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The influence of cross-linking and clustering upon the nanohole free volume of the SHI and γ-radiation induced polymeric material

Paramjit Singh [a], Rajesh Kumar [a,*], Rajinder Singh [b], Anirban Roychowdhury [c], D. Das [c]

[a] University School of Basic and Applied Sciences, Guru Gobind Singh Indraprastha University, New Delhi 110078, India
[b] Department of Physics, Guru Nanak Dev University, Amritsar, Punjab 143005, India
[c] UGC-DAE Consortium for Scientific Research, III/LB-8, Bidhannagar, Kolkata 700098, India

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ABSTRACT

The effects of swift heavy ions and gamma radiations upon the nano-scale free volume of the polymethylemethacrylate (PMMA) polymer were investigated using positron annihilation lifetime spectroscopy. The polymer samples were (a) irradiated by 50 MeV Li^{3+} ion beam to the fluences ranging from 1×10^{11} to 5×10^{12} ions/cm^2 and (b) exposed to gamma radiation at various doses ranging from 250 to 1000 kGy. The amorphization was observed in XRD study after ion irradiation and gamma exposure. The absorption edge in the UV–visible study shifted towards the higher wavelength regime leading to decrease of the band gap energy in both cases of irradiations. The formation of new bands at positions 1570, 1560 and 1542 cm^{-1} were observed in FTIR study of gamma radiation exposed sample at 750 kGy. The cluster formation was seen in the SEM images. The nano-scale free volume (V_f) of the Li^{3+} ions irradiated PMMA samples was observed to be decreased at fluences of 1.0×10^{11}, 5.0×10^{11} and 2.5×10^{12} ions/cm^2 due to ion induced cross-linking of the polymeric chains. The values of hole radius (R) and V_f were increased at fluence of 5.0×10^{12} ions/cm^2, it could be due to the clustering induced at higher fluences. The gamma exposures of the samples lead to decrease of the values of R and V_f.

1. Introduction

Over the past few decades, ion beam technology has become an increasingly important tool for the surface and in-depth characterization of polymeric materials [1,2]. In the similar perspective, gamma radiation processing has been widely used to modify the polymeric properties to improve their performance in certain directions [3,4]. The polymeric properties can be engineered by their controlled and calibrated irradiations. Various polymeric materials have been investigated by ion beam and radiation processing for changes in their physical and chemical properties in the last decade [5–7]. Industries are utilizing radiation for producing cross-linked wire insulation, and also for heat shrink products such as food wrap and tubing for electrical connections using polymers [8].

Polymethylmethacrylate (PMMA) is one of the radiation sensitive polymers and it has wide range of applications in biomaterials, semiconductors, lithography and organic electronics [9,10]. PMMA has been widely utilized in medical purposes; such as acetabulor cups, patellar prostheses, and as cements for fixing hip and joint prostheses and filler in dentistry or vertebraplastry [11,12]. Some reports of drawbacks of PMMA in medical applications are also reported [13]. The radiation induced degradation process of PMMA has been reported by Wagner [14]. The ion beam induced PMMA polymers can be used for improved surface and mechanical properties as well as for lithography and electronic applications. Hong et al. have reported the proton implantation upon PMMA for the applications in optical devices [15]. Lee et al. reported that high LET ion treatment of PMMA can improve surface mechanical properties for the use in the industry where highly cross-linked surfaces are needed [16]. Surface-conductivity enhancement of PMMA by keV-energy metal-ion implantation has been reported [17]. Unai et al. had optimized the irradiation conditions for PMMA thin films to induce cross-linking in the polymeric chains by irradiating it with 2 MeV proton beam while maintaining the exposed region free of blisters [18]. In a recent report by Hossain et al., the online and post irradiation analyses of the effects of high energy (4.5 MeV/u gold and 8.3 MeV/u uranium) ions were carried out upon PMMA. They also proposed the molecular scission mechanism for the degradation products after ion beam treatment [19]. Similarly, there are some other recent reports upon the ion irradiation

* Corresponding author. Tel.: +91 9718876101.
E-mail address: rajeshkumaripu@gmail.com (R. Kumar).

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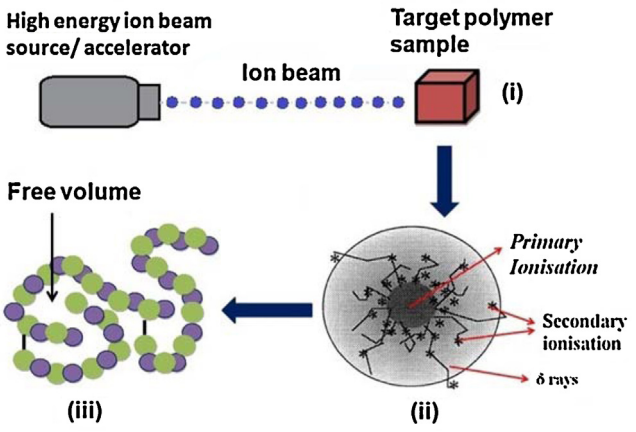

Fig. 1. Schematic diagram showing experimental method: (i) ion irradiation upon target polymer sample, (ii) polymer modification during irradiation and (iii) modification of the polymeric free volume.

and implantation on PMMA polymer [20–25]. But there is limited literature available on the free volume study of PMMA and there is no data available on the hole radius distribution and the free volume study of the ion beam and gamma radiation exposed PMMA polymer to the best of our knowledge. The ion irradiation of the polymer results in the excitation and/or ionization of electrons as well as free radical formation. These modifications are considered to be the primary reasons for scissoring and cross-linking in the polymeric chains and result to the free volume alteration of the polymeric material. Positron annihilation lifetime spectroscopy (PALS) technique is one of the successful and non-destructive ways for estimating the free volume of polymeric materials. This technique calculates the annihilation rate (or lifetime, τ_3) of ortho-positronium (o-Ps) and its formation probability (I_3). These two parameters are associated with the free volume average dimension and its relative concentration [26]. In the literature, the PALS technique has been used to correlate the low energy (300 keV He^+) ion beam induced depolymerization of PMMA with its transport properties [27]. The present paper deals with changes in the hole size distribution after ion beam and gamma treatment of the PMMA polymer using PALS technique; which has not been studied so far. Our objective is to study the influence of gamma rays and lithium ions irradiations on the free-volume content in the PMMA polymer. Fig. 1 [28] explains the clear objective of the present study. The choice of PMMA is such (as has been earlier discussed) that it is a radiation sensitive polymer and mainly degrades or cross-links after ion beam irradiation and the radiation induced modified polymer can be used in electronic applications [28,29]. The irradiation of ions and gamma rays affects the surface, structural, chemical, optical and surface properties of the polymers, so the SEM, X-ray diffraction, FTIR and UV–visible studies are also carried out in the present study.

2. Experimental method

2.1. Materials and characterization techniques used

The PMMA films of thickness ~125 μm were purchased commercially from Goodfellow, U.K. The as-received PMMA films were cut into samples of size 1.5 cm × 1.5 cm and exposed to 50 MeV Li^{3+} beam from 15 UD Pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi, India in the general purpose scattering chamber (GPSC) under high vacuum (~6×10^{-4} Pa). The ion fluence (number of ions per square centimeter area) was controlled by calculating the irradiation time in seconds. Fluences were taken approximately 1.0×10^{11}, 5.0×10^{11}, 2.5×10^{12} and 5.0×10^{12} ions/cm^2.

The gamma exposure of the same sized (1.5 cm × 1.5 cm) PMMA samples was carried out at different doses (250, 500, 750 and 1000 kGy). The gamma exposure was carried out from the gamma chamber (Co^{60} source, dose rate 6.88 kGy/h) at the IUAC, New Delhi, India. X-ray diffraction (XRD) studies were made using Cu Kα radiation (1.54 Å) for a wide range of Bragg's angle 2θ ($5^\circ < 2\theta < 50^\circ$) using Bruker AXS system. UV–visible (UV–vis) measurements were carried out using Hitachi U-3300 spectrophotometer in the range 200–800 nm. The chemical studies were carried out by Fourier transform infrared spectrophotometer using Thermo Nicolet Nexus 670 FTIR. Positron annihilation lifetime measurements were made at UGC-DAE Consortium for Scientific Research, Kolkata Centre, India. The source-sample arrangement and associated electronics has already been reported in our previous study [30].

2.2. Stopping and range of ions in materials (SRIM) calculations

The SRIM 2010 code [31] was used to calculate the projected range and electronic energy loss (S_e) of 50 MeV lithium ions in PMMA polymer; the values are 440 μm and 6.44 eV/Å, respectively. The projected range of lithium ions in PMMA was adequate enough to penetrate our samples (125 μm thickness) ensuring the negligible nuclear energy loss.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy studies

The FTIR spectra of the lithium ions irradiated and gamma rays exposed PMMA samples are compared with the spectra of pristine sample in Fig. 2a and b, respectively. The main characteristic peaks appear at 750 cm^{-1} [γ(C–C) skeletal mode], 844 cm^{-1} [γ(CH_2) rocking mode], 910 cm^{-1} (C–O–C group) and 1636 cm^{-1} (C=C stretching vibrations). In addition to it, some strong absorptions occur at some characteristic bands such as 1066–1397 cm^{-1} (C–O stretching vibrations and C–H stretching vibrations), 1425–1495 cm^{-1} (bending vibrations of C–CH_3 and CH_2) and 2828–3038 cm^{-1} (C–H symmetric stretching vibrations) [19]. Fig. 2a indicates that the characteristic peaks of the irradiated samples show increase in absorbance with increase of the ion fluence. The similar effects are observed in the gamma exposed PMMA samples in Fig. 2b except for the sample exposed at the dose of 750 kGy. The reduction in the intensity (decrease in absorbance) of this sample is attributed to the breakage of some chemical bonds, formation of free radicals followed by unsaturation and emission of gaseous molecules. The inset in Fig. 2b shows the closest view of the band in the range 1600–1430 cm^{-1}. The formation of new bands at positions 1570, 1560 and 1542 cm^{-1} represent the C=C stretching vibration [32] and it attributes to the formation of double bonds after the gamma exposure.

3.2. UV–visible studies

The optical absorption edges of lithium irradiated and gamma exposed PMMA samples shifted towards the longer wavelength region (from the ultraviolet wavelength region towards the visible region), as shown in the UV–visible spectra of pristine and irradiated PMMA samples in Fig. 3a and b. It indicated that ion beam and gamma induced radiation damage leaded to the formation of new bonds, such as the pi-bonds in either isolated or conjugated double bonds [33,34]. These shifts in the optical absorption edges affected the band gap energy and number of carbon hexagon rings per cluster of irradiated samples. The band gap energy was calculated by