

# The Influence of Low- and High-Linear Energy Transfers on Some Physical Properties of Poly(methyl-methacrylate) Samples

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**ABSTRACT:** Clear poly(methyl-methacrylate)—PMMA—dosimeter is widely used in food irradiations. Positron annihilation lifetime spectroscopy (PALS) is one of the unique tools used for studying free-volumes and open-volume type defects in solid media. The Vicker's microhardness measurements offer a simple and nondestructive tool for investigating the mechanical behavior of polymer materials. PALS as well as microhardness measurements were carried out for PMMA samples, irradiated with low- and high-linear energy transfers (LET). The low-LET irradiations were provided at lethal doses of gamma radiations for vegetative bacteria. Such irradiations showed a chain scission in the PMMA samples. High-LET irradiations showed behavior different from the low-LET ones.

The observed behavior depends on the alpha particle fluence. The microhardness testing was carried out for virgin and irradiated PMMA samples at high-LET. A negative correlation was found between PALS measurements and microhardness results. The optical characteristics and structural studies for the virgin and irradiated PMMA samples were in agreement with the PALS and microhardness measurements. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** poly(methyl-methacrylate); gamma ray doses; alpha particles fluences; Positron annihilation lifetime spectroscopy; microhardness test; optical characteristics; structural studies

## INTRODUCTION

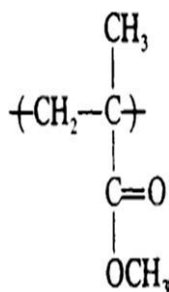
Poly(methyl-methacrylate), PMMA, has a molecular formula of  $(C_5H_8O_2)_n$  as shown in Figure 1. It is often used as an alternative to glass, in competition with polycarbonate (PC). PMMA is used in many fields like aeronautics, medical applications, electronics, and microelectronic industries.<sup>1</sup>

PMMA has a good degree of compatibility with human tissues and can be used for replacement intraocular lenses in the eye<sup>2</sup> when the original lens has been removed in the treatment of cataracts. Clear PMMA dosimeter is widely used for determining the absorbed dose<sup>3,4</sup> in radiation processing of materials. It is sensitive to ionizing radiation and its specific absorbance at 315 nm increases with increasing gamma ray dose.<sup>5,6</sup> However, the wavelength at 305 nm has high optical response<sup>4</sup> and, therefore, is more sensitive in determining the absorbed dose. PMMA molecules favor chain scission more than crosslinking when irradiated with  $\gamma$ -rays.<sup>7,8</sup> Scission and crosslinking not only depend upon polymer

structure but also upon the energy deposited per unit track length or linear energy transfer (LET).<sup>9–11</sup> Also, carbon clusters are formed from the interaction of radiation with polymeric material.<sup>12</sup> Free volume has long been proposed to explain both the molecular motion and physical behavior of polymers.<sup>13</sup> In general, the free volume can be calculated as the total volume minus the occupied volume.

Positron annihilation lifetime spectroscopy (PALS) is one of the unique tools used for studying free-volumes and open-volume type defects in solid media.<sup>14</sup> Positron can be trapped and annihilated in the defect site with the emission of two  $\gamma$ -rays. In polymers, a positron is known to form a bound state with an electron in the medium, resulting in the so-called positronium atom (Ps). Ps atom has two spin states; para-positronium (p-Ps) with antiparallel spin (lifetime in vacuum  $\sim 125$  ps) and ortho-positronium (o-Ps) with parallel spin (lifetime in vacuum  $\sim 142$  ns). The o-Ps lifetime is reduced due to interaction of o-Ps with electrons from surrounding matter (pick-off annihilation) and decays into two gamma rays. Positron lifetime gives information about the electron density by measuring the time elapsed from the emission of the birth ray to the emission of the death  $\gamma$ -ray. On the basis of the free volume model, the o-Ps lifetime can be quantitatively correlated with the size of the free

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**Figure 1** Chemical structure of PMMA polymer sample.

volume and its intensity can be correlated with the number of free spaces.<sup>15</sup> The effect of electron irradiation (0–300 kGy) on the free volume and optical properties of PMMA polymers has been studied using positron annihilation and other techniques.<sup>15</sup> The positron annihilation results show that electron irradiation affects the free volume and the carbonaceous clusters may act as positron scattering centers. The microhardness test, however, offers a simple and nondestructive tool for investigating the mechanical behavior of polymer materials.<sup>16,17</sup>

In this work, we present a study of the effect of lethal doses of gamma radiations (3.00, 5.00, and 8.00 kGy) on PMMA polymer samples by PALS. Also, we have irradiated PMMA with different fluencies of 5.486 MeV alpha particles. The radiation-induced defects in the PMMA samples were studied using PALS, Vicker's microhardness measurements, structural and optical characteristics.

## EXPERIMENTAL TECHNIQUES

### Irradiation processes

PMMA samples were purchased from Beijing Huajin Yuanyang Chemical products Ltd., China. The samples (1.50 cm × 1.50 cm × 0.19 mm) were divided into two categories. In the first category, the samples were irradiated with various doses of gamma rays (3.00, 5.00, and 8.00 kGy) as a low-LET at room temperature from a <sup>60</sup>Co-source at Egyptian Atomic Energy Authority. The source has a dose rate of 2.43 kGy/h. The samples in the second category were irradiated with various doses of alpha particles as high-LET using <sup>241</sup>Am radioactive source (0.1 μCi) in contact with the samples. The irradiation times were fixed at 1 and 5 min.

### Positron annihilation lifetime measurements

PALS measurements for PMMA virgin and irradiated samples were carried out using fast-fast coincidence system with two plastic scintillator detectors. The two identical PMMA samples were placed on each side of the positron source; <sup>22</sup>Na source depos-

ited on a pure thin kapton foil of 7.5 μm in thickness. The <sup>22</sup>Na decays with the emission of a β<sup>+</sup> with 511 keV followed by a 1274 keV γ-ray. The source-sample sandwich configuration was placed between the two detectors for lifetime measurements. For each spectrum, more than 2 × 10<sup>6</sup> counts were accumulated in the analyzed region. The lifetime spectra were analyzed into three lifetime components [τ<sub>1</sub> (self-annihilation), τ<sub>2</sub> (free annihilation), and τ<sub>3</sub> (pick-off annihilation of o-Ps) with corresponding intensities I<sub>1</sub>, I<sub>2</sub>, and I<sub>3</sub>] with the help of the LT-9 computer program.<sup>18</sup> PALS measurements were carried out for the two samples categories.

The positron energy, E<sub>p</sub> (keV), emitted from <sup>22</sup>Na-source is related to the mean implantation depth,  $\bar{Z}$  (nm), through the relation.<sup>19</sup>

$$\bar{Z} = \frac{4.0}{\rho} E_p^{1.6} \quad (1)$$

where ρ is the density of the PMMA sample. The positrons emitted from <sup>22</sup>Na source with energy of 540 keV, were implanted into the virgin PMMA sample with a depth of 79.13 nm, which is enough for complete annihilation to take place. In PALS, the o-Ps lifetime is directly correlated to the free volume hole size. This component is very sensitive to structural changes in the polymer and attributed to o-Ps pick-off annihilation in free volume. The intensity of this component contains information about free volume hole concentration.<sup>20</sup> The quantum mechanical calculations<sup>21,22</sup> give a semi-empirical equation, relating the mean free volume hole radius, R, to the measured o-Ps lifetime, τ<sub>3</sub>, of a spherical hole:

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right]^{-1} \quad (2)$$

where R<sub>0</sub> = R + ΔR and ΔR = 1.66 Å, ΔR is an empirical parameter, related to the penetration of Ps wave function in to the virgin sample and has been determined by fitting the experimental data of τ<sub>3</sub> obtained from materials with known hole size.<sup>23</sup> The average free volume hole size, V<sub>f</sub> is given as V<sub>f</sub> =  $\frac{4}{3}\pi R^3$ . The fractional free volume (F<sub>v</sub>) can be estimated as:

$$F_v = CV_f I_3 \quad (3)$$

where C is a structural constant and is determined empirically to be ~ 0.0018.<sup>24</sup>

### Microhardness test

The microhardness test for the second category was studied with the help of hardness tester equipped

**TABLE I**  
**Lifetime, Intensity, Mean Radius, Free Volume Hole Size, and the Fractional Free Volume in Virgin and Gamma Ray Irradiated PMMA Samples**

Sample	$\tau_3$ (ns)	$I_3$ (%)	$R$ (Å)	$V_f$ (Å <sup>3</sup> )	$F_V$
Virgin	1.540 ± 0.050	14.20 ± 0.38	2.39 ± 0.05	57.54 ± 3.83	1.47 ± 0.10
3kGy	1.686 ± 0.023	13.19 ± 0.11	2.55 ± 0.02	69.34 ± 1.98	1.65 ± 0.05
5kGy	1.662 ± 0.014	13.10 ± 0.68	2.52 ± 0.02	67.32 ± 1.21	1.59 ± 0.09
8 kGy	1.777 ± 0.032	12.73 ± 0.08	2.64 ± 0.03	77.30 ± 2.84	1.77 ± 0.07

with a Vicker's diamond pyramidal indenter having a square base and 136° pyramid angle attached to a Leitz microscope. The following relation has been used to calculate the Vicker's hardness number,  $H_v$ <sup>17</sup>:

$$H_v = \frac{1.854xL}{d^2} \text{ kg/mm}^2 \quad (4)$$

where  $L$  is the applied load in kg and  $d$  is the average diagonal length of the indentation in mm. Indentations at 50 and 100 g loads were obtained in replicate number and average Vicker's hardness number was calculated.

### Optical absorption spectra

The optical absorption spectra of the second category were measured using double beam UV–vis spectrophotometer (Shimadzu UV 3101 PC) in the wavelength range of 200–900 nm.

### Structural studies

The structural studies for the samples in the second category were carried out using X-ray diffractometer for wide range of Bragg angle  $2\theta$  ( $4^\circ \leq \theta \leq 100^\circ$ ).

## RESULTS AND DISCUSSION

### PALS measurements for gamma ray irradiations

The <sup>60</sup>Co-source emits two gamma rays with an average value of 1252.5 keV. By using WinXCom computer program at energies from 1 keV to 100 GeV based on the mixture rule,<sup>25</sup> the total mass absorption coefficient of the gamma ray irradiated PMMA samples can be calculated. The Compton scattering, gives dominant contribution about 99.93% to the total mass attenuation coefficient. A higher Compton interaction reflecting that there is more photon scattering in the irradiated samples. Since, the electron density in the irradiated samples is less than that in the virgin samples, the o-Ps lifetime in virgin PMMA sample is smaller than irradiated ones by an amount which depends mainly on the free volume.

This result was verified in the present data as in Table I. The positron annihilation for gamma irradiations has short lifetime component ( $\tau_1 = 0.143$ –

0.266 ns and  $I_1 = 27.70\%$ – $65.10\%$ ), intermediate component ( $\tau_2 = 0.373$ – $0.395$  ns and  $I_2 = 21.70\%$ – $59.10\%$ ), and long-lived component ( $\tau_3 = 1.54$ – $1.78$  ns and  $I_3 = 12.73\%$ – $14.20\%$ ). The probability of free positron annihilation ( $I_2$ ) is greater than the pick-off annihilation probability ( $I_3$ ) and lowers than self-annihilation ( $I_1$ ).

In addition to variations of lifetime and intensity, Table I also shows the mean radius, free volume hole size, and the fractional free volume in virgin and irradiated PMMA samples with lethal doses of gamma radiations for vegetative bacteria (3.0, 5.0, and 8 kGy). It was observed that the free volume hole size and the fractional free volume increase with irradiation doses [positive correlation ( $r$ ) = 0.85]. This can be attributed to chain scission in the samples taking place due to increasing  $\gamma$ -ray doses. However, the chain scission causes an increase in the free volume.<sup>26</sup> Accordingly, the o-Ps lifetimes increased with radiation leading to reduced  $I_3$  intensities.

### PALS measurements for alpha particle irradiations

The PMMA samples were irradiated with different  $\alpha$ -particle fluencies at 1 and 5 min irradiation times. The samples were in contact with the <sup>241</sup>Am- source. The fluence ( $\phi$ ) of alpha particles was calculated for the two irradiation times by the following equation<sup>27</sup>:

$$\phi = \frac{Q}{2\pi Z^2} \left( 1 - \sqrt{\frac{H^2}{H^2 + Z^2}} \right) \quad (5)$$

where  $Q$  represents the  $\alpha$ -disintegration rate,  $Z$  is the radius of the evaporated circle of the source, and  $H$  is the distance from the source to the sample. Due to the direct contact between the samples and source during the irradiations, the value of  $H$  was diminished. The fluencies corresponding to the irradiation times 1 and 5 min were  $1.15 \times 10^6$  and  $5.77 \times 10^6$  / cm<sup>2</sup>, respectively. The linear energy transfer of alpha particles for all irradiations<sup>28</sup> was 10.16 eV/Å. The thickness of the polymer sample is larger than the projected range (35.30  $\mu\text{m}$ ) of the alpha particle in the sample. Therefore, the alpha particle fluence was totally dissipated in the polymer samples.

The PALS for alpha irradiations has shortest lifetime component ( $\tau_1 = 0.178$ – $0.249$  ns and  $I_1 = 10.58\%$ – $45.60\%$ ) and free annihilation component

**TABLE II**  
Lifetime, Intensity, Mean Radius, Free Volume Hole Size, and the Fractional Free Volume in Virgin and Alpha Particle Irradiated PMMA Samples

Sample	$\tau_3$ (ns)	$I_3$ (%)	$R$ (Å)	$V_f$ (Å <sup>3</sup> )	$F_V$
Virgin	1.540 ± 0.050	14.20 ± 0.38	2.39 ± 0.05	57.54 ± 3.83	1.47 ± 0.10
1 min irradiation time	1.855 ± 0.048	12.25 ± 0.07	2.70 ± 0.07	82.45 ± 6.38	1.82 ± 0.14
5 min irradiation time	1.550 ± 0.060	15.00 ± 1.05	2.40 ± 0.07	58.05 ± 4.92	1.57 ± 0.17

( $\tau_2 = 0.358$ – $0.400$  ns and  $I_2 = 39.40\%$ – $77.17\%$ ). The long-lived component for alpha irradiations has  $\tau_3 = 1.54$ – $1.86$  ns and  $I_3 = 12.25\%$ – $15.00\%$ , as shown in Table II. The probability of free positron annihilation ( $I_2$ ) is greater than the pick-off annihilation probability ( $I_3$ ) and self-annihilation ( $I_1$ ).

The free volume hole size and the fractional free volume were measured for the virgin and irradiated samples, as shown in Table II. The average free volume hole size and the fractional free volume at 1 min irradiation time have the highest value. Accordingly, the chain scission in the samples would occur.<sup>26</sup> The irradiation at 5 min starts restoring the state of the virgin sample. This result suggests that a high concentration of free radicals was produced over many neighboring molecular chains at higher fluencies, facilitating track overlap and enhancing crosslinking over scission.<sup>29</sup> Therefore, the crosslinking at this irradiation time could cause a decrease in available free volume.<sup>26</sup>

Generally, it is observed that irradiations with low-LET dose show scission in PMMA sample while high-LET show different behavior depending on the alpha particle fluence. The effects of low-LET on PMMA were previously reported in the literature.<sup>4,15,30,31</sup> So, we conclude that it is important to focus on the study of high-LET irradiations.

#### Vicker's microhardness measurements for samples irradiated with high-LET

The Vicker's hardness number ( $H_v$ ) at different indentation loads (50 and 100 g) for virgin and the two irradiated samples (1 and 5 min) were calculated, as shown in Table III. It was observed that the  $H_v$  for 50 g is smaller than that for 100 g for the present samples. Also, the values of  $H_v$  for the two indentation loads, decrease with increasing irradiation

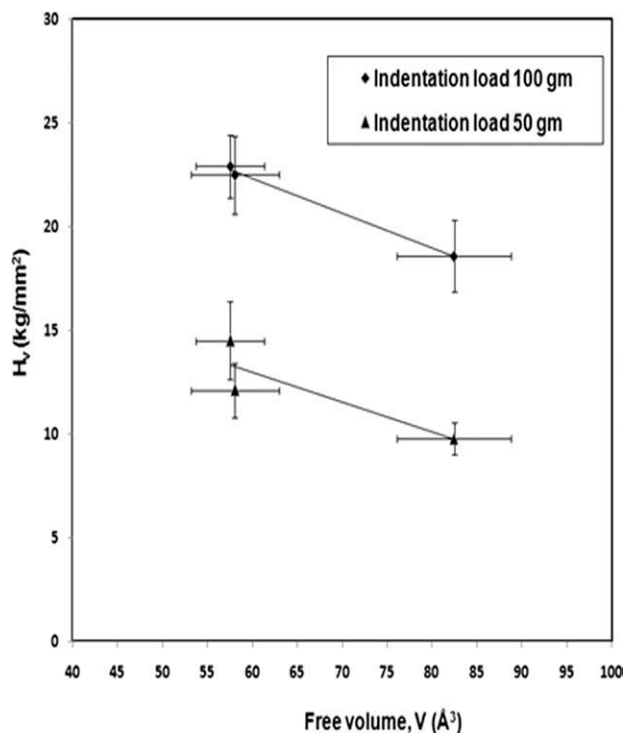
**TABLE III**  
The Values of Vicker's Hardness Number ( $H_v$ ) at Different Indentation Loads for Virgin and the Two Irradiated Samples

Load (gm)	$H_v$ (kg/mm <sup>2</sup> ) for virgin sample	$H_v$ (kg/mm <sup>2</sup> ) for 1 min irradiation time	$H_v$ (kg/mm <sup>2</sup> ) for 5 min irradiation time
50	14.49 ± 1.88	9.76 ± 0.77	12.11 ± 1.29
100	22.91 ± 1.53	18.56 ± 1.73	22.49 ± 1.86

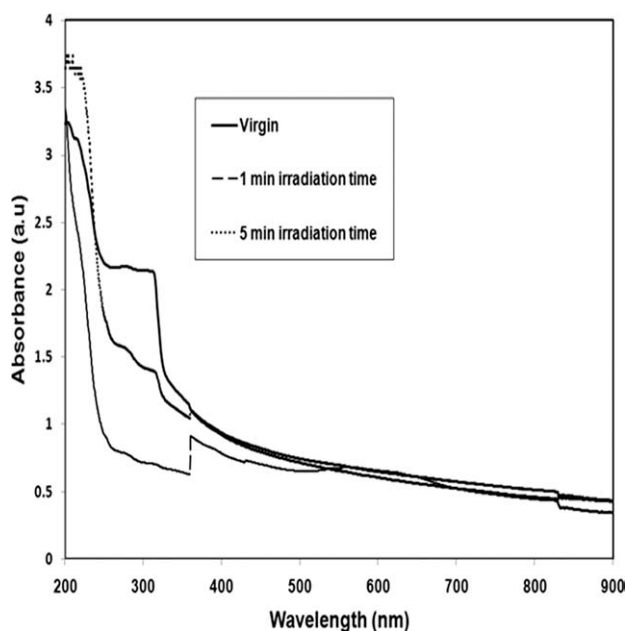
time up to 1 min and then increase. The increase of the value  $H_v$  at 5 min irradiation time is due to the irradiation hardening of the PMMA specimens. This can be attributed to radiation crosslinking. However, the crosslinking can occur only when two dangling radical pairs are in neighboring chains and generally increase hardness.<sup>32</sup> This result confirmed the previous results of PALS at 5 min irradiation time measurements. Similar result was previously reported.<sup>33</sup>

#### The Correlation between Vicker's hardness number ( $H_v$ ) and free volume hole size ( $V_f$ ) for high-LET

The study of the variations of hardness number with free volume hole size for present PMMA samples at the indentation loads 50 and 100 g is shown in Figure 2. It is noticed that there is a linear dependence between the  $H_v$  and  $V_f$  for the two the indentation loads. The dependence behavior has negative correlations of 0.99 and 0.87 for the two different loads,



**Figure 2** Variations of the Vicker's hardness number with free volume hole for present PMMA samples at the indentation loads 50 and 100 g.



**Figure 3** Optical absorption spectra of virgin and irradiated PMMA samples.

respectively. This leads to the conclusion that samples having small  $H_v$  show large free volume hole size.

### Optical response for high-LET

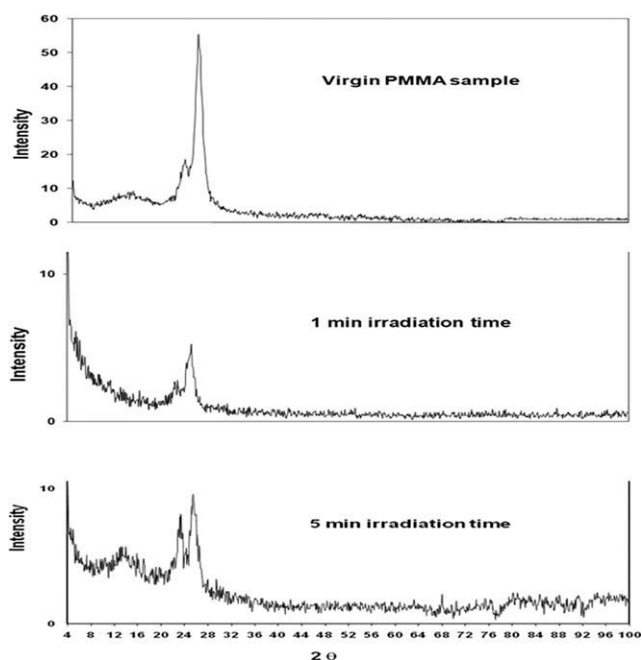
The absorption spectra of PMMA samples (virgin, 1 and 5 min alpha particles irradiation times) are shown in Figure 3. The wavelength at 305 nm has the highest optical response and was used as the characteristic wavelength for the present samples. It is observed that the absolute change in the absorption of PMMA as a result of high-LET at 305 nm for 1 min irradiation time has the minimum value. The absorbance at 5 min irradiation time starts in the attempt to restore the virgin form. The UV spectrum for 1 min irradiation time shows a shift in the absorption edge towards shorter wavelength. By increasing the irradiation time to 5 min, the absorption edge shifts toward higher wavelength. These shifts can be correlated with the optical energy band gap.<sup>34</sup> The optical energy band gap ( $E_g$ ) of the virgin as well as the alpha-irradiated samples was calculated in direct allowed transition.<sup>31,35</sup>

It was found that, the optical energy band gap,  $E_g$ , has values of 4.77, 5.12, and 5.01 eV for virgin, 1 and 5 min irradiation times, respectively. The  $E_g$  for 5 min irradiation time sample attempts to restore to the virgin form. The variations in the optical band gap suggest formation of defects (radicals and organic species) after irradiations and/or the presence of carbon enriched clusters. The overlapping tracks formed by irradiation with low light particles are

known to produce clusters.<sup>12</sup> The presence of such defects may create new energy levels within the polymer.<sup>36</sup> The cluster size (number of carbon atoms formed along the tracks) is inversely proportional to the optical energy band gap.<sup>34</sup> Therefore, it can be concluded that, the cluster size at 1 min irradiation is smaller than that for 5 min irradiated samples. The clusters may act as scattering centers for the positron. The scattered positron may get trapped in the “vacancy like” defects within the polymer.<sup>15</sup> The trapping process may lead to an increase in the positronium formation. The cluster size at 5 min irradiation may scatter more positrons than at 1 min irradiation. This may tend to increase the intensity ( $I_3$ ) and decrease ( $\tau_3$ ) at 5 min irradiation time, as shown in Table II.

### Structural response for high-LET

Figure 4 shows the X-ray diffraction pattern of virgin PMMA and irradiated samples at 1 and 5 min in contact with the radioactive source. The appearance of the two prominent crystalline diffraction peaks in the present samples was observed. The virgin sample shows a semicrystalline (i.e., a mixture of small crystalline and amorphous states within the material) with dominating amorphous content on it. The decrease in the peak intensity at 1 min irradiation time is generally associated with the decrease in crystallinity of the polymer. This result shows that the amorphous nature of the PMMA increase may be due to chain scission. This result was similar to



**Figure 4** X-ray diffraction pattern of virgin and irradiated PMMA samples at irradiation times 1 and 5 min in contact with the radioactive source.

electron irradiation of PMMA.<sup>15</sup> As a result; an increase of free volume by the chain scission causes increase the o-Ps lifetime resulting in a decrease in the intensity ( $I_3$ ), as shown in Table II.

The PMMA sample subjected to 5 min irradiation time shows improved crystallinity which may be due to enhancement of the crosslinking. The free volume decrease results in a decrease the o-Ps lifetime leading to an increase in the intensity ( $I_3$ ).

### CONCLUSIONS

PALS was carried out for PMMA virgin and irradiated samples with low-LET and high-LET. The samples were irradiated with some lethal doses of gamma radiations for vegetative bacteria, low-LET. The irradiations with high-LET were carried out for samples in contact with <sup>241</sup>Am source at 1 and 5 min. The probability of free positron annihilation for irradiations with alpha particles is greater than its value for gamma rays. The free volume hole size increases with irradiation dose for the samples irradiated with low-LET due to occurring scission. However, the free volume at high-LET shows different behavior depending on the alpha particle fluence. The results reveal degradation at 1 min irradiation time with enhancement of the amorphous nature of the polymer leading to increasing the available free volume hole size and decreasing the o-Ps intensity. Irradiation at 5 min reduces the available free volume hole size, indicating that the facilitation of crosslinking with crystallinity improvement of the PMMA polymer and an increase of the o-Ps intensity. The values of  $H_v$  decrease with increasing irradiation time up to 1 min and then increase. The increasing in  $H_v$  at 5 min irradiation time is due to radiation crosslinking in the PMMA specimens. The optical measurements of the PMMA samples at high-LET suggested the presence of carbonaceous clusters. The cluster size at 5 min irradiation may scatter more positrons than at 1 min irradiation. Accordingly, the UV-vis spectroscopic analysis for high-LET is in agreement with the PALS and microhardness measurements. The existence of correlation between PALS and microhardness measurements show that samples having reduction in the free volume hole size also have large  $H_v$ .

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