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ION BEAM MODIFICATION OF POLYMERIC MATERIALS USING ACCELERATORS

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Abstract

Accelerators are widely used for medical and industrial applications. With the advent of accelerators, material science research gets immensely benefited. Ion beam modification of materials using heavy ions at Nuclear Science Centre, New Delhi have been studies. The paper presents the results of the studies.

1. Introduction

Accelerator based materials science research is of recent origin in India. Materials science in general and devices in particular have always prospered immensely from the advent of accelerators. Low energy (keV) ion accelerators have become part of industry and medium energy (MeV) accelerators have become available for commercial exploitation. It has become possible to accelerate ions of any element to desirable energies (GeV range) using cyclotrons and linear accelerators. At Nuclear Science Centre (NSC), New Delhi, a 15 UD Pelletron facility is set up, which is a 15 MV tandem Van de Graaf machine. Lower energy Pelletrons are already functioning at TIFR, Mumbai and Institute of Physics, Bhubneshwar. Some of the old machines, Van de Graaf accelerators at BARC, Trombay and B.H. U. Varanasi had been used in materials science research also. We are yet at the threshold of accelerator based materials science research in India. Our group has also been involved in ion beam modification of materials^{1,2} since 1985 using heavy ion beams available from GSI, Darmstadt, JINR, Dubna and NSC, New Delhi. A brief review of the results obtained will be given here.

Mechanism

When an ion beam is incident on a polymer, there is a linear energy transfer (LET) along the path of the beam. The transfer of energy from the ions to the molecular solid is usually described in terms of electronic excitations and nuclear encounters. The interaction takes place in three steps. First, when the incident energy and velocity are large, electronic excitation dominates in time shorter than 10^{-15} s; intense ionization takes place with the emission of fast delta rays. The de-excitation of atoms and molecules continue for a longer time, say up to 10^{-9} s, till the thermal equilibrium is established with the formation of free radicals, radical ions, unsaturated groups, and broken chains etc. In this phase, some amount of thermal energy may also trigger a significant atomic reorganization. This is followed by a chemical equilibrium, in which recombination of radicals, crosslinking of chains may take place together with formation of new species as per the laws of hot atom chemistry. With decreasing energy and velocity of the incident ion as it penetrates deeper in polymer, the electronic excitation decreases and gives place to the loss of energy by nuclear encounters. The effects of ion beam modification of polymers are manifested by radiolytic evolution of gases, surface blistering, void formation, exfoliation, changes in crystallinity, solubility and dielectric behaviour, etc. In some cases, useful improvements in the mechanical, optical, and electrical properties are also observed as radiation induced effects. Hardness often improved over 50 times, exceeding hardness value of steel³. Similarly, the conductivity increases by an order of 18 to 20 magnitudes^{4,5} by ion beam irradiation of Kapton.

2. Experimental

Various types of polymers studied are polycarbonates (CR-39, SR-86 & Markrofol, the most sensitive track detectors); polyimides (Kapton-H) and Polyvinylidene fluorides (PVDF). Polycarbonate samples were irradiated in high vacuum scattering chamber using ^{12}C ion beam and others by ^7Li ion beam, available from the 15 UD pelletron accelerator at the Nuclear Science Centre (NSC), New Delhi. In order to expose the whole area of the target an oscillating beam in the x-y plane was used, with a fluence range of 10^{11} – 10^{14} ions/cm². The nature and extent of radiation damage, or in other words, structural modifications in polymers, have been characterized by Fourier transform infrared (FTIR) and UV-visible spectroscopy as well as XRD analysis.

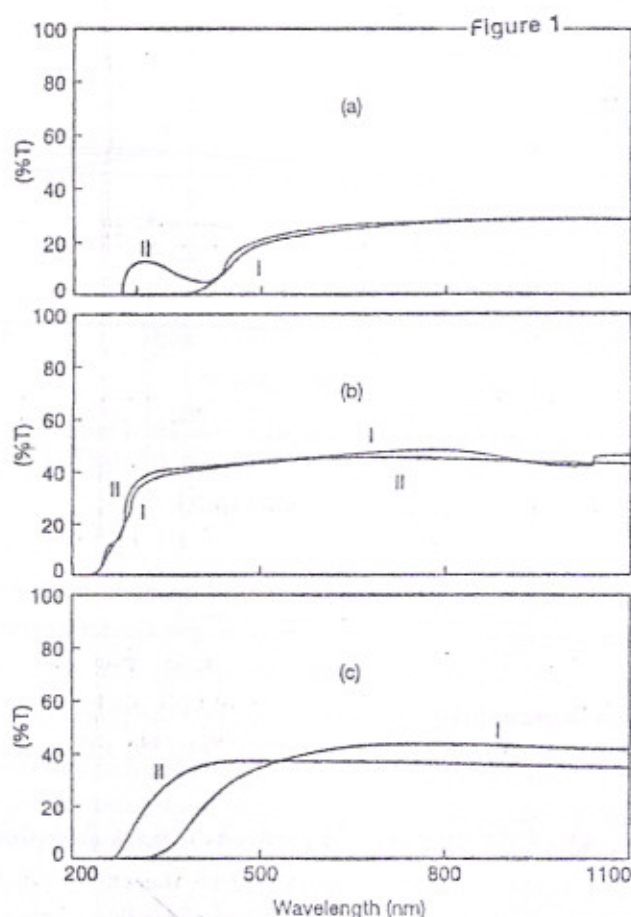


Fig. 1 UV-visible spectra of irradiated (I) (dose 10^{12} ions cm^{-2}) and unirradiated (II) samples of (a) Makrofol, (b) CR-39 and (c) SR-86.

3. Results and Discussion

a) Radiation Effects in Polycarbonates using 60 MeV $^{12}\text{C}^{+5}$ Beam

The results of optical absorption studies carried out with an UV-visible spectrophotometer on unirradiated and irradiated samples of Makrofol-KG, CR-39 and SR-86 are illustrated in Figure 1. It is observed that for all the three polymers, there is 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 with CR-39 whereas it is quite evident for Makrofol-KG and SR-86. The effect disappears at higher wavelengths for Makrofol but, on the contrary, there is a reversal in the case of SR-86. Figure 2 shows the UV-visible

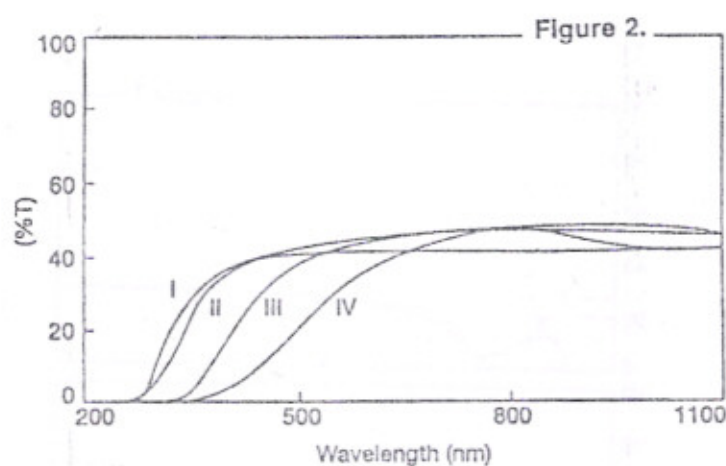


Fig. 2 UV-visible spectra of SR-86 samples irradiated with $^{12}\text{C}^{5+}$ at various doses (I, virgin sample; II, 10^{11} ions cm^{-2} , III, 10^{12} ions cm^{-2} and IV, 10^{13} ions cm^{-2}).

spectra of SR-86 for three different irradiation doses in comparison with the spectrum of an unexposed sample. The region of optical absorption extends to higher wavelengths for higher irradiation doses. The reversal effect also disappears at a fluence of 10^{13} ion cm^{-2} .

Most of the observed chemical modifications in polycarbonates are due to large amount of energy transferred to electronic-molecular environments in polymers. The bulk etch rates of CR-39, SR-86 and Makrofol polycarbonate are summarized in Table 1. For all three polymers, the enhancement of the bulk etching rate after irradiation confirms the hypothesis that damage is created by deposition of heavy ions' energy in ion-polymer interaction in the MeV/ μ range.

Table 1 : Bulk etch rates of CR-39, SR-86 and Makrofol-KG, by thickness measurement method ($V_b = \Delta x/2t$)

Samples	Etchant (NaOH)	Etching time	Etchant temperature	Bulk etch rate ($\mu\text{ m/h}$)	
				Unirradiated	Irradiated
CR-39	6.25 N	2 h	60°C	1.25	1.75
SR-86	6.25 N	2 h	60°C	2.00	3.50
Makrofol-KG	6.25 N	2 h	60°C	0.75	1.00

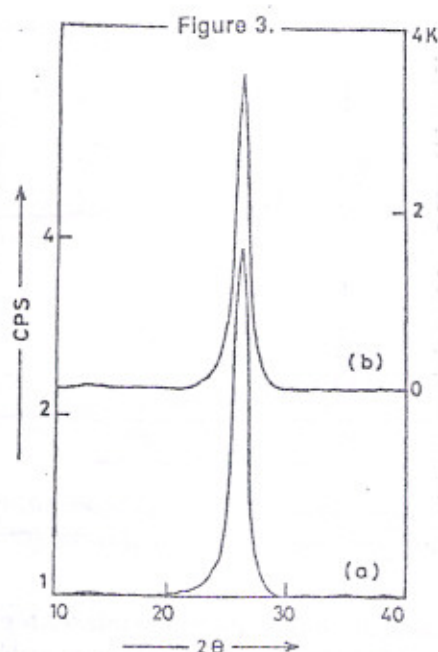


Fig. 3 X-ray diffraction pattern of Kapton-H polymer; (a) virgin, (b) irradiated with 50 MeV ${}^7\text{Li}^{3+}$ ion beam at the dose of 10^{14} ions cm^{-2} .

(b) Radiation Effects in Kapton-H Using 50 MeV ${}^7\text{Li}^{3+}$

The UV-visible and FTIR spectra of this polymer before and after irradiation is almost same, indicating that this polymer is highly stable towards high energy ${}^7\text{Li}^{3+}$ ion beam irradiation. This may be due to the presence of three phenyl rings linked to each other with stiff bonds at the backbone of polymer.

The diffraction pattern of the virgin and irradiated Kapton-H is shown in Fig. 3. It clearly shows that this polymer is crystalline in nature with a sharp peak at $2\theta = 25.82^\circ$ and $d=3.447\text{\AA}$. Due to irradiation there is a decrease in the intensity of about 10.3% and an increase of crystallite size by 5.4%. The diffraction pattern of virgin and irradiated Kapton are more or less identical. Hence we may conclude that the kapton-H is stable under 50 MeV Li ion beam irradiation.

(c) Radiation Effects in PVDF using 50 MeV ${}^7\text{Li}^{3+}$ beam

The UV-visible and FTIR spectra of this polymer before and after irradiation up to the dose of 1.45×10^{12} ions/ cm^2 are almost identical, indicating

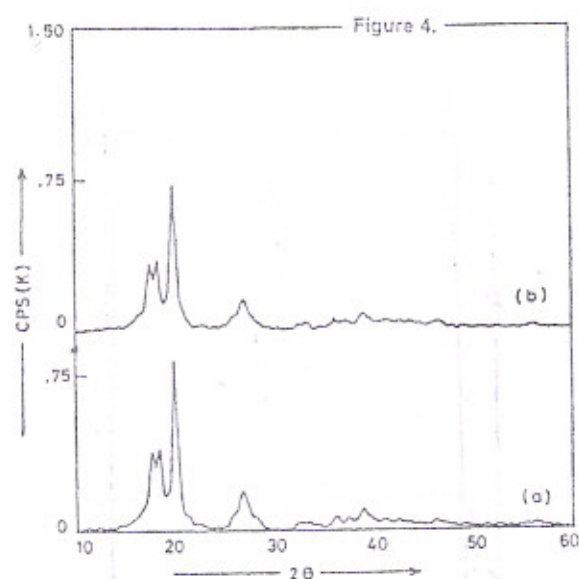


Fig. 4 X-ray diffraction pattern of PVDF polymer; (a) virgin, (b) irradiated with 50 MeV $^7\text{Li}^{3+}$ ion beam at the dose of 10^{13} ions cm^{-2} .

that this polymer, is optically and chemically stable. At higher doses, the stability decreases at faster pace with the formation of carbon-carbon double bond due to irradiation.

The diffraction pattern of the virgin and irradiation PVDF shown in Fig. 4. It clearly shows that this polymer is semicrystalline with a sharp peak at $2\theta = 20.02^\circ$ and $d = 4.432 \text{ \AA}$. The diffraction pattern of virgin and irradiated PVDF are almost identical.

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