$^{12}C^{5+}$ radiation effects in some polymers

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Abstract

Polycarbonates like CR-39, SR-86 and Makrofol have been irradiated with $^{12}C^{5+}$ ions of energy 5.0 MeV/u and fluences of 10^{11}, 10^{12} and 10^{13} ions/cm^2. The optical studies show an increase in absorption in the shorter wavelength region (250–500 nm) which is more pronounced in SR-86. The study also reveals that the increase in radiation dose extends the optical absorption region to longer wavelengths. The annealing of radiation damaged polymer samples at 120°C for 75 min partially recovers the damage. It is observed that the bulk etch rates of these polymers increase after irradiation. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Polymers are a familiar part of everyday life, and because of the ability of chemists to tailor-make their properties, have found widespread applications in the recent past especially in microelectronics fabrication, space and nuclear technologies. Earlier, the most valued property of polymers was their capacity to inhibit electrical conduction as insulators, now they are attracting considerable attention as conducting polymers [1,2]. Polymers exhibit properties of ion transport, redox behaviour, electrochemical effects, photoactivity, catalytic agents, and electronic junction effects, in addition to light weight, flexibility, low cost, ruggedness and other beneficial physical properties.

Swift heavy ions (SHI) (velocity around and above K-shell electrons), interact with target atoms mainly by collision processes leading to the ionisation of the target atoms and excitation of the target electrons. The slowing down of the projectile ion, and consequently the energy transfer to the target, is dominated by the electronic stopping power $(dE/dx)_e$, which may be upto some tens of keV/nm. As a general rule, SHI irradiations induce a continuous damage all along the ion path. Hence, the irradiation damaged region surrounding the ion path is referred to as "latent track" before chemical etching and called a "nuclear track" after its revelation by chemical or electrochemical etching. Consequently, polymers have been used as solid state nuclear track detectors (SSNTDs) in recent years [3–5].

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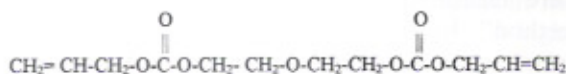
SHI irradiation produces both surface and bulk modifications in polymers [6]. The atomic and electronic structure of polymer films is modified from a molecular solid to an amorphous material and irreversible changes are induced in their macromolecular structure and other physical properties. These effects depend on target parameters (composition, molecular weight, temperature, etc). and on ion beam parameters (energy, mass and fluence). At low energy density (10^{22}–10^{24} eV/cm^3), primary phenomena associated with ion-polymer interaction are chain scission, chain aggregation, double bonds and molecular emission [7]. Molecular emission from polymers always occurs with a release of neutral hydrogen and carbon-hydrogen groups and with a significant change of the polymer stoichiometry.

SHI irradiation modified most of the physical and chemical properties, e.g., optical, electrical, mechanical, etc., of polymeric materials depending on the irradiation dose and energy of the ion beam used. Optical properties of polymers have been characterised by various authors [8–11] by correlating the change in optical properties with the mode of energy deposition. Marletta et al. [12] have found a correlation between chemical structure modifications and change in electrical properties by some polymers. Improvements in surface smoothness, hardness and wear resistance of polymers by multiple ion implantation has been studied by Lee et al. [13]. The aim of the present investigations is to study the change in chemical behaviour, nature of radiation damage produced and its recovery, change in optical properties and morphology of radiation damage latent tracks produced in track recording polymers of common use.

2. Materials and methods

Polymers used in our study, viz. polycarbonates with trade names CR-39 (Pershore Moulding, UK) and SR-86 (Fukuvi, Japan), are of common use as track recorders due to their high resolution and sensitivity. Makrofol polycarbonate (Bayer, Germany) has been used extensively for preparation of ion track filters and allied applications [14].
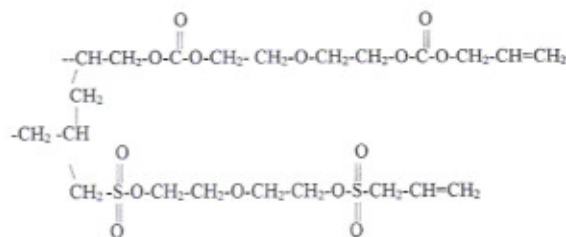
The three dimensional network of CR-39 consists of polyallyl chains cross-linked by diethylene glycol dicarbonate linkages. The monomer of CR-39 plastic is represented as follows

$$\text{CH}_2\text{= CH-CH}_2\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-CH}_2\text{- CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-CH}_2\text{-CH=CH}_2$$

SR-86 is a co-polymer of DEAS (Diethylene glycol bis of allyl sulphonate) and CR-39 in the ratio 20:80, respectively. Monomer of DEAS is given by

$$\text{CH}_2\text{=CH-CH}_2\text{-S-O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-S-CH}_2\text{-CH=CH}_2$$
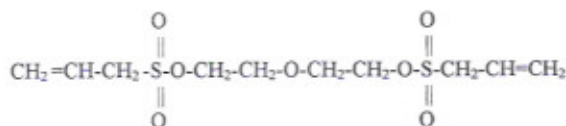
Co-polymer of DEAS and CR-39 can be represented by

$$\text{--CH-CH}_2\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-CH}_2\text{- CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-CH}_2\text{-CH=CH}_2$$

DEAS monomer was synthesized by condensation of diethylene glycol and allyl sulphonyl chloride in the presence of pyridine. Makrofol polycarbonates are prepared from diphenylolalkanes in which the commonest monomer is 2,2-diphenylol-propane or Bisphenol-A(BPA).

SHI irradiation was carried out at Nuclear Science Centre (NSC), New Delhi, India using a 60 MeV ^{12}C^{5+} ion beam available from 15 UD Pelletron accelerator. Samples of polymer films (2 cm^2) were prepared as targets and mounted on a target ladder before irradiation. Six targets can be irradiated in a single mount in a general purpose scattering chamber (GPSC) evacuated to 10^{-6} mbar. Remote control is provided for various motions of target ladder and the detector arms. The ion beam fluence was varied from 10^{10} to 10^{13} ions/cm^2 (with a beam area of 1.6×1.2 cm^2) during irradiation in different runs by changing the targets for each run. All targets were exposed at room temperature using normal incidence in GPSC.

Both irradiated and unexposed polymer samples were etched in the laboratory under identical conditions using 6.25 N NaOH at 60°C for 2 h in a constant temperature bath. The bulk etch rates were measured [3] by "thickness measurement method". In this technique, the thickness of the sample is measured before and after etching for a certain period of time using a sensitive micrometer. If y and y' be the thickness of the sample before and after etching for a time, t, then the bulk etch rate, V_b is given by

$$V_b = (y - y')/2t.$$

The nature and extent of radiation damage, or in other words, structural modifications in polymers can be characterised by different techniques such as UV-visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy, ultraviolet photoemission spectroscopy (UPS), electron energy loss spectroscopy (EELS), Rutherford backscattering (RBS) and solubility measurements [15]. We have used the first two techniques for our characterisation and the spectrophotometers employed are UV-visible-166 and FTIR-8101M (Shimadzu, Japan).

3. Results and discussion

SHI–polymer interaction is a complex process where a lot of primary and secondary effects are involved. In a very short-time (10^{-15}–10^{-13} s) the ion energy is transferred to the electrons in the polymer chain within a small volume surrounding the ion track. The energy spike is very high, reaching values of the order of 100 eV/atom for a single ion track. For $^{12}C^{5+}$ ions of energy 5 MeV/u, the energy transfer occurs only through electronic excitations and ionisations, extending upto 100 Å around the core of latent track for energetic secondary electrons (or δ-rays) [15].

Due to a large amount of energy transfer to the electronic-molecular environment in polymers, the energy spike induces breaking of original bonds, production of excited and ionised species, of radicals and bonds rearrangement which are responsible for most of the observed chemical modifications. The bulk etch rates of CR-39, SR-86 and Makrofol polycarbonate are summarized in Table 1.

It is observed that bulk etch rates of all polymers are enhanced after irradiation and the maximum effect is noticed in SR-86. The dissolution rate of bulk material is affected by the available free energy associated with the creation of damage zones around the ion path in crystalline materials. However, in polymers the bulk etch rate enhancement may be explained by the processes of chain scission or cross-linking resulting in modification of molecular weight of the irradiated polymer. The case of SR-86 is enigmatic. The bulk etch rate of this co-polymer may be explained on the basis of unzipping phenomenon which is due to the scission of C–SO$_x$ linkage or rupture of the chain at the C–O site. Marletta [16] has reported the unusual reduction of –SO$_2$– to –S– by electronic excitation occurring due to heavy ion bombardment in PES. A similar process of chemical modification may be in operation for SR-86.

Table 1
Bulk etch rates of polymers (CR-39, SR-86 and Makrofol), measured by thickness method ($V_G = \Delta x/2\Delta t$)

Samples	Etchant conc. (N NaOH)	Etching time (h)	Etchant temperature (°C)	Bulk etch rate (μm/h)	
				unirradiated	irradiated
CR-39	6.25	2	60	1.25	1.75
SR-86	6.25	2	60	2.00	3.50
Makrofol-N	6.25	2	60	0.75	1.00

The anomalous behaviour of environmentally affected CR-39 at elevated temperatures has been studied by Bhatia et al. [17]. They observed the effect of post-irradiation oxidation of the samples, increasing the percentage scission of the hydrocarbon chain and hence an increase in the bulk etch rate of CR-39. Generally in plastics, free radicals will be formed from the decomposition of primarily formed hydroperoxides [18]

$$RH + O_2 \rightarrow ROOH,$$

$$ROOH \rightarrow RO^+ + OH^-.$$
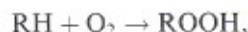
The results of optical absorption studies by the UV-visible spectrophotometer carried out on unirradiated and irradiated samples of Makrofol, CR-39 and SR-86 are illustrated in Fig. 1. It is observed that all the three polymers show an increase in optical absorption in the short wavelength range (250–500 nm) after SHI irradiation (fluence 10^{12} ions/cm^2). The effect is hardly perceptible in CR-39 while it is quite evident in Makrofol and SR-86. The effect disappears at higher wavelengths for Makrofol but, on the contrary, there is a reversal in case of SR-86. Fig. 2 shows the UV-visible spectra of SR-86 for three different irradiation doses in comparison to an unexposed sample. The region of optical absorption extends to higher wave lengths for higher irradiation doses. The reversal effect phenomenon also disappears at a fluence of 10^{13} ions/cm^2. It proves that radiation damage effects are complex and non-linear in this most-sensitive of SSNTDs for track registration.

To further investigate the nature and extent of radiation damage in SR-86, recourse is taken to FTIR spectroscopy. The optical absorption results of IR spectra of SR-86 are shown in Fig. 3. The comparison of IR spectra of unirradiated and irradiated samples indicates that the infrared absorption increases around 3600 cm^{-1}. This absorption can be assigned to the breakage of the sulphonate groups.

In the spectrum of pristine SR-86 sample (Fig. 3a), band corresponding S–O stretching is found in the region of 600–700 cm^{-1}. In the same region, CH bending bands are also overlapped. So these bands cannot be taken as the characteristic bands of S–O linkage clearly. The band at ~1600 cm^{-1}

Fig. 1. UV-visible spectra of irradiated (I) (dose 10^{12} ions/cm^2) and unirradiated (II) samples of: (a) Makrofol; (b) CR-39 and (c) SR-86.
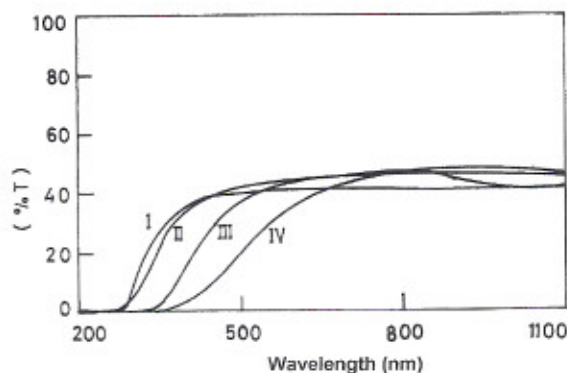

Fig. 2. UV-visible spectra of SR-86 sample irradiated with $^{12}C^{5-}$ at different doses (I – virgin, II – 10^{11}, III – 10^{12} and IV – 10^{13} ions/cm^2).
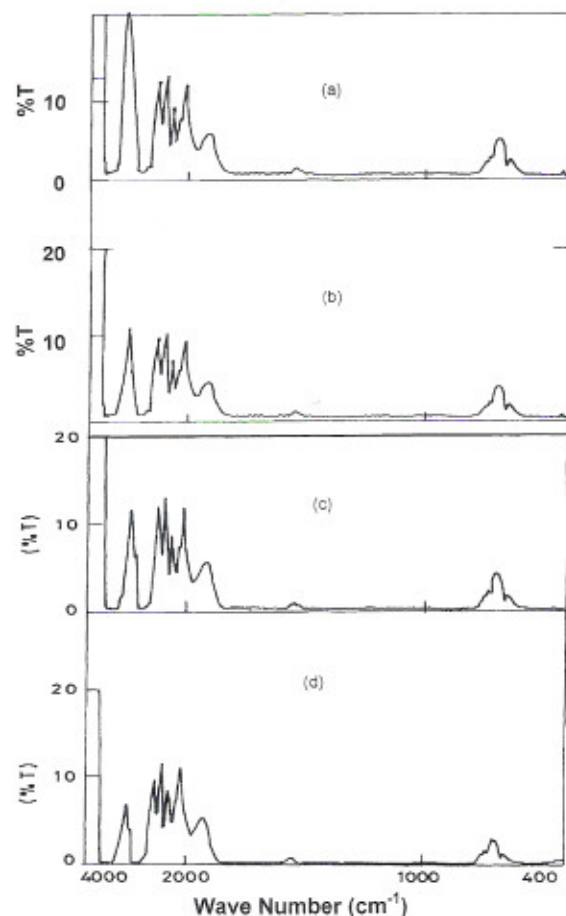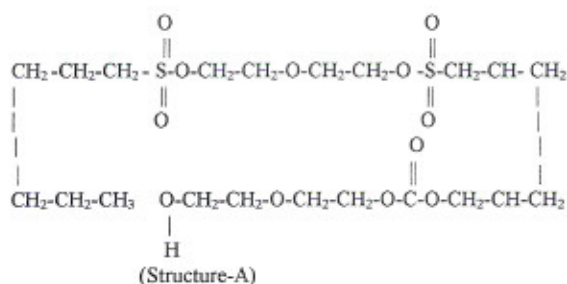
Fig. 3. IR spectra of SR-86 irradiated with $^{12}C^{5-}$ at different doses: (a) virgin; (b) 10^{11}; (c) 10^{12} and (d) 10^{13} ions/cm^2.

corresponding to unsaturated double bond is also observed. The band around 1800 cm^{-1} corresponds to C. The weak band around 3600 cm^{-1} corresponds to terminal OH– end group. The other bands between 3200 and 2000 cm^{-1} correspond to CH$_2$ stretching and bending of CH. The bands corresponding to S are expected in the region of 1260–1150 cm^{-1} (SO$_2$ asymmetric) and 1080–1010 cm^{-1} (SO$_2$ symmetric). But these bands are not observed in the present case. This may be due to the low amount of DEAS (20% only) in the co-polymer.

At a fluence of 10^{11} ions/cm^2 (Fig. 3b), the increment in absorption at 3600 cm^{-1}, 600–700 cm^{-1} and 1800 cm^{-1} indicates increase in number of

OH, S–O, C and CH per molecule. This is possible if cross-linking is taking place. As the fluence is increased to 10^{12} and 10^{13} ions/cm^2 (Figs. 3c and d), the absorption increased at the similar sights indicating that cross-linkage increased with fluence.

There is also a possibility of CO$_2$ and SO$_2$ gas evolution during the irradiation process. If CO$_2$ is evolved on irradiation, the possible structure after irradiation can be represented as

$$CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{S}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{S}\text{-}CH_2\text{-}CH\text{-}CH_2$$

(Structure-A)

If SO$_2$ is evolved on irradiation, the possible structure after irradiation can be represented as
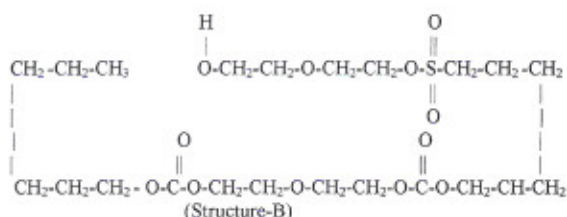
(Structure-B)

If both SO$_2$ and CO$_2$ are evolved, the cross-linking may take place for some of the molecules in the form of structure-A and for some molecules in the form of structure-B simultaneously. However, this can be established only when gasses evolved on irradiation are analysed by quadrupole mass spectrometer, a facility which was not in operation during our experiment.

Annealing kinetics of radiation damage in track recording SSNTDs has been studied in our laboratory for more than two decades and a new model was proposed [19,20]. The irradiated polymer samples under investigation were kept exposed to the laboratory environment for 3–4 weeks before annealing experiments were carried out in a muffle furnace in ambient air. It is felt that some active species tend to stick to the open ends of the broken chains, thereby preventing broken polymer chains
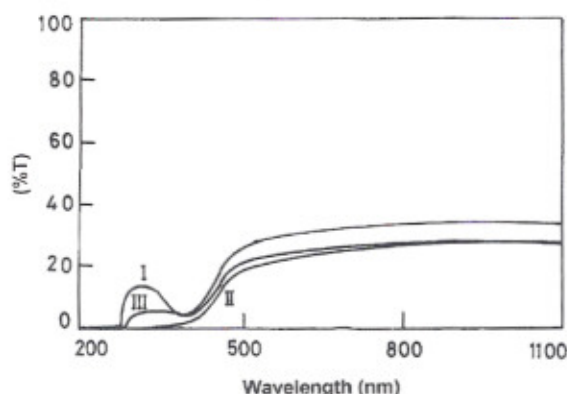
Fig. 4. UV-visible spectra of Makrofol irradiated with $^{12}C^{5+}$ (10^{12} ions/cm^2) and annealed at 120°C (I) virgin, (II) irradiated and (III) annealed.

from reuniting and repairing the radiation damage to the structure.

It is observed that radiation damage produced by $^{12}C^{5+}$ (fluence 10^{12} ions/cm^2) ions in Makrofol gets partially annealed at 120°C for 75 min heating as shown in Fig. 4. The UV-visible spectra of Makrofol reveals that there is a partial damage recovery due to the thermally induced evolution of the species formed by exposure of the irradiated samples to the atmosphere. The emission of neutral hydrogen and ejection of other atomic species from Makrofol during irradiation will inhibit full recovery of radiation damage in annealing experiments. Partial annealing is also observed in CR-39 and SR-86. The work is in progress for detailed investigations of the annealing process and its correlation with the structural modifications.

Acknowledgements

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