Modification of optical, chemical and structural response of polymethyl methacrylate polymer by 70 MeV carbon ion irradiation

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Polymethyl methacrylate (PMMA) foils were irradiated under vacuum with 70 MeV C 5+ ions to the fluences of 3.1×10 11, 3.7×10 12, 1.8×10 13, 5.6×10 13 and 1.2×10 14 ions cm −2. Ion induced optical, chemical and structural modifications were studied by ultraviolet, visible (UV-Vis) and Fourier Transform Infrared (FTIR) spectroscopy and X-ray diffractometer (XRD). PMMA suffers degradation under irradiation, UV-Vis data show the increase of optical absorbance and the shift of absorption edge from the UV towards visible with the increase of the fluences, attributing to the formation of conjugated system of bonds. The intensity of infrared bands and characteristics of different chemical functional groups are found to decrease with Swift Heavy Ion (SHI). Crystallite size of irradiated sample shows a decrease of 8%.

Keywords: Polymethyl methacrylate polymer, C 5+ Ion irradiation, Ion beam modification, FTIR, UV-Vis, X-ray diffraction

1 Introduction

Poly (methyl methacrylate), PMMA, known as a positive photo-resist for its degradation upon irradiation, has been the subject of more investigations in radiolysis than many other polymers. This was partly due to a growing interest in the applications of PMMA in ion beam lithography in the semiconductor industry and partly due to the non-gelling nature of PMMA at low dose irradiation, which allowed investigators to study the mechanisms of scission and cross-linking. The first polymer studied was PMMA, which is an excellent material because it is easy to structure and has the desired optical properties. Aromatic polymers such as polymethyl methacrylate (PMMA) are finding extensive use in expanding optical networks in the field of telecommunication.

The usage of polymers is increasing day-by-day owing to their higher strength to weight ratio, lower cost, ease of moulding and lightness. Interest in ion beam treatment of polymers has increased in recent years, prompted by the ion beam induced improvements of the mechanical, optical and electrical properties of various polymer substrates. A wide variety of material modification in polymers has been studied by using ion irradiation technique. Extensive research has focused onto Swift Heavy Ions (MeV’s energy) probably because of good controllability and the large penetration length in polymers. High energy ion irradiation tends to damage polymers significantly by electronic excitation and ionization. It may result into reactions in the polymers, creation of latent tracks and can also cause formation of radicals such as ablation, sputtering, chain scission and intramolecular cross-linking creation of triple bonds and unsaturated bonds and loss of volatile fragments. Free radicals are created due to chemical changes caused by ionizing radiation in the polymers. These may initiate modifications such as formation of chemical bonds between different molecules; inter...
molecular cross-linking; irreversible cleavage of bonds (scission) in the main chain, resulting into the fragmentation of molecules and the formation of saturated and unsaturated groups with stimulated evolution of gases\textsuperscript{23}.

In the present study, 70 MeV C\textsuperscript{5+} ion induced modifications in the chemical structure and physical properties of PMMA films and their dependence on ion fluences are investigated through UV-Vis and FTIR spectroscopy and XRD technique. The structure of polymethyl methacrylate (PMMA) is given as:

\[ \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2\text{CH}_2\text{CO} \]

3 Results and Discussion

The energy lost by Swift Heavy Ion (SHI) in a solid is mainly dominated by two mechanisms known as electronic and nuclear stopping. The electronic energy loss is dominant for ions with high energy and involves the energy transfer to the target electronics. The SRIM calculation\textsuperscript{23} indicates that 99.95\% of energy lost by 70 MeV C\textsuperscript{5+} ions in 125 µm thick PMMA sheet is due to electronic energy loss. The electronic stopping power of the beam, (dE/dX)\textsubscript{e}, is 2.938×10\textsuperscript{2} keV/µm. The irradiation doses deposited in the PMMA at different fluences, 3.1×10\textsuperscript{11}, 3.7×10\textsuperscript{12}, 1.8×10\textsuperscript{13}, 5.6×10\textsuperscript{13} and 1.2×10\textsuperscript{14} ions cm\textsuperscript{-2} are 1.1, 13.5, 66.0, 205.5 and 440.4 Joules, respectively.

3.1 Optical response

The absorption of light energy by polymeric materials in the ultraviolet and visible regions involves promotion of electrons in σ, π and n-orbitals from the ground state to higher energy states which are described by molecular orbitals\textsuperscript{24}. High-energy ion beam interaction with PMMA produces cross-linking while low energy radiation sources (-e-beams and γ-rays) result in the production of chain scission\textsuperscript{25}.

The results of optical absorption studies with UV-visible spectrophotometer carried out on virgin and irradiated samples are shown in Fig. 1(A-E). The optical absorption spectrum of virgin sample shows the maximum absorbance at 200 nm with a narrow peak at 260 nm and a broad peak at 337 nm. The optical spectra of irradiated samples in Fig. 1(B-E) show some interesting features. At a fluence of 3.1×10\textsuperscript{11} ions/cm\textsuperscript{2} [Fig. 1(B)], the absorption decreases over the hole range of wavelengths from 200 to 800 nm with a maximum decrease of 35\% at 200 nm. When the fluence is increased to 3.7×10\textsuperscript{13} ions/cm\textsuperscript{2}, the optical absorption is again increased over the full spectrum [Fig. 1(C)] as if the polymer sample has recovered its virgin form. Further irradiation to 1.8×10\textsuperscript{13} and 5.6×10\textsuperscript{13} ions/cm\textsuperscript{2}...
produces almost identical patterns [Fig. 1(D-E)] with sharp peaks at 300, 345 and 411 nm with low absorption in low wavelength region and high absorption in the high wavelength region. There is a complete reversal of the properties of virgin polymer after irradiation. Such a strange behaviour in the polymer studies has not been observed by us, viz. polyimides and polycarbonates in our laboratory\(^\text{26,27}\).

The periodic nature of radiation effects in PMMA needs further investigation using low LET and high LET radiation sources. Other researchers have also observed such an anomalous\(^\text{28,29}\) behaviour of PMMA also.

### 3.2 Structural response

X-ray diffraction pattern of the virgin (A) and one of the irradiated \((1.8\times10^{13}\text{ ions/cm}^2)\) PMMA samples (B) are shown in Fig. 2 (A-B). The diffraction pattern indicates that the pristine PMMA is semi-crystalline in nature with dominating amorphous content in it. The six peaks to be seen in the X-ray spectrum of the virgin sample, are presented in Table 1. The two sharp peaks are shown in the virgin sample at \(2\theta = 21.22^\circ\) and \(25.56^\circ\) with lattice spacing \(d = 4.183\) and \(3.482\) Å, respectively. However, in case of the irradiated sample, a truly significant change in the diffraction pattern has been observed with one sharp peak only, corresponding to \(2\theta = 21.26^\circ\) and \(d = 4.175\) Å (Table 2). The disappearance of five X-ray peaks for irradiated sample indicates a clear increase in the amount of amorphous content of PMMA.

The crystallite size of the virgin and the irradiated PMMA have been calculated (Table 3) using Scherrer’s equation\(^\text{30}\):

\[
b = K\lambda/L \cos\theta
\]

where \(b\) is Full Width at Half Maxima (FWHM) in radians, \(\lambda\), the wavelength of X-ray beam (1.5418 Å) and \(K\), a constant\(^\text{31}\) which is assumed to be 1. The crystallite size of irradiated sample decreases by 8%.

### 3.3 Chemical response (FTIR spectroscopy)

Chemical response or the nature of chemical modifications can be studied through the characterization of the vibration modes determined by infrared spectroscopy. Figure 3(a-c) shows the FTIR
Fig. 3 — FTIR spectra of PMMA (a) Virgin; irradiated to the fluence of (b) $3.1 \times 10^{11}$ (c) $3.7 \times 10^{12}$ ions/cm$^2$
spectra of the virgin (a) and two of the four irradiated samples (b & c) using the fluence of $3.1 \times 10^{11}$ and $3.7 \times 10^{12}$ ions/cm$^2$, respectively.

Figure 3 shows clearly the general decrease in intensity of the peaks of irradiated samples compared to the virgin sample. There is a maximum absorption (0% transmittance) in the range 2800-3000 cm$^{-1}$ corresponding to C-H stretching vibrations. The peak around 1716.56 cm$^{-1}$ [Fig. 3(a)] corresponding to C = O vibrations in the virgin sample is slightly shifted to 1705.44 and 1720.12 cm$^{-1}$ in the irradiated samples [Fig. 2(b-c)]. A regular trend in the variation of the peak positions is not observed with increase of fluence. This type of anomaly has been observed in the UV-Vis spectra also (Fig. 1). The peak corresponds to the CH$_2$ symmetric bending at 1455.92 cm$^{-1}$ and the peak around 1380 cm$^{-1}$ corresponding to CH$_2$ asymmetric bending, which is to be overlapped in the above peak, are not showing any appreciable change at higher fluence of $3.7 \times 10^{12}$ ions/cm$^2$. This indicates that gas evolution (either methane or hydrogen) is not taking place after irradiation. The band around 3000 cm$^{-1}$ corresponding to CH$_2$ is also not showing any change after irradiation, indicating that CH$_2$ groups are also intact. The peak at 1637 cm$^{-1}$ corresponding to C=O is also not showing any change indicating that C=O groups are not abstracted by the ionic radiation. The bands corresponding to the C-O-C stretching groups around 1260 and 1150 cm$^{-1}$ have not been observed in both the virgin and irradiated samples giving rise to an anomalous behaviour of the PMMA polymer.

4 Conclusions
UV-Vis spectroscopic analysis of irradiated PMMA samples reveals an anomalous behaviour with fluence, which may be due to both degradation (scission) and cross-linking of polymer chains competing simultaneously. FTIR analysis reveals that ionic radiation results in decrease of intensity of some of the prominent peaks without causing significant changes in their position. X-ray diffraction pattern reveals a characteristic increase in the amorphous nature of the irradiated PMMA. The crystallite size of irradiated sample shows a decrease of 8%. However, further experiments are necessary to establish the true nature of anomalies observed in the physical and chemical behaviour of PMMA polymer.

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