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Study of Gamma - irradiation effects on the Polymethylmethacrylate (PMMA) Using (PAL) Method

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Abstract: *Gamma - irradiation effect on polymethylmethacrylate (PMMA) samples has been studied using Positron Annihilation Lifetime (PAL) method . The ortho - positronium (o-Ps) lifetime τ_3, hence the o-ps parameters , the -volume hole size (V_h) and the free volume fraction (f_h) in the irradiated samples were measured as a function of gamma-irradiation dose up to 28.05 kGy. It has been shown that τ_3, V_h and f_h are increasing in general with increasing gamma-dose, to reach a maximum percentage increment of 22.42% in τ_3, 60% in V_h and 29.5% in f_h at 2.55 kGy , whereas τ_2 reaches maximum increment of 119.7% at 7.65 kGy. The results suggest that gamma-irradiation induces structure changes in PMMA, causing degradation in the main chains, and the presence of oxygen causes reduction in the amorphous regions ; oxygen and the peroxy radicals form cross-linking at reactive sites between neighboring chains, giving a net reduction of the degradation yield.*

دراسة تأثيرات التشعيع بأشعة كاما على البولي ميثيل ميثا اكرليت (PMMA) باستخدام طريقة زمن عمر فناء البوزترون (PAL)

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الخلاصة : *درست تأثيرات التشعيع بأشعة كاما على نماذج من البولي ميثيل ميثا اكرليت (PMMA) مستخدمين طريقة زمن عمر فناء البوزترون ، حيث قيس زمن عمر البوزترونيوم التعامدي (o-Ps) (τ_3) وحجم الفجوة للجسم الحر (V_h) وجزء الحجم الحر (f_h) كدوال لجرع التشعيع حتى (28.05) كيلوكري (kGy). لوحظ من النتائج ان τ_3 و V_h و f_h تزداد بزيادة جرعة كاما وتصل زيادة عظمى هي 22.42% و 60% و 29.5% على التوالي عند جرعة مقدارها (2.55) كيلوكري . اما τ_2 ، زمن عمر فناء البوزترون الحر ، فتصل زيادته العظمى الى 119.7 % عند جرعة (٧,٦٥) كيلوكري. وهكذا تشير النتائج الى ان التشعيع باشعة كاما احدث تغيرات في (PMMA) مسببا تهديما في السلاسل الاساسية وان وجود الاكسجين سبب نقصا في المناطق غير البلورية، كما ان الاكسجين مع جذور البيروكسي (Peroxy) تكون ترابطا جدائيا عند الجوانب النشطة بين السلاسل المتجاورة معطية حصيلة نقصان في حصيلة التهدم .*

Introduction:

Positron annihilation spectroscopy (PAS) has been recently developed to determine the defect properties at the atomic level for polymer materials (1). The sensitivity of PAS is due to the localization of positronium (Ps) in those holes range from 1 A° to 20 A°. Positron annihilation spectroscopy has emerged as a unique and potent probe for characterizing the free - volume properties of polymers (2).

In PAS, the antiparticle of electron, the positron is employed as a nuclear probe. Because of its positively charged nature , the positron is repelled by the ion cores and preferentially localized in the atomic - size free-volume holes (V_h) of a polymeric material. Therefore , the positron and positronium (a bound atom which consists of a positron and an electron) annihilation signals are found to be contributed mainly from the free-volume holes in a polymer. Currently , PAS has been mainly developed in monitoring the ortho-Positronium (o-Ps , a triplet state) annihilation lifetime (PAL) for polymeric applications . The results for o-Ps lifetime and its probability are related to free-volume hole size , fraction and distribution. Experimental (3,4) and theoretical efforts (5,6,7) suggested that PAL is a unique probe which can directly measure the free-volume hole size in amorphous polymers. The results for o-Ps lifetime and its probability , are related to free-volume hole radius R (8) as :

$$\tau_{o-Ps} = 0.5[1 - \frac{R}{Ro} + 0.159 \sin \frac{2\pi R}{Ro}]^{-1} ns \qquad (1)$$

where R = Ro + ΔR, ΔR = 0.1656 nm, the electron layer thickness, and R_o= the radius of the volume before irradiation.

The free volume fraction (f_h) has been expressed (9) as an empirical equation of the form:

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

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 (in %) is the intensity , and A is a constant , which is empirically determined to be (1-2) (nm^{-3}) in solid polymers.

PMMA is an amorphous polymer that usually suffers from degradation in the side chain (scission) by irradiation. One important result of this effect is its molecular weight reduction . The number of molecules per unit mass is proportional to the reciprocal of molecular weight (10,11) . It was found that 60-65 eV deposited energy (of ^{60}Co γ-ray) causes one scission in PMMA (12) at room temperature . If the reciprocal of the polymer molecular weight is plotted against the absorbed dose , there must be a linear relation (a straight line) of a positive slope proportional to the radiation energy absorbed per unit scission in the polymer chain (10,13).

Ito and Tabata (14) reported the polymerization of the (PMMA) methylmethacrylate monomor using γ-rays irradiation by means of Positron Annihilation Lifetime Spectroscopy (PALS). They found that both τ_3 and I_3 were increasing with increasing the absorbed dose up to 1MGY.

Al-Bayati et al., (15,16) investigated γ-irradiation effects on PMMA using PALS. They concluded that a reduction of the amorphous regions of PMMA occurred as the dose increased up to 880 KGy. The reduction of the lifetime indicated that free volume size

reduction and therefore the expected effects are due to the cross-linking , due to the oxygen presence and the interactions with the proxy radicals at reactive sites of PMMA. More recently, Rubilio et al. (17) have investigated the effects of γ-irradiation on PMMA with a total dose of 200 kGy using PALS, as well as the mechanical properties of that polymer. The free volume content of non irradiated and the irradiated polymers clearly demonstrated increment as the dose increased . They explained the results due to the scission and the rapture of the polymer chains.

Experimental and Data Analysis

The PMMA samples were prepared in the laboratory , with a diameter of 32 mm and thickness of 1.5 mm.

The samples were irradiated in air at room temperature to energetic γ-rays using a Co-60 gamma cell, with a dose rate of 0.425 kGy/hour , up to a total dose of 28.05 kGy.

The positron lifetime measurements were performed using a fast-slow coincidence system (15) with a time resolution of 400 ps. The positron source activity was 2.14 uci (^{22}Na) and the fraction of positrons absorbed in the source was found to be 8%.

The lifetime spectra were measured for each individual dose value with a total integral counts of 0.5×10^6. The peak - to- back ground ratio was better than 2200 : 1. The lifetime spectra were analyzed in three-lifetime components using PFPOSFIT program (18). 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.

Results and Discussion

The results of the analysis of PMMA lifetime spectra for γ-doses are given in Table (1). The o-Ps lifetime, τ_3 and the corresponding intensity I_3 are plotted as a function of irradiation doses in Figures (1-a) and (1-b) respectively. The free positron lifetime τ_2 and its corresponding intensity I_2 are also plotted as a function of the irradiation doses in Figures (2-a) and (2-b), respectively. The free volume hole size, V_h, and its corresponding free volume hole fraction (f_h) are illustrated as a function of the absorbed doses in Figures (3-a) and (3-b) respectively. The initial values of τ_3 and τ_2 for the unirradiated samples are in agreement with those found in the literature (15,20).

At low γ-dose only small changes occur in τ_3 as shown in Table (1) . At γ-dose of 0.425 kGy a 10% increment occurs in τ_3 (relative to the unirradiated samples parameters), associated with a 4.7% reduction in I_3 and a 21.9% increment in V_h and a 6.1% increment in f_h . The values of τ_3 then remain constant up to a total γ-dose of 0.743 kGy, while I_3 decrease rapidly at that dose by 18.5% . Above that dose τ_3 decreases continuously up to a total γ-dose of 0.956 kGy , where its value reaches 2054 ps, which is only a 4.5% higher than its initial value. This causes an increment in V_h of about 9.1%.

After that , τ_3 reaches its maximum value of 2442 ps, which is 27.6% more than the initial value , associated with a 58% increment in V_h and a 29.5% in f_h. At doses above 1.7 kGy, τ_3 slightly decreases up to a total γ-dose of 28.05 kGy. As shown in Figure (1-b) , I_3 is slightly decreasing as γ-dose increases . The general behavior of τ_3 indicates that chain scission occurs in PMMA as

γ-dose increases. Chain scission causes increasing of the free volume hole size. An important reason of that is the reduction of the number-average molecular weight of the polymer, M_n, where each chain scission produces a new free molecule from the polymer chain. Since reducing M_n causes increasing in the available free volume size , the o-Ps pick-off annihilation rate will decrease and thus the value of τ_3 will increase.

Table (1) . The lifetime Parameters of γ-Irradiated PMMA (τ_1 fixed at 182 ps)

Dose (kGy)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	V_h (nm^3)	f_h (%)
0	442±71	67.56±5.0	1913±37	7.78±0.42	0.089	1.043
0.106	312±12	64.26±2.4	1981±24	8.10±0.14	0.096	1.170
0.212	380±33	66.50±2.6	1932±29	7.74±0.20	0.091	1.059
0.318	378±36	67.21±2.7	1926±28	8.13±0.20	0.091	1.107
0.425	394±37	64.80±1.8	2121±30	7.91±0.20	0.109	1.293
0.531	395±28	63.18±1.7	2114±29	8.22±0.18	0.108	1.336
0.637	386±33	64.00±3.7	2117±28	7.86±0.20	0.109	1.281
0.743	512±186	62.00±3.6	2132±38	6.34±1.34	0.110	1.047
0.850	339±25	63.60±2.7	2050±26	8.47±0.16	0.102	1.298
0.956	374±36	63.60±3.8	2054±25	8.21±0.16	0.103	1.263
1.062	383±40	65.90±2.8	2108±28	7.40±0.60	0.108	1.194
1.275	341±22	63.90±1.9	2104±24	8.26±1.41	0.107	1.330
1.700	450±21	60.28±1.5	2000±62	6.77±1.30	0.097	0.990
2.550	628±35	55.40±2.4	2442±82	6.38±2.40	0.141	1.351
4.678	811.196	53.60±1.4	2335±70	7.19±0.50	0.130	1.406
7.650	971±112	54.60±1.6	2397±83	6.70±1.40	0.137	1.387
14.45	704±156	54.10±1.5	2134±53	8.40±1.02	0.110	1.398
28.05	708±82	52.65±2.5	2323±66	6.38±1.20	0.129	1.235

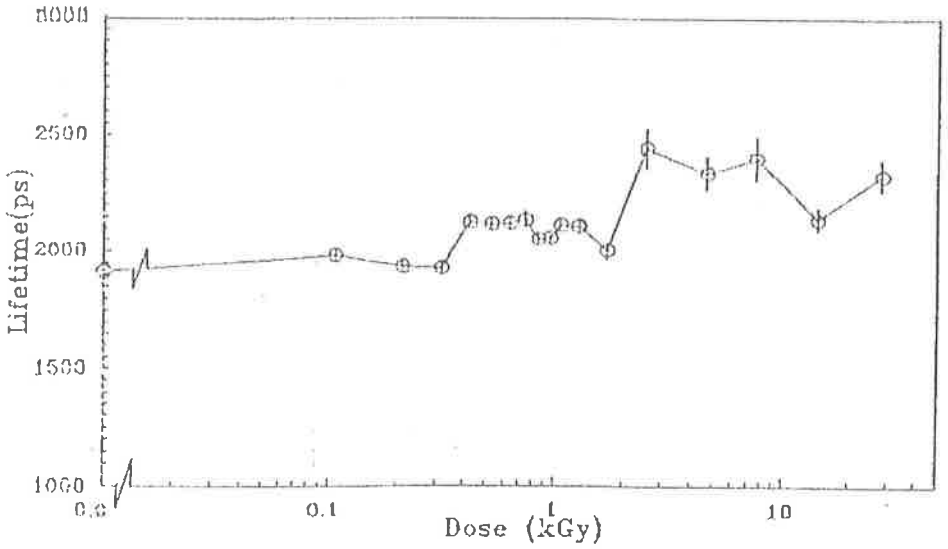


Figure (1-a) Gamma-ray irradiation effects on τ_3 in PMMA.

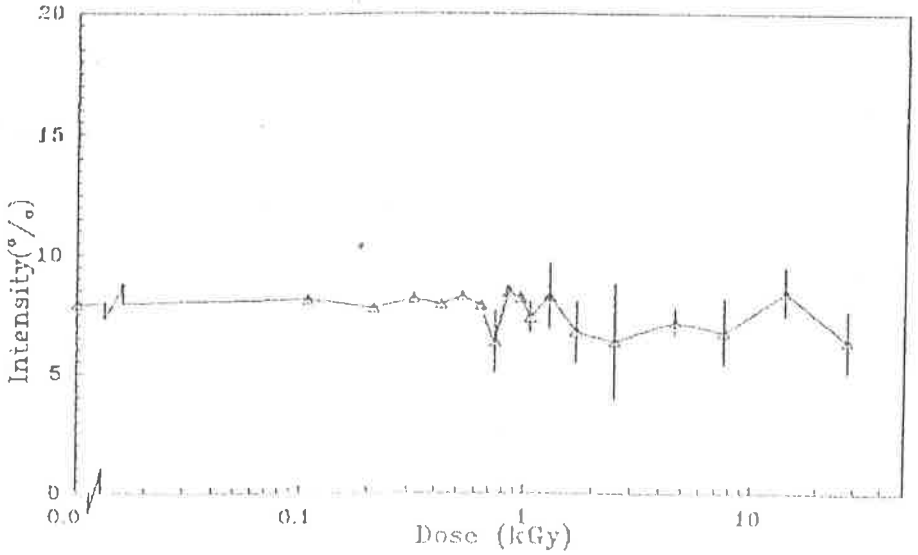


Figure (1-b). Gamma-ray irradiation effects on I_3 in PMMA.

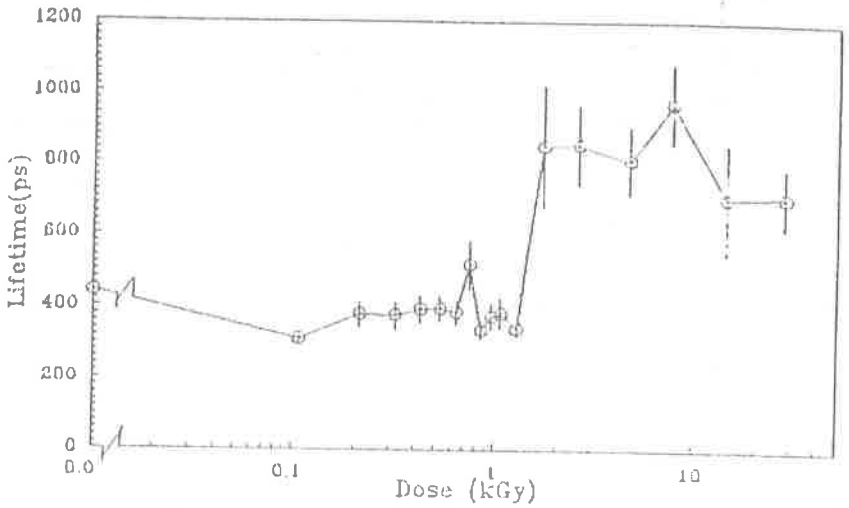


Figure (2-a). Gamma-ray irradiation Effects on τ_2 in PMMA.

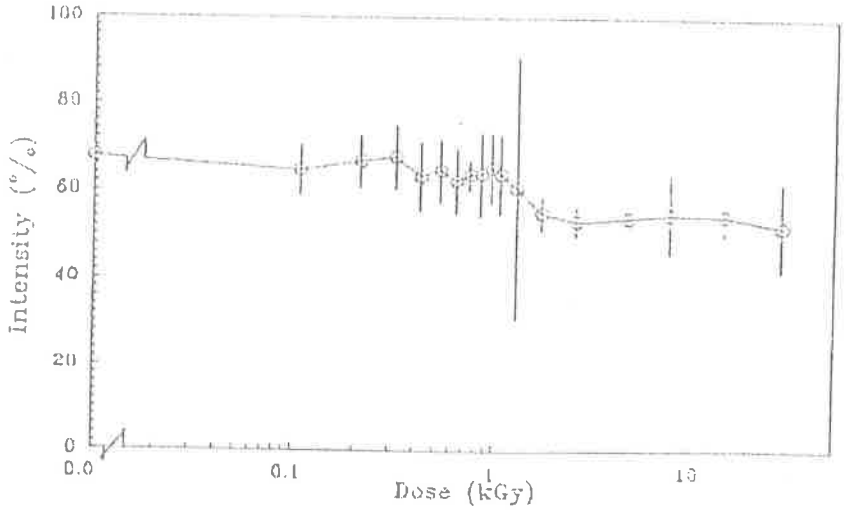
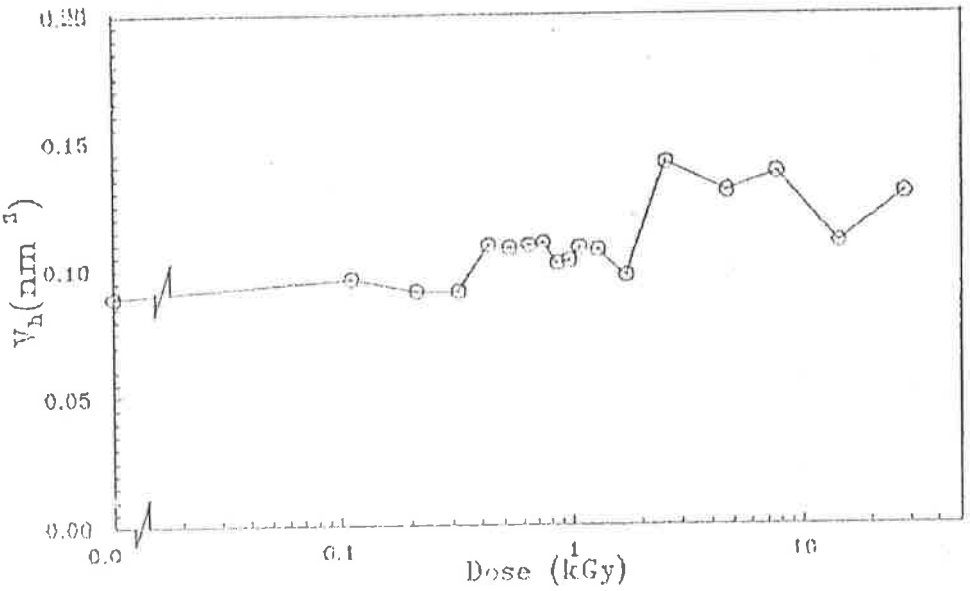
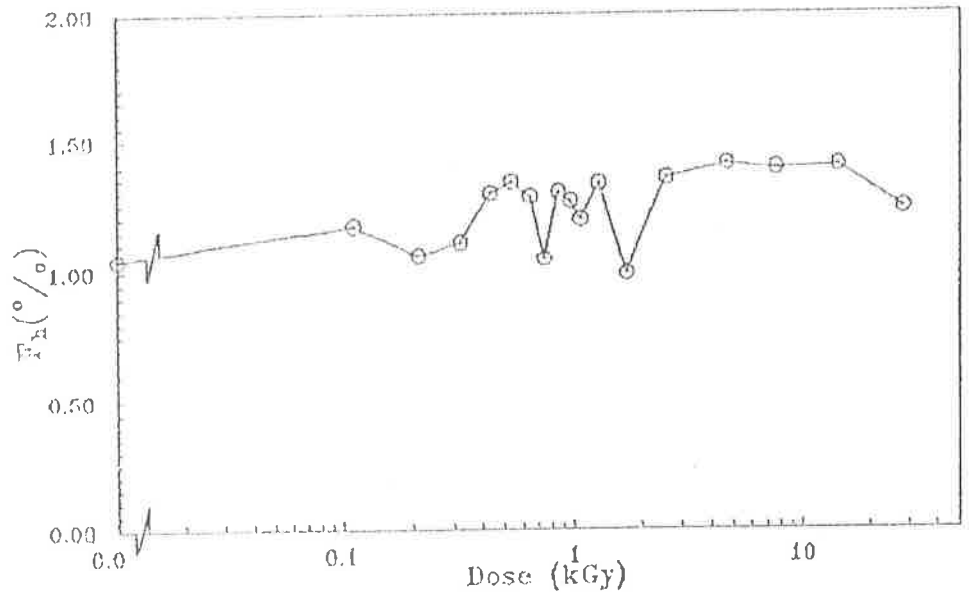


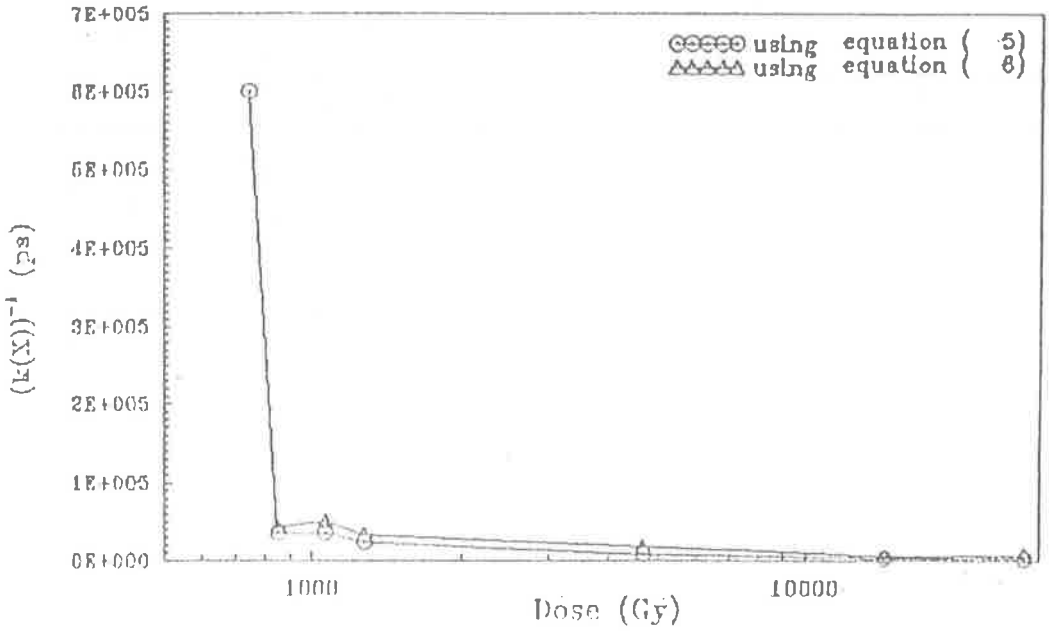
Figure (2-b). Gamma-ray irradiation effects on I_2 in PMMA.



Figure(3-a) . Gamma-ray irradiation effects on V_h in PMMA.



Figure(3-b). Gamma-ray irradiation effects on F_h in PMMA.



Figure(4) The $(k(X))^{-1}$ values (in ps) for gamma-irradiated PMMA.

This should be the only reason of increasing τ_3 as γ-dose increases up to at least 0.637 kGy, because at such low doses the participation of the free radical's concentration in the o-Ps lifetime quenching is negligible due to their low concentration. The constancy of τ_3 values for γ-dose interval from 0.850 kGy to 1.7 kGy reflects the high formation rate of the free radicals in such a way that the effect of the o-Ps lifetime quenching in this interval of dose is equivalent to the increment of τ_3 due to the reduction in M_n of PMMA . Above γ-dose of 1.7 kGy the increment in τ_3 might be due to the fact that M_n of PMMA starts to decrease with a higher rate, or that the formation rate of the free radicals begins to be slower . It is the preferred reason because the first reason is not likely , where it is known (10,27) that the change in M_n of PMMA polymer is contantly behaving as a function of the absorbed dose.

The contribution of the free radicals could be estimated from τ_3 values and the calculated values of M_n. To do that , we take the values of M_n found in references (10) and (17) . Using those values and fitting them to the formula :

$$Y = \frac{1}{M_n} = A \times D(Gy) + B \qquad (3)$$

where D (Gy) is the absorbed dose (in Gy), A and B are empirical constants, then the following empirical formulae could be deduced .

$$\frac{1}{M_n} = 1.8440 \times 10^{-10} D\,(Gy) + 9.738 \times 10^{-7} \quad (4)$$

for the values given in reference (21) , and ,

$$\frac{1}{M_n} = 1.5504 \times 10^{-10} D\,(Gy) + 3.803 \times 10^{-7} \quad (5)$$

for the values reported in reference (17). In both references the irradiation was performed under vacuum and the results could be applied for irradiating PMMA with both γ-rays from ^{60}Co and 2 MeV electrons. Since the constants A and B in formulae (4) and (5) could not be applied for any high doses because of the presence of oxygen, which might add a noticeable effect. These formulae could be applied for low doses only , say < 500 Gy where the effects of the free radicals are expected to be negligible. For γ-dose, the dose interval from 0 to 0.425 kGy is chosen. Then the approximate values of M_n became as given in Table (2) for both formulae.

Table (2) : The approximate values of M_n for γ-irradiated PMMA polymer as calculated from formulae (2) and (3)

Dose (kGy)	$M_n \times 10^6$ (from eq. 2)	$M_n \times 10^6$ (from eq. 3)
0	1.026	2.629
0.106	1.006	2.520
0.212	0.986	2.421
0.318	0.967	2.327
0.425	0.948	2.241

It has been shown (22) that the relation between M_n and τ_3 may be given by:

$$\tau_3 = \frac{1}{\lambda_o + \Omega M_n} \quad (6)$$

where Ω and λ_o are empirical constants Thus using M_n values given in Table (2) and fitting them to formula (6), it could be found that :

$$\tau_3 = \frac{1}{5.78\times10^{-5} + 4.547\times10^{-10} M_n} (Ps) \quad (7)$$

for the values of formula (4), and :

$$\tau_3 = \frac{1}{2.928\times10^{-4} + 8.827\times10^{-11} M_n} (Ps) \quad (8)$$

for those values of formula (5). Both formulae (7) and (8) indicate that τ_3 decreases as M_n increases. Such behavior is expected from the free volume theory (21).

Furthermore it is suggested (22) that in an environment where a chemical reaction is taking place between the o-Ps and some chemical specie of a concentration [X] , then the following relation holds :

$$\lambda_3 \propto \lambda_{P_o} + k[X] \quad (9)$$

where λ_3 is the experimentally measured o-Ps total annihilation rate , λ_{po} is that rate corresponding to the

pick-off annihilation rate only and k is the reaction speed. It is also stated (22) that the presence of the term k [X] (or the chemical effect rate) will alter the physical meaning of τ_3 and that the measured annihilation rate then will not express the free volume hole size , unless the participation of the chemical effect rate given in formula (9) is negligible. We think that the chemical effect rate terms do not change the physical meaning of the measured o-Ps annihilation rate , at least in irradiated polymers , because the presence of the free radicals will increase the observed lattice potential so the net effect of the term k [X] appears to quench the o-Ps lifetime by pick-off reaction mostly. It is confirmed (22,23,24,25) that the o-Ps measured annihilation rates in irradiated polymers do reflect the free volume hole size. Thus one can rewrite formula (9) as :

$$\lambda_3 \propto \lambda_3^- + k[X] \qquad (10)$$

where: λ_3^- is proportional to the o-Ps pick-off annihilation rate at [X] = 0. Formula (10) could be extended to include other possible affecting terms such as that due to changes in M_n. Thus the following empirical formula holds :

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{\lambda_3^- + \Omega M_n + k[X]} + \Delta \qquad (11)$$

where Δ is the term corresponding to any additional effects , such as those due to crystallinity and density changes, for simplification it is ignored in this work.

At very low doses, the term of the chemical effect rate is negligible and formula (6) holds. For higher doses where the effect of that term (Δ) is important, one can extrapolate the relation between M_n and the absorbed dose and then the participation of k[X] could be found. For γ-doses the calculated values of the chemical effect term are listed in Table (3).

These values are helpful in comparing γ and β^- irradiation effects when β^--irradiation effect is studied. The values of $(k[X])^{-1}$ are shown in Figure (4). Both curves indicate the continuous increment in k[X] values as γ-dose increases. If the value of k is assumed to be constant, then the changes in the chemical rate effect reflect the trend increment in the free radicals concentration [X].

This causes a reduction in τ_3 because of the increment of the probability of the (o-Ps - free radical) compound formation. When this compound is formed, the potential that affects the o-Ps pick-off annihilation rate will increase, thus leading to increase the pick-off annihilation rate and to reduce τ_3. The formation of other systems, such as the Ps-system is of a high probability only when the free radicals` concentration is very high (26). Therefore the chemical effect rate terms` contribution in the reduction of τ_3 is negligible comparing to the effect of the reduction in M_n and the probability of Ps- formation is also small.

Furthermore, the small effects of k[X] could be observed from the inhibition of the o-Ps, which is correlated with the reduction in I_3 given in Figure (1-b). Beside their effects on τ_3, the free radicals may also attract the free electrons generated due to the primary radiation effects, or they may attract the positron itself. Also there is a possibility to change I_3 due to the free radicals interaction with the o-Ps, where they may affect it by ionization or oxidation.

Table (3) . 1/k[X] for γ-irradiated PMMA as calculated using formulae (7) and (8) and the values of Table (2)

Dose (kGy)	τ_3 (ps)	1/k[X] (ps) (from eqs. 4 and 7)	1/k[X] (ps) (from eqs. 5 and 8)
0.743	2132	614632	-
0.850	2050	36052	44148
1.062	2108	36184	51191
1.275	2104	24387	33811
4.678	2335	4140	17968
14.45	2134	3500	7036
28.05	2323	3348	8402

All such interactions inhibit Ps formation. Consequently the value of I_3 will be reduced in some way depending on the free radicals concentration. Therefore, the general decreasing behavior of I_3 in Figure (1-b) reflects the free radicals` concentration increment. By fitting the values of I_3 to the empirical formula :

$$I_3 = I_{o3}\, e^{-\phi D(Gy)} \qquad (12)$$

it could be found that the values of I_3 taken from Table (1) satisfy the formula :

$$I_3 = 7.682\, e^{-5.333\times10^{-6} D(Gy)} \qquad (13)$$

Some researches (23) showed that the favorable formula , which could be used to fit the results of I_3, is :

$$I_3 = I_{o3} + I^{-}\, e^{-\phi D(Gy)} \qquad (14)$$

However, it is found that the results in this work could not be fitted to this type of formula due to the relatively high standard deviation in I_3 values. Since the irradiation is performed in low doses, the form of the formula (12) is convenient.

The bahavior of τ_2 shows a rise at a total γ-dose of 7.65 kGy as shown in Figure (2-a). There should be an appropriate explanation for its existence. Since the irradiation of a polymer in air form proxy radicals (27,28) , therefore it is expected for a fraction of the free positrons to form a bound system with the proxy radicals (30) . (The expression of free positrons annihilation is used here to refer to any annihilation event for positrons not forming Ps atom, although the positrons may be bounded into another system). The changes in the free positron's lifetime due to the (e^+ - free radical) bound system formation is not observed clearly before. In the present work , this effect may be shown because of the small amount of doses given for the polymer sample each time, which allows small changes to occur in the polymer's properties.

The initial value of τ_2 is 442±71 ps, and it remains almost constant (within the standard deviations) to γ-dose of 1.27 kGy where it starts to increase continuously to a total γ-dose of 7.65 kGy, reaching a maximum value of 971 ± 112 ps. Although the standard

deviation at that value is relatively high , the lower limit , 859 ps, is still higher 94% than the initial τ_2 value. At higher γ-doses , τ_2 decreases. The effect of post-irradiation on PMMA at such low doses is not important (12) , therefore it is ignored . The carbonyl group produced from the decomposition of the proxy radical is a favorable site for the formation of the system (e+-carbonyl) (27). The lifetime of positron annihilation from that system is changed due to the high electronegativity of the oxygen atom that may act as a trap for free positrons . Initially when the free radical's concentration is low the efficiency of such traps is small. As the absorbed dose increases, the efficiency increases as a function of the free radicals concentration and hence the annihilation rate of the free positrons decreases and their lifetimes increase. The values tabulated in Table (3) reflect that approximately. This will cause a slower annihilation rate for the free positrons and thus a longer lifetime. This behavior appears to continue to a certain dose , which is 7.65 kGy in this case. We call such a dose as the ``Threshold Dose``, (TD). Above that dose the free positrons lifetime decreases. The reduction of τ_2 value above TD is explained on the basis of free radicals` presence. When the concentration of the free radicals is high , they will be distributed rather closer to each other, thus the free positrons will sense the competition between the closer free radicals to attract it. Such closer potentials appear as an increment in the electron density where the annihilation rate increases and as a consequence, the lifetime decreases. Furthermore , the effects of the free radicals could be seen from the behavior of I_2, shown in Figure (2-b) . I_2 decreases after irradiation from 67.5% to 60.2% at a total γ-dose of 1.7 kGy. After that I_2 remains unchanged . From Table (1) , it is observed that the first constant value occurs at about the same dose range where τ_2 increases rapidly at a dose of 2.55 kGy. This indicates the reduction in the probability of the free positron annihilation event from the -so named- free state. The extracted fraction of the positrons is added to the p-Ps intensity I_1, not given in Table (1), its value is given as I_1 (%) = 100 - I_2-I_3. It could also be observed from the small changes in I_3. This is due to the big value of τ_2 , where the existence of the free positrons in an unstable format (such as the terminal spur or the free radicals) provides a better chance for the Ps atom formation, and that atom is suffering from a high transition rate from the o-Ps state to the p-Ps state due to spin conversion. The p-Ps conversion to the o-Ps is not likely due to its short lifetime.

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