



Modification of optical, chemical and structural response of CR-39 polymer by 50 MeV lithium ion irradiation

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Abstract

CR-39 polymer samples were irradiated with 50 MeV lithium ion beam; the fluence was varied in the range 10^{11} – 10^{13} ions cm^{-2} . Irradiation effects were studied using UV–visible, FTIR spectroscopic and X-ray diffraction techniques. The observation of the recorded spectra shows that the detector is sensitive to swift ions irradiation and its UV absorption is influenced by the stopping power $(dE/dx)_s$. The FTIR spectra does not show any considerable changes due to the irradiation indicating that the detector is chemically stable. No appreciable change in the diffraction pattern of CR-39 polymer after irradiation upto the fluence level of 10^{13} ions cm^{-2} is observed, showing its structural stability also. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: CR-39 polymer; Lithium ion irradiation; UV-visible and FTIR spectroscopy; X-ray diffraction

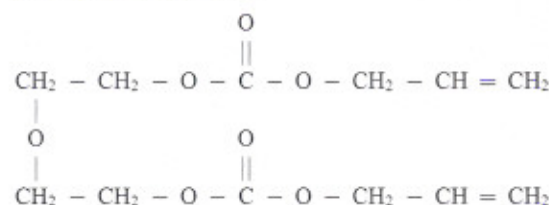
1. Introduction

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 (Lee, 1996; Venkatesan et al., 1978; Wielunski et al., 1997). The polymer used in this study is a homopolymer commonly known by its trade name CR-39, which is found to be a high-grade optical plastic and has an intrinsic property of ion track detection (Singh et al., 1982, 1988; Virk et al., 1986). Ion irradiation in polymers destroys the initial structure by cross-linking, scission and emission of atoms, molecules and molecular fragments (Marletta, 1990). This leads to changes of their properties like density (Schiessel et al., 1994), conductivity (Calgagno and Foti, 1987), optical absorption (Davenas et al., 1990), molecular-weight distribution and solubility (Puglisi et al., 1987; Virk et al., 1998). The effectiveness of these changes produced in the polymer depends on the structure of the polymer and the experimental condition

of the ion irradiation like ion energy, fluence, mass, charge and the nature of the targeted material itself.

The absorption of light energy by organic polymers in the visible and ultraviolet region involves promotion of electrons in σ , π and n orbitals from the ground state to a higher energy state. Many molecules contain electrons that are not directly involved in bonding; these are called non-bonding or n -electrons and are mainly located in atomic orbitals of oxygen, sulphur, nitrogen and halogens. The polymers containing these molecules in the structure are expected to play an important role in UV–visible absorption. The three-dimensional network of CR-39 polymer consists of polyallyl chains cross-linked by diethylene glycol dicarbonate linkages.

The monomer unit of CR-39 plastic (Cartwright et al., 1978) is given as follows:



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2. Experimental

The self-supporting polymer CR-39 specimen samples in the form of flat, polished sheets of thickness 250 μm were obtained from Pershore Moulding (UK). These were used in as-received form in the size of 1 cm \times 1 cm without any further treatment. Three identical samples were mounted on a vertical vacuum-shielded sliding ladder and irradiated in a general purpose scattering chamber by using 50 MeV $^7\text{Li}^{3+}$ ion beam available from the 15 UD Pelletron in the Nuclear Science Center (NSC), New Delhi. The ion beam fluence was varied in the range of 10^{11} – 10^{13} ions cm^{-2} . In order to expose the whole target area, the beam was scanned in the x – y plane. The ion beam energy and the thickness of the target are so chosen that the material modification will occur only due to electronic energy loss of lithium ions in the exposed sample. The nature of the ion beam-induced changes has been analysed by using UV–visible spectrophotometer (UV-160 Shimadzu) in the absorption mode. The Fourier Transform Infrared (FTIR) spectroscopy was performed in the transmission mode, using Nicolet Avatar 320 FT-IR.

The preliminary structural study was carried out by an X-ray powder diffractometer (Rigaku D Max IIIC) using Cu-K_α radiation (1.5418 Å) for a wide range of Bragg angles 2θ ($10^\circ \leq 2\theta \leq 60^\circ$) at the scanning rate of $5^\circ/\text{min}$.

The projected range of 50 MeV $^7\text{Li}^{3+}$ ion beam were calculated to be around 449 μm by using SRIM-97 code (Ziegler, 1997). The SRIM calculation indicates that 99.95% of the energy lost by the 50 MeV $^7\text{Li}^{3+}$ ion beam in 250 μm thick CR-39 is electronic in its nature. The average electronic stopping power of the beam $(dE/dx)_e$, is 6.31 eV/Å.

3. Results and discussion

The nature and extent of radiation damage induced in CR-39 has been studied by both UV–visible and FTIR spectroscopy as well as XRD analysis. The results of optical absorption measurements with UV–visible spectro-photometer carried out on unirradiated and irradiated samples are shown in Fig. 1. The optical absorption spectrum of the virgin sample Fig. 1(I) shows two distinct sharp peaks occurring at 200 and 210 nm with more or less equal magnitude of absorption. Beyond the second peak, the absorption falls exponentially and comes to base level at 320 nm. Fig. 1 (II–IV) shows the UV–visible spectra of irradiated samples at the fluences of 10^{11} , 10^{12} and 10^{13} ions cm^{-2} , respectively. It is observed that due to the irradiation the two peaks of the virgin sample Fig. 1(I) disappear and there is a decrease in optical absorption in the range of 190–330 nm. However, a reversal effect is observed in the behaviour when the fluence is increased from 10^{11} to 10^{13} ions cm^{-2} . Due to the irradiation, a change in band shape, and band width, have also been observed in the same wavelength range.

The FT-IR spectra of the virgin and irradiated CR-39 polymer sample are shown in Fig. 2 in the transmission

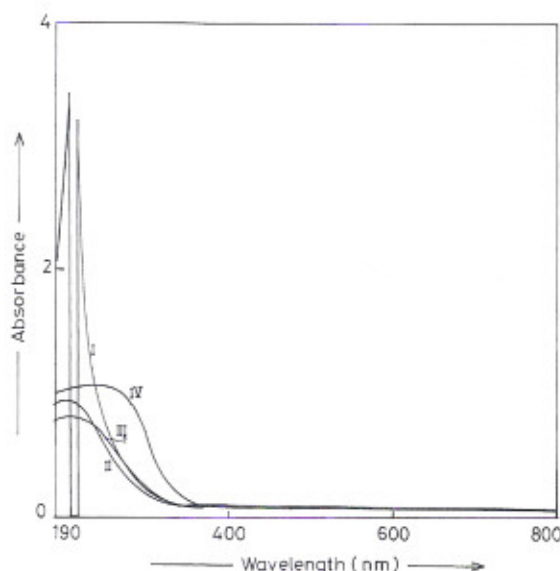


Fig. 1. UV–visible spectra of virgin sample (I) and of the samples irradiated (II–IV) with 50 MeV $^7\text{Li}^{3+}$ ion beam at the fluences of 10^{11} , 10^{12} , 10^{13} ions cm^{-2} , respectively.

mode without using the normalisation technique. It shows the characteristic peaks at 3450, 3520 and 3620 cm^{-1} as belonging to double bond carbonate stretching group, respectively. The intensity of the peaks is very high. The FT-IR spectra of irradiated samples does not indicate any considerable change due to irradiation with the increase in the fluence level of radiation. From the above results, it may be interpreted qualitatively that the polymer CR-39 has chemical stability up to the fluence level of 10^{13} ions cm^{-2} .

Fig. 3 (I and II) shows the diffraction pattern of the virgin and irradiated CR-39 polymer at the fluence level of 10^{13} ions cm^{-2} . The diffraction pattern of CR-39 virgin polymer clearly indicates that this polymer is amorphous in nature and shows the maximum intensity at the angle around 20° . The irradiated one also shows an identical diffraction pattern except that the maximum intensity point is slightly shifted towards the higher angle.

4. Conclusions

On the basis of the UV–visible spectroscopic analysis, it may be concluded qualitatively that there is a chain scission in the polymer backbone and the scission increases with increasing fluence level. A shift in the absorption edge towards the higher wavelength indicates the decrease in band gap energy of the polymer samples. It may be inferred from the FTIR spectra that the CR-39 polymer has chemical stability up to the fluence level of 10^{13} ions cm^{-2} , particularly in the case of electronic energy loss by the 50 MeV lithium ions. A comparison of diffraction pattern of the virgin and

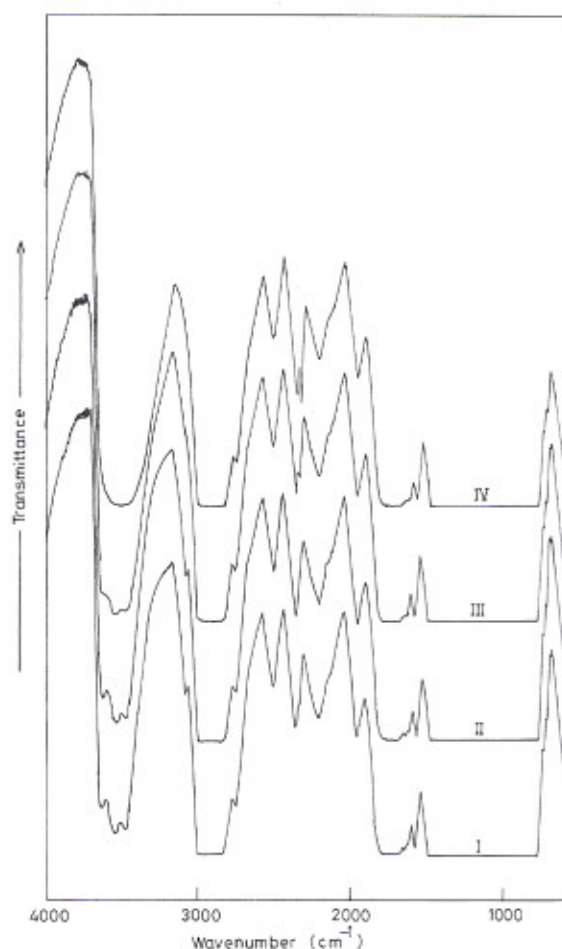


Fig. 2. FTIR spectra of virgin sample (I) and of the samples irradiated (II–IV) with 50 MeV ${}^7\text{Li}^{3+}$ ion beam at the fluences of 10^{11} , 10^{12} , 10^{13} ions cm^{-2} , respectively.

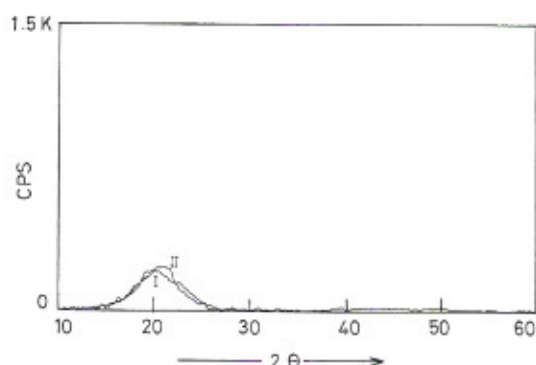


Fig. 3. X-ray diffraction pattern of virgin sample (I) and of the sample irradiated (II) with 50 MeV ${}^7\text{Li}^{3+}$ ion beam at the fluence of 10^{13} ions cm^{-2} .

irradiated polymer shows that the electronic energy loss in CR-39 does not induce any appreciable change in the physical structure of the polymer.

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