

## Modification of the optical, chemical and structural properties of 50 MeV ${}^7\text{Li}^{+3}$ ion bombarded polyimide kapton-H

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The ion beam induced modification of polyimide (kapton-H) by  ${}^7\text{Li}^{+3}$  at 50 MeV has been studied by using UV-visible and FTIR techniques. The ion fluences ranging from  $7.8 \times 10^{10}$  to  $0.94 \times 10^{14}$  ions  $\text{cm}^{-2}$  have been used in order to study the optical, chemical and structural changes in polyimide. The observation of the recorded UV-visible spectra clearly shows three characteristics peaks at 338, 348, 360 nm, which shows an oscillatory behaviour corresponding to the magnitude of absorption with increasing dose. The FTIR spectra clearly indicate that there is only breakage of one of the bonds in imide ring of the repeating system without any scission in the back bone of the polymer. The general behaviour of the spectra of the polymer before and after irradiation is almost the same, indicating that this polymer is highly stable towards the electronic energy loss. The diffraction pattern of kapton indicates that mostly this polymer is in crystalline form along with a very small part in amorphous state. However, an appreciable change in diffraction pattern has been observed after irradiation.

### 1 Introduction

The development of polymers containing aromatic rings linked by various functional groups in the main chain (aromatic polymers) was extensively made during the 1970's to assist the production of thermo-resistant engineering plastics. Because of the versatility, these polymers are used in the nuclear energy field. Radiation resistivity is a very important property for use in the radiation field and the studies of the radiation effects on ladder polymers are necessary. Polyimides such as kapton were extensively studied and reported having resistivity for gamma rays and electron beam up to  $\approx 100$  MGy of radiation<sup>1,2</sup>. Coltman *et al.*,<sup>3</sup> reported that these polymers have also an excellent resistivity under reactor irradiation.

When a highly energetic charged ion strikes a polymer target, it loses most of its energy in exciting electrons and/or ionizing atoms. Target ionization causes bond cleavages; the formed free radicals are expected to come to rest and may react in a molecular site of a different type from their original site. These radicals are responsible for most of the chemical modifications observed in the polymer film: chain scission, cross-linking and double and triple bond formation<sup>4</sup>. The very value of the energy transferred induces an unusual density of electron-hole pair close to the ion path and consequently the polymer modification differs from those observed with low energy ionizing projectiles<sup>5,7</sup>. Irreversible

cleavage of bonds within the macromolecules results in the production of volatile species. The particular bonds which are broken in such a process may be delineated by FTIR analysis of both virgin and irradiated samples. In general the energy spent in ionization is such larger that the bond energies found in polymers<sup>8,9</sup>.

The ion beam induced modification in polyimide attracted a great interest in view of the very interesting drop of the resistivity<sup>10,14</sup> from about  $10^{16}$  to  $10^{-3} \Omega\text{-cm}$ . The property modification is related to ion induced chemical modifications occurring in various successive steps, at fairly well defined fluence range<sup>13,14</sup>. Polymers are a promising class of materials for optical components such as splitters, which are needed for the expanding optical networks in the field of telecommunication. The first polymer studied was PMMA, which is an excellent material because it is easy to structure and has the desired optical properties<sup>15</sup> with one single exception that its temperature stability<sup>16</sup> is limited to 80 °C.

The polyimide (kapton) is made by the poly-condensation of aromatic di-anhydrides and aromatic amines. The first step is a soluble polyamic acid, which is converted to the polyimide by further condensation. The polyimides retains usable properties at 300°C for months, and at 400°C for a few hours, can withstand exposures of a new minutes to temperatures well over 500°, depending on degree of condensation and struc-



ture. The polyimide kapton has  $T_g$  beyond  $300^\circ\text{C}$ . The monomer of kapton-H polymer is represented as follows:

The optical, chemical and structural modification induced by 50 MeV lithium ion beam on kapton-H films, mostly due to electronic energy loss have been investigated.

### Experimental Details

The kapton-H polyimide (Du Pont, UK) polymer specimens in the form of flat, polished sheet of thickness  $200\mu\text{m}$ , were prepared in the size of  $1\text{ cm} \times 1\text{ cm}$ . They were used in as received condition without any further treatment. Four samples of same type were mounted on a vertical vacuum shield sliding ladder, and irradiated in general purpose scattering chamber by using 50 MeV  $\text{Li}^{+3}$  ion beam available from the 15 UD pelletron accelerator at the Nuclear Science Centre (NSC), New Delhi. The ion beam fluences were varied in the range of  $7.8 \times 10^{10}$  to  $0.94 \times 10^{14}$  ions  $\text{cm}^{-2}$ . In order to expose the whole area of the target, an oscillating beam in the x-y plane was used. The ion beam energy and the thickness of the target is so chosen that the modification will occur only due to the electronic energy loss in the exposed sample. The nature of optical, chemical and structural modifications have been analysed by UV-VIS, Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction analysis.

### 3 Results and Discussion

The projected range of 50 MeV  $\text{Li}^{+3}$  ion beam in kapton-H was calculated to be  $392\mu\text{m}$ , using SRIM-97 code<sup>17</sup>, which is more than the thickness of the polymer. The energy lost by the ions in a solid is mainly dominated by two mechanisms known as electronic and nuclear stopping. Electronic energy loss is dominant for ions with high energy and involves kinetic energy transfer to atoms in the target due to inelastic ion-electron interaction. Nuclear processes produce lattice vibration and the displacement of the target atoms. Displacement damage is usually considered the most important cause of material modification in solids; however, in polymers ionization processes are also important since purely ionizing radiation such as UV and gamma rays are known to cause significant modification in polymers<sup>18</sup>.

The nature and extent of radiation induced changes, viz., optical, chemical and structural modifications in kapton-H polymer are studied by UV-VIS, FTIR spectroscopy and XRD analysis. The results of optical absorption studies with UV-visible spectrophotometer carried out on virgin and irradiated samples are illustrated in Fig. 1. The optical absorption spectrum of the virgin sample (Fig. 1a) shows a constant absorption region from 190-310 nm. After the constant absorption region, three distinct peaks are occurring at 316, 328 and 360 nm. Further it shows two distinct constant absorption regions between 364-418 nm and 430-480 nm, there

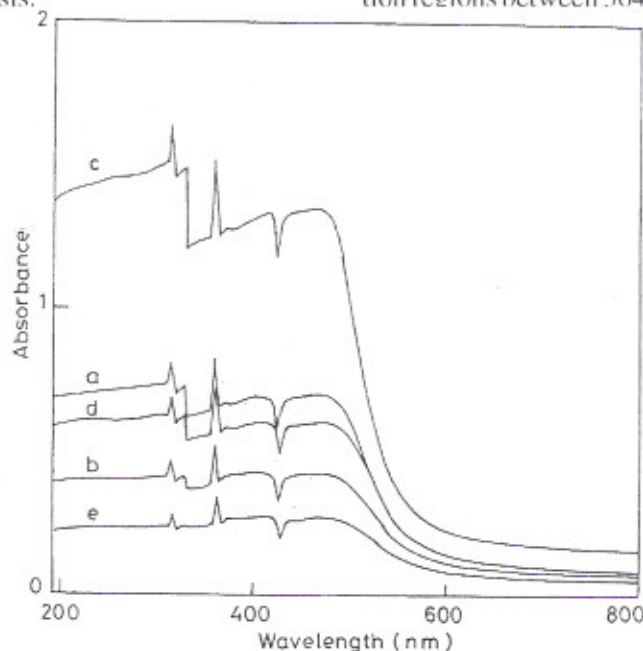


Fig. 1 — Optical absorption spectra of polyimide kapton-H polymer irradiated with 50 MeV  $\text{Li}^{+3}$  ion beam: (a) virgin (b)  $7.8 \times 10^{10}$ , (c)  $8.55 \times 10^{11}$ , (d)  $1.03 \times 10^{13}$  and (e)  $0.94 \times 10^{14}$  ions  $\text{cm}^{-2}$

after the absorption falls exponentially and comes to the base value. The three characteristic absorption peak may be correlated with the electronic transition occurring in imide ( $\text{NC}=\text{O}$ ); it is well known that the compounds like oxygen, nitrogen containing non-bonding electrons are capable of showing these types of characteristic absorptions. Fig. 1(b,c,d,e) shows the optical absorption spectra of irradiated samples at the doses of  $7.8 \times 10^{10}$ ,  $8.55 \times 10^{11}$ ,  $1.03 \times 10^{13}$  and  $0.94 \times 10^{14}$  ions  $\text{cm}^{-2}$  respectively. It is observed that due to irradiation up to the dose level of  $7.8 \times 10^{10}$  ions  $\text{cm}^{-2}$  there is a decrease in the optical absorption along the whole range of wavelengths. However, a reversal effect in optical absorption has been observed when dose is further increased to a value of  $8.55 \times 10^{11}$  ions  $\text{cm}^{-2}$ , giving a maximum absorption at this dose. When dose is further increased, it shows a decrease in optical absorption along with the wavelengths. It is surprising why this polymer shows an oscillatory behaviour as the dose increases. It has also been observed that this polymer retains more or less the

original nature of optical absorption pattern up to the dose level of  $0.94 \times 10^{14}$  ions  $\text{cm}^{-2}$ .

The FTIR spectrum of the virgin and irradiated kapton-H polymer is shown in Fig. 2. The FTIR spectrum of the un-irradiated kapton-H (Fig. 2a) shows the characteristic peaks in the region  $3500\text{--}3650 \text{ cm}^{-1}$  corresponding to OH stretching frequencies. The characteristic imide ( $\text{NC}=\text{O}$ ) peak of the polymer is observed at  $2260 \text{ cm}^{-1}$ . The corresponding peak to carbonyls is observed around  $1700 \text{ cm}^{-1}$ . The all other usual peaks corresponding to aromatic ring system and other linkages are also observed in the corresponding region. Fig. 2(b, c, d, e) shows the FTIR spectrum of the irradiated polymer at the fluences of  $7.8 \times 10^{10}$ ,  $8.55 \times 10^{11}$ ,  $1.03 \times 10^{13}$  and  $0.94 \times 10^{14}$  ion  $\text{cm}^{-2}$  respectively. The general behaviour of the spectrum in all irradiated samples is intact without much change either in the peak position or in the intensity of the peaks. This indicates that there is no scission in the back bone of the polymer. Fig. 3(a,b) shows the diffraction pattern of the virgin and

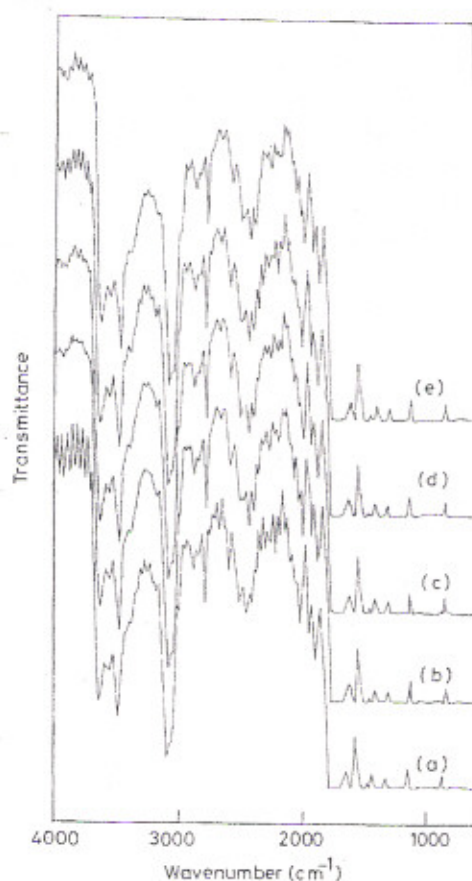


Fig. 2 — FTIR spectra of polyimide kapton-H polymer irradiated with 50 MeV  $^7\text{Li}^{+3}$  ion beam : (a) virgin (b)  $7.8 \times 10^{10}$  (c)  $8.55 \times 10^{11}$  (d)  $1.03 \times 10^{13}$  and (e)  $0.94 \times 10^{14}$  ions  $\text{cm}^{-2}$

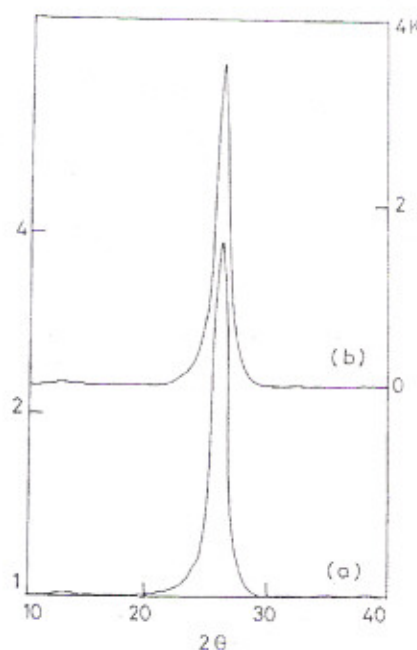
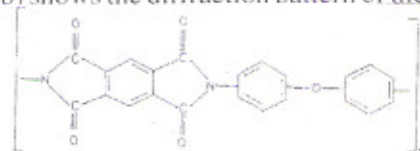


Fig. 3 — X-ray diffraction pattern of kapton-H polymer: (a) virgin (b) irradiated with 50 MeV  $^7\text{Li}^{+3}$  ion beam at the dose of  $0.94 \times 10^{14} \text{ cm}^{-2}$



irradiated kapton-H polymer respectively, at the dose level of  $0.94 \times 10^{14}$  ions  $\text{cm}^{-2}$ . The diffraction pattern of virgin polymer clearly indicates that this polymer is crystalline in nature. It shows a sharp peak at  $2\theta = 25.82^\circ$  with  $d = 3.447 \text{ \AA}$  and full width at half maxima (FWHM) = 1.65. However, the diffraction pattern also shows a very small portion in the amorphous phase which corresponds to the diffused pattern observed at  $2\theta = 13.1^\circ$ . The diffraction patterns of virgin and irradiated one are more or less identical but with slightly changed values. Due to irradiation there is a decrease in the intensity of about  $10.3^\circ$  and also in FWHM by 5.4%. The broadening of diffraction maxima on X-ray diagrams is usually associated with a decrease in the crystallite size. It has also been observed that maximum intensity position is slightly shifted towards the lower angle from  $25.82^\circ$  to  $25.72^\circ$ . Hence it clearly indicates that the physical structure of this polymer is quite stable under high energy irradiation.

#### 4 Conclusion

The general behaviour of the spectra of this polymer before and after irradiation is almost the same, indicating that, this particular polymer, kapton-H is highly stable towards high energy  $^7\text{Li}^{+3}$  ion beam irradiation. This can be due to the presence of three phenyl rings linked to each other with stiff bonds at the backbone of polymer. Such type of behaviour may be specific to the ladder type of polymers. On the basis of X-ray diffraction analysis of virgin and irradiated kapton-H polymer, it is concluded that the size of crystallite increases by 5.4 % due to irradiation.

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