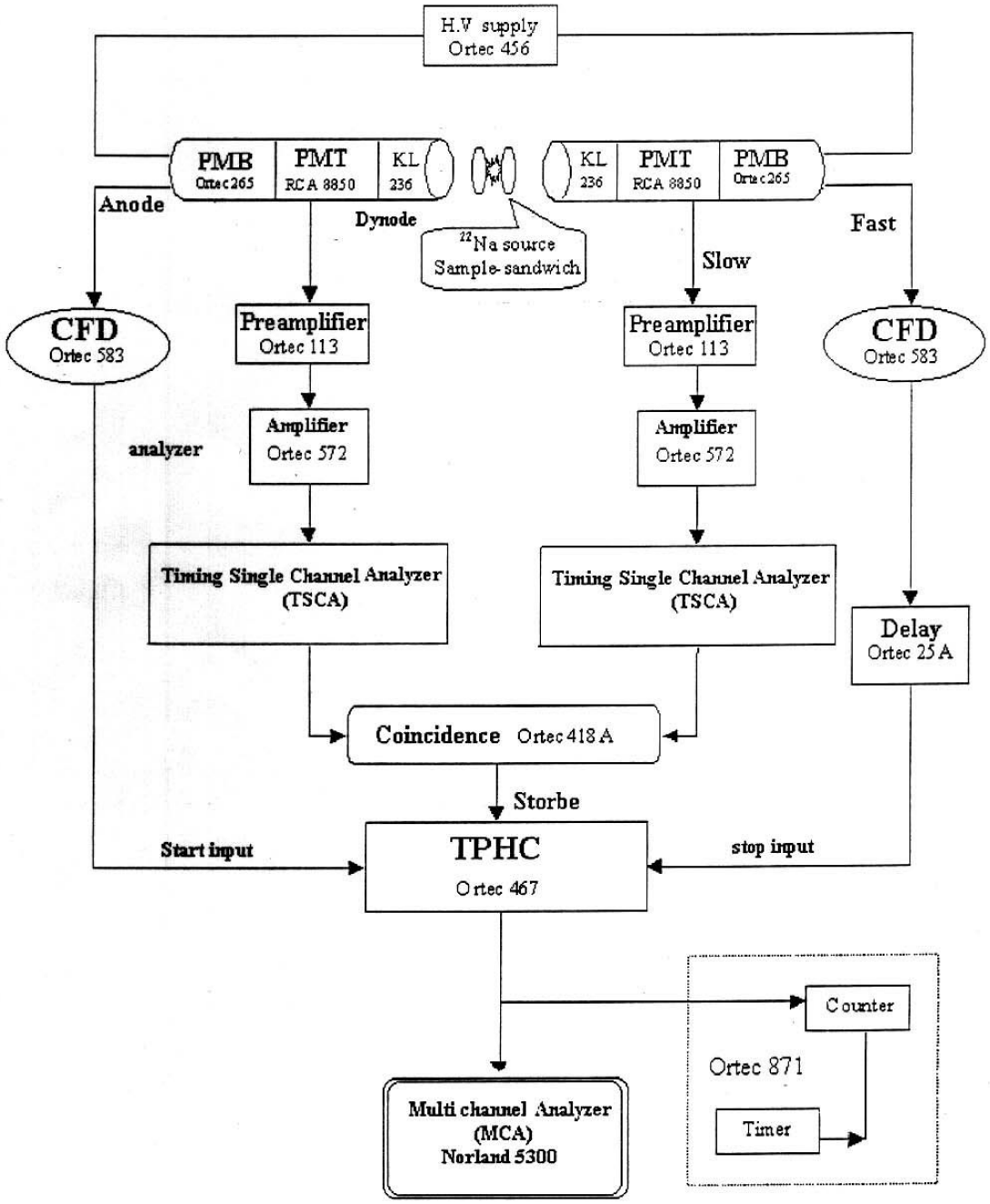
$$Ps + R^{*(n)} \rightarrow e^- e^+ e^- + R^{*(n+1)} \quad (5\text{-b})$$

$$Ps + R^{*(n)} \rightarrow [Ps - R^{*(n)}]^* \rightarrow e^- e^+ e^- + R^{*(n+1)} \quad (5\text{-c})$$

The value of τ_2 is increasing to a maximum value of 920 ps at a Threshold Dose (TD) of β-rays of 1.59 kGy, which is about 211% greater than the initial value (295 ps). The higher peroxy free radicals formation rate makes the value of τ_2 reaching its maximum at such a relatively low β-dose, as shown in Figure (2-a), but I_2 decreases at this dose, which is due to the same causes which was mentioned before. At TD the transition between the positron physical systems (Para-Positronium to o-Ps and vice versa) is expected due to the higher free radicals concentration.

Figures caption

Figure (E) A block diagram of the experiment setup.
Figure (1-a). beta- ray irradiation effect on τ_3 in LDPE.
Figure (1-b). beta- ray irradiation effect on I_3 in LDPE.
Figure (2-a). beta- ray irradiation effect on τ_2 in LDPE.
Figure (2-b). beta- ray irradiation effect on I_2 in LDPE.
Figure (3-a). beta- ray irradiation effect on V_h in LDPE.
Figure (3-b). beta- ray irradiation effect on F_h in LDPE.



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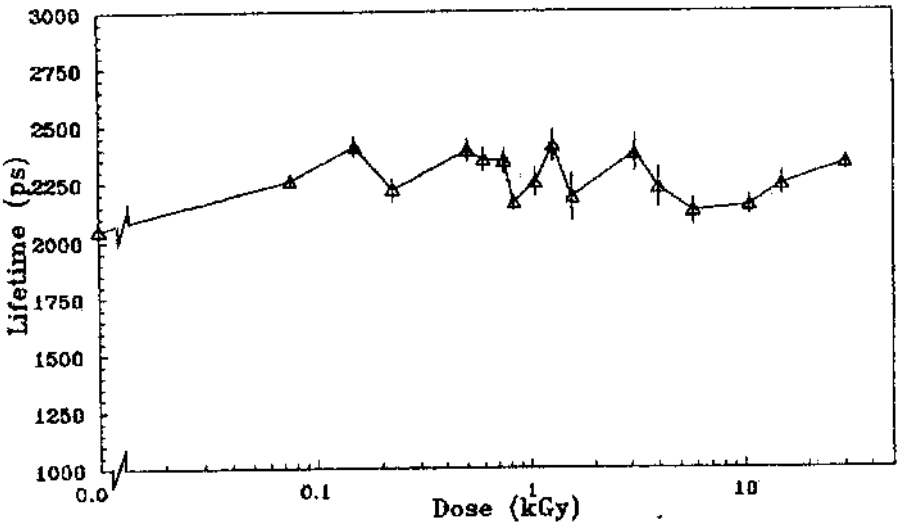
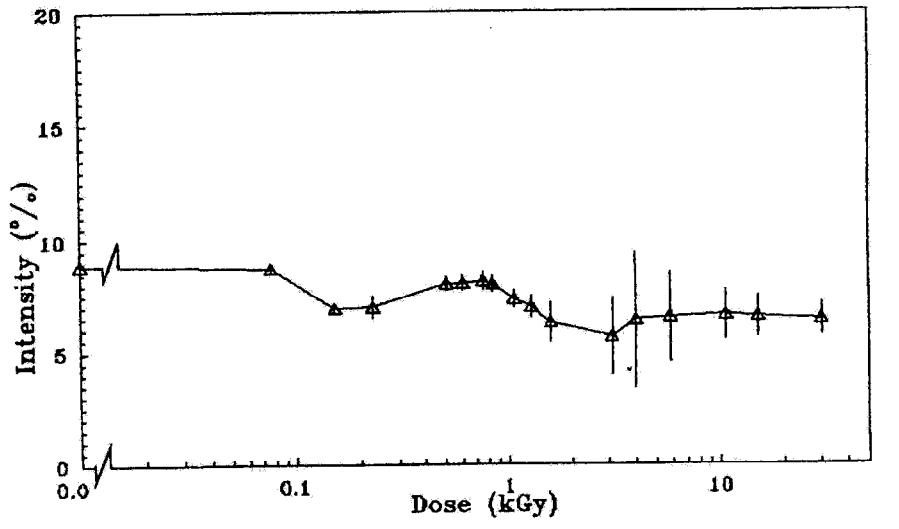


Figure $(1-a)$. Beta-ray irradiation effects on τ_3 in LDPE.



Figur $(1-b)$. Beta-ray irradiation effects on I_3 in LDPE.

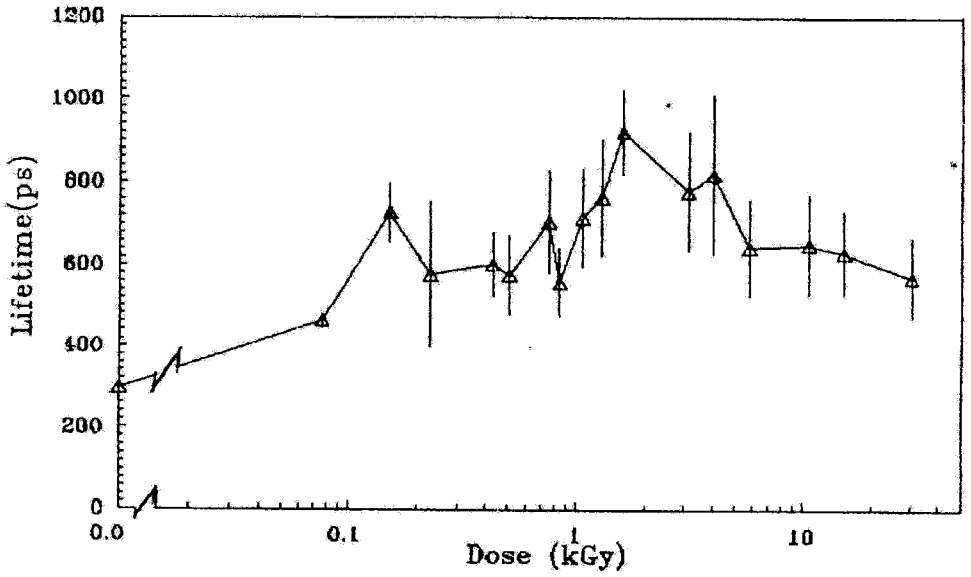


Figure $(2-a)$. Beta-ray irradiation effects on τ_2 in LDPE.

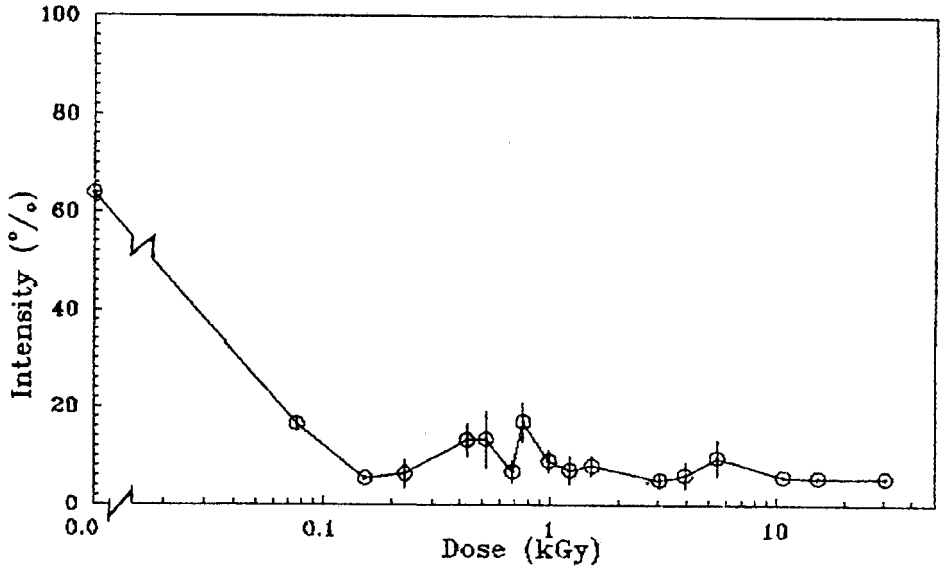


Figure $(2-b)$. Beta-ray irradiation effects on I_2 in LDPE.

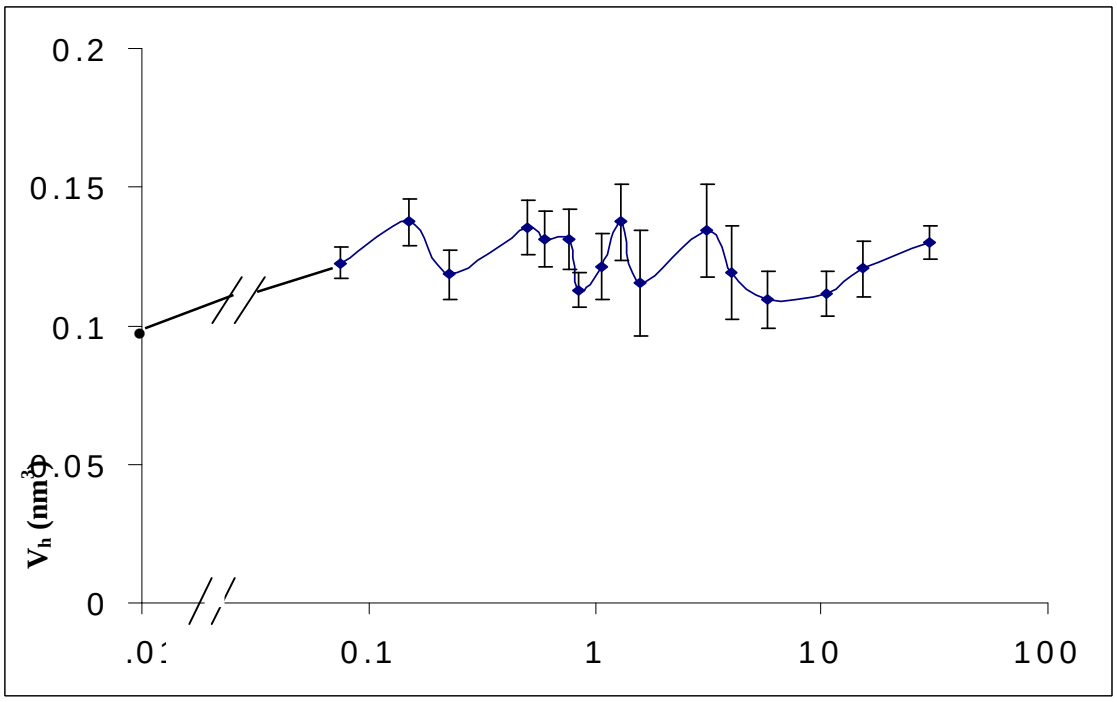


Figure (3 – a). Beta – ray irradiation effects on V_h in LDPE

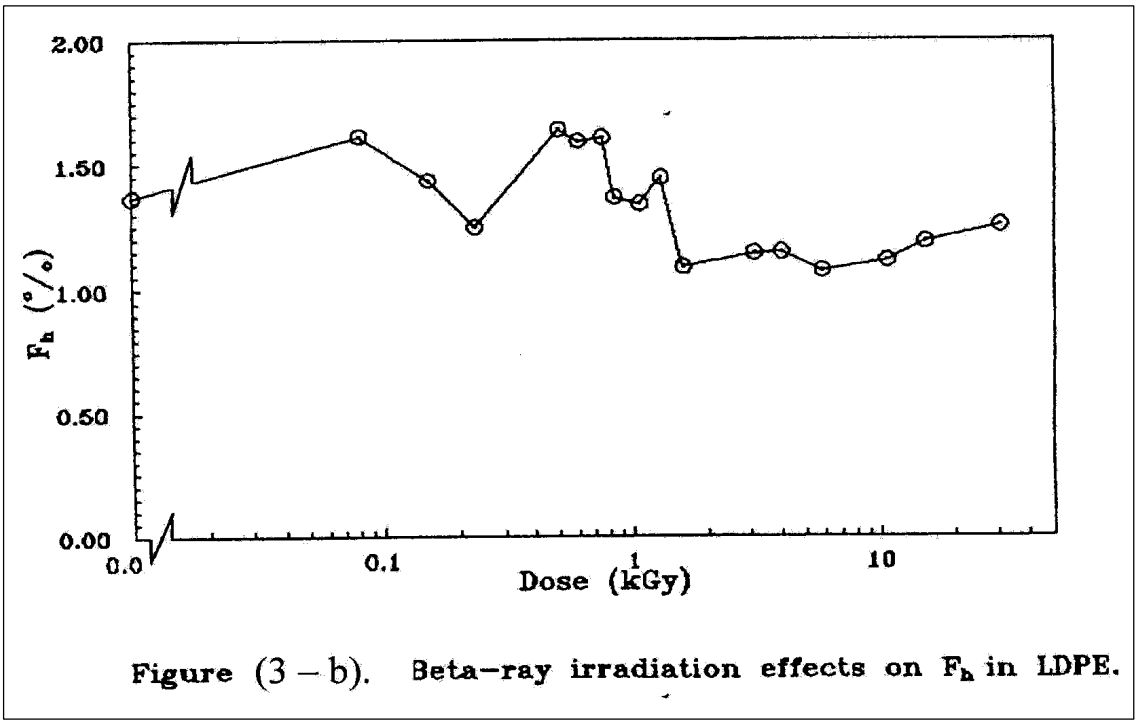


Figure (3 – b). Beta-ray irradiation effects on F_h in LDPE.

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