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Study of optical band gap, carbonaceous clusters and structuring in CR-39 and PET polymers irradiated by 100 MeV O^{7+} ions

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ABSTRACT

Commercially purchased CR-39 and PET polymers were irradiated by 100 MeV O^{7+} ions of varying fluences, ranging from 1×10^{11} to 1×10^{13} ions/cm^2. The effects of swift heavy ions (SHI) on the structural, optical and chemical properties of CR-39 and PET polymers were studied using X-ray diffraction (XRD), UV–visible spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The XRD patterns of CR-39 show that the intensity of the peak decreases with increasing ion fluence, which indicates that the semicrystalline structure of polymer changes to amorphous with increasing fluences. The XRD patterns of PET show a slight increase in the intensity of the peaks, indicating an increase in the crystallinity. The UV–visible spectra show the shift in the absorbance edge towards the higher wavelength, indicating the change in band gap. Band gap in PET and CR-39 found to be decrease from 3.87 to 2.91 and 5.3–3.5 eV, respectively. The cluster size also shows a variation in the carbon atoms per cluster that varies from 42 to 96 in CR-39 and from 78 to 139 in PET. The FTIR spectra show an overall reduction in intensity of the typical bands, indicating the degradation of polymers after irradiation.

1. Introduction

Ion irradiation of polymer can induce irreversible changes in their macroscopic properties. Electronic excitation, ionization, chain scission, cross-linking and mass losses are the fundamental events for macroscopic changes in polymers [1,2]. In early years, ion beam modifications were made using low ionizing beams comprising mainly of fast electrons, low energy ions, gamma rays and X-rays. But now, modification of materials using swift heavy ions (SHI) bombardment is well established. When a high energetic charged ion strikes a polymer target, it loses most of its energy in exciting electrons and/or ionizing the atoms. By using high-energy heavy ions, dramatic modifications in the polymer material have been observed [3,4]. In general, most of these modifications can be traced back to changes taking place in chemical structure of polymer. Some of the changes have been attributed to the scission of polymer chains by incident ions, breaking of covalent bonds, cross-linking, formation of carbon clusters and liberation of volatile species and in some cases even formation of new chemical bonds [5–8]. The liberation of volatile species almost always takes place under irradiation as soon as the ion beam modifies the polymer. Any modification of material depends on the structure, the ion beam parameters (energy, fluence and the charge state) and the nature of target material itself.

The modifications in the chemical structure of polymers like polypropylene, polyimide and polymethyl methacrylate/polystyrene blend have been reported by the use of 60 MeV silicon ions beam [9]. Some chemical modifications in the CR-39 were also found after irradiation with 100 MeV Si^{8+} ions beam [10]. The Fourier transform infrared (FTIR) spectroscopy studies of polycarbonate are also carried out using low energy argon ions [11]. The present work reports the results of the physical and chemical changes produced by the bombardment of 100 MeV O^{7+} ions on PET and CR-39 (DOP) polymer films with special reference to properties like optical, chemical and structural.

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2. Experimental methods

Commercially available CR-39 (0.2% DOP) and PET (polyethylene terephthalate) of thickness 200 and 100 μm, respectively, were used in the present study. Self-standing films of PET and CR-39 (DOP) of 1 cm^2 were irradiated at room temperature in a Material Science Beam Line under high vacuum (5×10^{-6} Torr), using the 100 MeV O^{7+} ions beam with a current of 1 pnA (particle nano ampere), available from the 15 UD Pelletron at the Inter University Accelerator Centre (IUAC), New Delhi using various fluences ranging from 1×10^{11} to 1×10^{13} ions/cm^2. In order to expose the whole area, the beam was scanned in the *X*–*Y* plane. The thicknesses of the films were selected thin enough to permit the beam transmission and the ion ranges were calculated using SRIM 2003 programme, as 130 and 220 μm, respectively, for PET and CR-39 (DOP) films. SRIM 2003 shows that the foils are irradiated throughout, with the energy transferred from the ion beam to the target being essentially due to electronic processes (electronic stopping power $S_e = 5.387\times10^2$ and 4.148×10^2 keV/μm for the PET and CR-39 (DOP) polymer films, respectively) and nuclear damage being negligible.

The nature of the changes induced by the ion beam has been analyzed using UV–visible spectrophotometry in the range 200–700 nm. The FTIR spectroscopy was performed in the transmission mode in the range 400–4000 cm^{-1} and the structural studies were carried out by a X-ray powder diffractometer with Cu-Kα radiation (1.54 Å) for a wide range of Bragg's angle 2θ ($15<\theta<40$) at the scanning rate of 1°/min using a Bruker AXS X-ray Diffractometer.

3. Results and discussion

The results of the structural and the optical measurements performed on the CR-39 (DOP) and PET films are given below.

3.1. X-ray diffraction

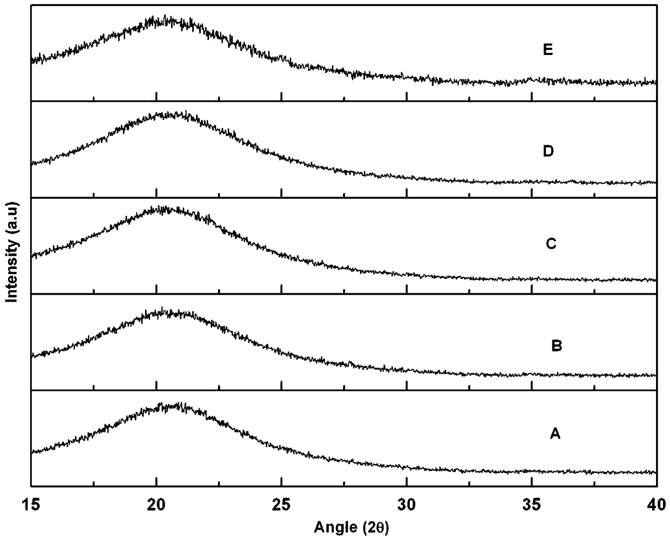

Fig. 1. X-ray diffraction of CR-39 (DOP): (A) unexposed and exposed with 100 MeV oxygen ion beams of different fluences: (B) 1×10^{11} ions/cm^2, (C) 3×10^{11} ions/cm^2, (D) 1×10^{12} ions/cm^2 and (E) 1×10^{13} ions/cm^2.

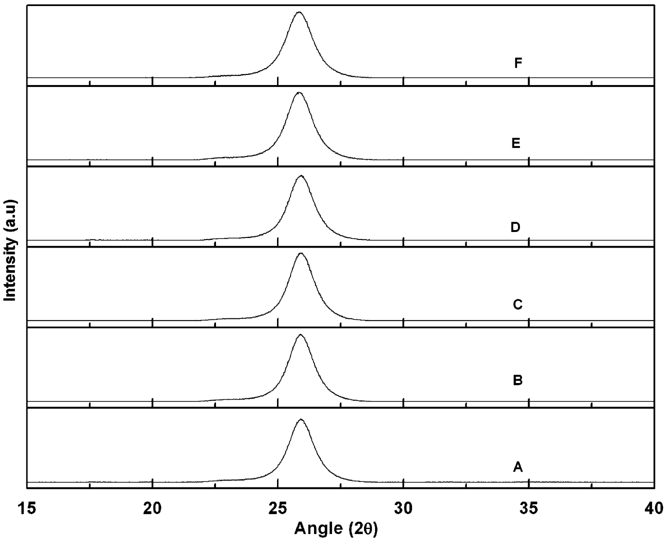

Fig. 2. X-ray diffraction of PET: (A) unexposed and exposed with 100 MeV oxygen ion beams of different fluences: (B) 1×10^{11} ions/cm^2, (C) 3×10^{11} ions/cm^2, (D) 1×10^{12} ions/cm^2, (E) 3×10^{12} ions/cm^2 and (F) 1×10^{13} ions/cm^2.

Table 1
The percentage crystallinity of CR-39 (DOP) and PET polymers irradiated by 100 MeV O^{7+} ions beams

Fluence (ions/cm^2)	%*K* of CR-39 (DOP)	%*K* of PET
Pristine	52.36	84.31
1×10^{11}	52.31	84.44
3×10^{11}	52.19	84.78
1×10^{12}	51.30	84.52
3×10^{12}	–	82.50
1×10^{13}	47.83	80.55

The X-ray diffraction (XRD) patterns of our pristine and irradiated CR-39 (DOP) and PET are shown in Figs. 1 and 2, respectively. These polymeric samples studied here are widely used materials falling in the class of majority of polymer material that consists of crystalline and amorphous region in different proportions. Prominent peak at $2\theta\approx20.51^\circ$ is the characteristic peak of CR-39 (DOP). The diffraction pattern of unexposed CR-39 (DOP) film peak at $2\theta\approx20.51^\circ$ shows a large peak and indicates the amorphous nature of the film. The exposed CR-39 (DOP) also shows an identical pattern in the XRD peak, except that the width of large peak increases (slight broadening) after irradiation with a change in intensity. The overall decrease in intensity and broadening of peak show the amorphization of CR-39 (DOP) after irradiation. A different pattern was observed with PET, which shows a slight increase in intensity with lower fluence indicating an increase in the crystallinity of the polymer but at higher fluence the intensity decreases suggesting the amorphization of the polymer. This observed change in intensity of XRD spectra may be due to the destruction of original structure of PET [12]. The change in the crystallinity of both of the polymers was calculated using the following formula:

$$K = \frac{A}{A'} \times 100\% \tag{1}$$

where *A* is the total area of the peaks (crystalline and amorphous) and *A′* is the total area under the diffractogram [13]. The percentage crystallinity calculated using Eq. (1) is shown in Table 1. A change in the crystallite size was also observed after irradiation. The average crystallite size was calculated using the Scherrer formula [14] as given by

$$L = \frac{\lambda}{b\cos\theta} \tag{2}$$