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**OPTICAL AND CHEMICAL RESPONSE OF 60 MEV CARBON ION IRRADIATED KAPTON  
-H POLYMER**

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**Sanjay Kumar<sup>a</sup>, Ajeet Kr. Srivastava<sup>a</sup>, Manvinder Singh<sup>b</sup>, A.K.Tiwari<sup>c</sup>**

<sup>a</sup>Bharat Institute of Technology, Sonipat- 131025

<sup>b</sup>G.L.Bajaj Institute of Technology and Management Greater Noida-201305

<sup>c</sup> Department of physics , K.N.Govt.P.G College, Gyanpur, Bhadohi U.P.

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**ABSTRACT**

Physical and Chemical response of 60 MeV Carbon ion irradiated Kapton-H Polymer has been studied by using UV-visible, FTIR and XRD techniques. The ion fluences ranging from  $8.6 \times 10^{11}$  to  $9 \times 10^{13}$  ions  $\text{cm}^{-2}$  have been used. Recorded UV-Visible spectra clearly show a decrease in absorption initially with dose, but for the higher doses it shows a recovery characteristic. A decrease in band-gap energy of 0.066 eV has been observed. The FITR analysis indicates about oxidative degradation of polymer. The diffraction pattern of Kapton - H indicates that this polymer is semi crystalline in nature. In case of irradiated one, there is an average increase of crystalline size by 23% but diffuse pattern indicates that there is decrease in crystallinity, which may be attributed to the formation of complex structure induced by the cross -linking of the polymeric chains.

**KEYWORDS:** Kapton -H polymer, Carbon ions; Radiation effects; UV and FT-IR spectroscopy; X-ray diffraction.

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**INTRODUCTION**

The rapid development of polymer science and the extensive utilization of polymeric materials in all fields of technology have led in recent years to the increased interest to the various problems of the physics and chemistry of polymers. It is known that one of the main objectives of polymer physics is the elucidation of the relationship between the chemical and physical structure and physical properties of polymers.

Polyimides are used extensively in situation requiring high- performance plastic materials because of their unique combination of superior mechanical, electrical, chemical, and thermal properties<sup>1</sup>. Kapton, a popular Polyimide, is able to operate in the temperature range of low as  $-269^{\circ}\text{C}$  and high as  $400^{\circ}\text{C}$ . In particular the radiation resistance, and fire resistance, has made this polyimide one of the favorite choice for applications in wire and cable insulation, electrical component seal assemblies, in nuclear power plants, military aircraft, and space shuttles<sup>3,4</sup>.

When the swift heavy ion (SHI) passes through a material medium, it loses its energy in the medium. If the thickness of the targeted medium is sufficiently less than the range of the projectile ion then the energy deposition is mainly due to electronic energy loss, which is generally denoted by  $(dE/dX)_e$  or by the equivalent quantity, the linear energy transfer, LET. This energy deposition leads to production of new reactive species (radicals, gas) and defects (instauration, scissions, cross links) and heat<sup>5</sup>.

When a highly energetic charged Ion strikes a polymer target, it loses most of its energy in exciting electron 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<sup>6</sup>. These radicals are responsible for most of the chemical transformation observed in the polymer films: The very high value of energy transferred induces an unusual density of electron - hole pair close to the ion path and consequently the polymer modifications differ from those observed with low ionizing projectiles.<sup>7-9</sup>

Analysis of the structure of polymers has been a problem of continuing interest for over four decades. Even to this day, the conception that has recently gained wide recognition consists in that the main

physical property of polymers depends not only on chemical structure but also on the super molecular organisation<sup>10</sup>.

This paper reports on the investigation of physical and chemical response of 60 MeV carbon ion bombarded on polyimide (Kapton-H) polymer and following properties like optical, chemical and structural changes. In order to study the effect of electronic stopping power  $(dE/dX)_e$  on these properties the energy of the projectile was so chosen that it could easily pass through the polymer sample.

### EXPERIMENTAL DETAILS-

The self- supporting polyimide (Kapton-H) commercial specimen in the form of a flat, polished film of thickness 100  $\mu\text{m}$  was obtained from Du Pont (UK). The samples were prepared in the size of 1 cm x 1 cm for irradiation. They were used in as-received condition without any further treatment. The irradiation were performed on a five identical samples, Polymer sample were mounted on a vacuum-shielded vertical sliding ladder and irradiated in a general purpose scattering chamber under high vacuum order of  $8 \times 10^{-7}$  Torr by using the 60 MeV  $^{12}\text{C}^{+5}$  ion beam with a beam current of 4.5 particle Nano Ampere, available from 15 UD Pelletron accelerator at Nuclear Science Centre New Delhi<sup>11-12</sup>. The Ion beam fluence was measured by integrating the ion charge on the sample ladder which was insulated from the chamber. The fluence was varied in the range of  $8.6 \times 10^{11}$  to  $9 \times 10^{13}$  ions  $\text{cm}^{-2}$ . In order to expose the whole target area The Beam was scanned in x-y plane. The range(as estimated by SRIM<sup>13</sup>) of the incident Ion was more than the thickness of polymer film The Ion beam energy and thickness of target were so chosen that only the modification due to electronic energy loss affected the exposed sample. The nature of ion beam induced changes has been analyzed by using the UV visible spectrophotometer (UV-160-Shimadzu) in the range of 200 to 800 nm. The Fourier transform infrared (FTIR) Spectroscopy was performing in the absorption mode using (Nicolet-Avatar 320 FTIR) in the range of 4000 to 400  $\text{cm}^{-1}$ . The preliminary structure studies were carried out by x-ray powder spectrometer(Rigaku D Max IIIC) with  $\text{Cu-K}\alpha$  radiation ( $1.5418 \text{ \AA}$ ) for a wide range of Bragg Angles  $2\theta(5^\circ < 2\theta < 60^\circ)$  at the scanning rate of  $5^\circ/\text{minute}$ . All the physical and chemical measurement has been carried out at the ambient temperature of 25 to 27<sup>0</sup> C.

### RESULT AND DISCUSSION

All our experiment can be divided into three type of measurement UV visible spectroscopy, FT- IR Spectroscopy and X-Ray diffraction of virgin and irradiated samples. The projected range of 60 MeV  $^{12}\text{C}^{+5}$  ion beams in polyamide (Kapton) was calculated to be around 133 $\mu\text{m}$ , using SRIM code<sup>13</sup>, which is more than 1.7 times 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. The electronic energy loss is dominant for ions with high energy and involves the energy transfer to atoms in the target due to inelastic electron-electron interaction. Coalitional processes produce lattice vibration and the displacement of the target atoms. Displacement damage is usually considered to be the most important cause of material modification in solids: however in the polymer ionization process are also highly important<sup>2</sup>. The SRIM calculation<sup>13</sup> indicate that 99.95% of energy lost 60 MeV  $^{12}\text{C}^{+5}$  in 100  $\mu\text{m}$  thick polyimide is electronic in its nature. The electronic stopping power of beam  $(dE/dX)$  is 32.62eV/ $\text{A}^0$ . The irradiation absorbed doses deposited in the Kapton-H at five different fluences  $8.6 \times 10^{11}$ ,  $9.3 \times 10^{12}$ ,  $1.53 \times 10^{13}$ ,  $4.53 \times 10^{13}$  ions  $\text{cm}^{-2}$  are 3.63, 36.32, 59.2, 176 and 3553 joules respectively.

### OPTICAL RESPONSE

Ultraviolet-visible spectroscopy, which gives us an idea what the value of band gap( $E_a$ ), is thus an important tool for investigation. The absorption of light energy by polymeric materials in the ultraviolet and visible regions involves promotion of electrons in  $\sigma$ ,  $\pi$  and  $n$ -orbitals from the ground state to the higher state in which are described by molecular orbital<sup>14</sup>. The electronic transition ( $\rightarrow$ ) that are involved in the ultraviolet and visible region are of the following types  $\sigma \rightarrow \sigma^*$ ,  $n \rightarrow \sigma^*$ ,  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$ . Many of the optical transitions which result from the presence of impurities have energies in the visible part of the spectrum, consequently the defects are referred to as the colour centres<sup>15</sup>. Ion beam interaction with polymers generates damage which leads to the formation of new defects and new charge states. In

order to obtain useful information from the ultraviolet or visible spectrum of the polymer the wavelength of maximum absorption ( $\lambda_{\max}$ ) and intensity of absorption must be measured accurately.

The result of optical absorption studies with UV visible spectrophotometer carried out on virgin and irradiated samples are illustrated in Fig- 1. For convenience of comparison between the virgin and the irradiated samples, the actual spectra are shifted along y-axis by regular displacement. The optical absorption spectrum of the virgin sample (Fig 1 a) shows three characteristic peak at around 302 nm, 351nm and 453nm a respectively, The first peak at 302nm appears in the form of a **kink** (Hidden Peak) which is usually observed in case of solid materials<sup>16</sup>, the second peak appear at 351nm in the form of a **dip**(Reverse Phase) which may be arising due to the  $180^\circ$  phase difference of outgoing signal. However the third peak at 453 nm appears in the form of a **hump** (broad peak); the magnitude of the absorption is more or less equal to the first and third peak. After the third peak, the absorption decreases very sharply and come to the minimum absorption (absorption-edge) at 536.8 nm ( $\lambda_g$ ) . We have calculated the band gap energy of the virgin as well as the irradiated sample from their respective value of  $\lambda_g$ .

Fig.1(B-F) shows the optical Spectra as a function of irradiation fluence for Kapton-H polymer samples at the fluence of  $8.6 \times 10^{11}$  ,  $9.3 \times 10^{12}$  ,  $1.53 \times 10^{13}$  ,  $4.53 \times 10^{13}$  and  $9 \times 10^{13}$  ions  $\text{cm}^{-2}$  , respectively. It is clear from the observation that the absorption decreases with increasing the fluence which may be attributed to scissioning of the polymer chains. However at Higher doses, the absorption increases, which may be correlated with the cross- linking of polymeric chains. A shift in the absorption is the absorption edge ( $\lambda_g$ ) towards higher wavelength by 21.8 nm indicates the decrease in the band gap energy of a polymer sample the quantitative value of irradiation dose deposited in Kapton-H at five different fluences and the energy band gap for the virgin and irradiated sample was given in table- 1. Due to the irradiation the kink in fig.1A disappears and has taken from a peak. The peak at 453 nm shifted to 467 nm, indicating about the possibility of formation of a new bond. Figure 2 shows the variation of absorbance which fluence on a log scale at three different characteristic wavelengths 302 nm, 351 nm, and 467 nm respectively, it is clear from the plots that the absorption is decreased initially, but for the higher doses the absorption increases. The decrease and increase in the absorption with increasing fluence may be correlated to the scissoring and cross linking of polymeric chains.

Fig.3 shows the variation of absorbance with fluence on a log-scale .It is clear from the plots that the band gap energy decreases initially with increasing fluence. However at higher doses, it shows a slight recovery characteristic which may be due to the cross-linking of polymeric chains.

### (b)FT-IR Spectroscopy of the irradiated Kapton–H polymer

The nature of chemical bonds of polymer can be studied through the characterization of the vibration modes determined by infrared spectroscopy<sup>18</sup>. The thickness of the analyzed film should be less than to the penetration depth of the ions in order to avoid an important background which would result from an undamaged polymeric thickness. We have used 100  $\mu\text{m}$  thick Kapton-H polymers to avoid the important background effect. Figure 4 (A B)shows the FT-IR spectra of the virgin(A) and one of the irradiated samples (B) at the fluence of  $9.0 \times 10^{13}$  ions  $\text{cm}^{-2}$ . The modes associated to the different characteristics absorption peaks are represented as the vibration of C = O at 1760 and 1700  $\text{cm}^{-1}$ , the CONH of the imide group at 1480/ $\text{cm}$ , the C-O-C vibration between two aromatic cycles at 1290 and 1275  $\text{cm}^{-1}$  and the substituted atomic cycles at 1220  $\text{cm}^{-1}$  Due to irradiation and considerable change has been observed in the range of 3000 -3700  $\text{cm}^{-1}$  the peak present at 3568  $\text{cm}^{-1}$  disappears due to irradiation which may be an evidence for oxidative degradation of polyimide. The analysis reveals that ring or ladder structure polymer are chemically highly resistant to electronic energy loss, this is because for a complete scission to occur at the imidic ring of Kapton, Two bonds at opposite positions of the Ring need to be broken simultaneously.

### STRUCTURAL PROPERTIES

Analysis of structure of polymer has been a problem of continuing interest for over four decades. Figure 5 (A,B) represents the diffraction pattern of a virgin and one of the irradiated kapton Polymer at a fluence

of  $9.0 \times 10^{13}$  ions  $\text{cm}^{-2}$ . The diffraction pattern of a virgin Polymer clearly indicates that this polymer semi-crystalline in its nature. The X-ray diffraction data (Table 1) of the virgin Kapton polymer clearly shows three peaks at  $2\theta = 13.76^\circ, 14.80^\circ$  and  $25.66^\circ$  with  $d = 6.430 \text{ \AA}, 5.981 \text{ \AA}$  and  $3.469 \text{ \AA}$  respectively. and the corresponding full width at Half Maxima (FWHM) are 1.26 1.0 5.1.26. The diffraction pattern of untreated sample shows partial Crystallinity and the most intense peak at  $2\theta = 25.66^\circ$ , however in the case of irradiated one a significant change in the diffraction pattern has been observed. The X ray diffraction data shows the most intense peak at  $2\theta = 13.98^\circ$ , the diffraction pattern of virgin and irradiated one are quite different and peaks are found slightly higher angular positions at  $2\theta = 13.98^\circ, 15.04^\circ$  and  $26.08^\circ$  with  $d = 6.392 \text{ \AA}, 5.885 \text{ \AA}$  and  $3.143 \text{ \AA}$  respectively. It is clear from the diffraction pattern of the irradiated Kapton sample that the diffraction patterns are broader (more diffused) than the virgin one, which indicates a decrease in crystallinity.

The concept of the crystalline in the case of polymers is quite different than other solids<sup>18</sup>. However, the decrease in intensity and shift in angular position towards the higher angle can be explained by decrease in lattice spacing<sup>19</sup>. The peaks suggest an evolution of the polymer toward a more disordered state and also a change in crystalline size. Due to irradiation, a shift in the peak angular positions towards the higher angle and an increase in crystalline size have been observed. The change in the crystalline size of the polymer has been calculated using Scherrer's equation<sup>20</sup>. In the case of virgin sample the average crystalline size is  $1.32 \text{ \AA}$  but in the case of irradiated one the average crystallite size is found to be  $1.64 \text{ \AA}$ , indicating an average increase in crystallite size by 24%. The decrease in crystallinity and increase in crystallite size has been observed due to heavy ion irradiation. However particularly in case of solid polymeric materials the exact nature of the interrelation between spacing, crystallite size and degree of disorder is yet to be understood.

## CONCLUSIONS

UV-Vis Spectroscopic analysis irradiated Kapton –H polymer reveals both degradation (scissioning) and polymerization (cross-linking) with change of fluence. It is also observed that the band gap energy decrease slightly by order of 0.07 eV at the fluence of  $9 \times 10^{13}$  ions/cm<sup>2</sup>. FTIR analysis reveals that ring or ladder structured polymers are chemically highly resistant to electronic energy loss, This is because for complete scission to occur at the imidic ring of Kapton. Two bonds at opposite position of the Ring need to be broken simultaneously Kapton-H has a partial crystallinity as evidenced by x-ray diffraction pattern. Heavy Ion irradiation induces a decrease in Crystallinity and increasing crystal size.

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**Table-1 Quantitative values of absorbed dose and decrease in band gap energy.**

<b>Irradiation fluence (ions/cm<sup>-2</sup>)</b>	<b>Absorbed dose (Jouies)</b>	<b>Absorption edge (nm)</b>	<b>Band-gap energy (eV)</b>
0	0	536.8	2.31
$9.3 \times 10^{11}$	3.6	546.6	2.27
$9.3 \times 10^{12}$	36.3	552.4	2.25
$1.53 \times 10^{13}$	59.8	557.7	2.23
$4.53 \times 10^{13}$	177.2	555.4	2.24
$9 \times 10^{13}$	352.0	557.8	2.23

**Table-2 Quantitative Value of X-Ray diffraction analysis for the virgin and one of the maximum irradiated Kapton –H polymer.**

Kapton (H) Virgin Sample					Kapton(H) Irradiated				
2 $\theta$	Intensity	d	width	I/I <sub>0</sub>	2 $\theta$	Intensity	d	width	I/I <sub>0</sub>
13.76	179	6.430	1.26	62	13.98	204	6.329	1.170	100
14.80	201	5.981	1.05	69	15.04	185	5.885	0.870	90
25.66	289	3.469	1.26	100	26.08	129	3.413	0.870	63

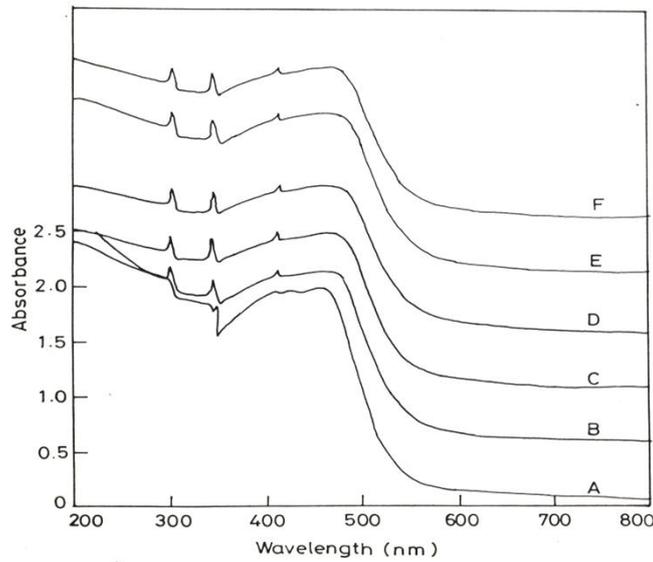


Fig-1 The Optical absorption spectra of polyimides (Kapton-H) irradiated with 60 MeV  $^{12}\text{C}^{+5}$  ion beam: (A) virgin, (B)  $9.3 \times 10^{11}$ , (C)  $9.3 \times 10^{12}$ , (D)  $1.51 \times 10^{13}$ , (E)  $4.53 \times 10^{13}$ , (F)  $9 \times 10^{13}$  ions  $\text{cm}^{-2}$ .

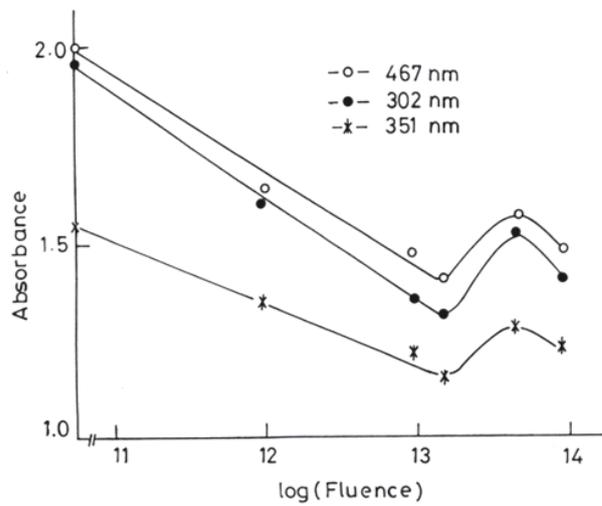


Fig-2 The variation of absorbance with fluence on a log-scale, at three different characteristic wavelengths, 302nm, 351nm, and 467 nm respectively.

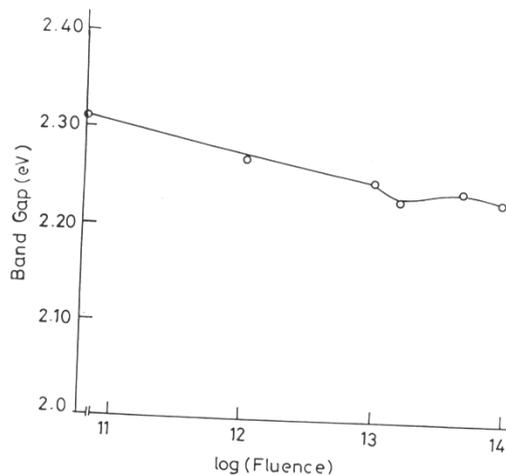


Fig 3- The variation in band gap energy with irradiation fluence on a log-scale

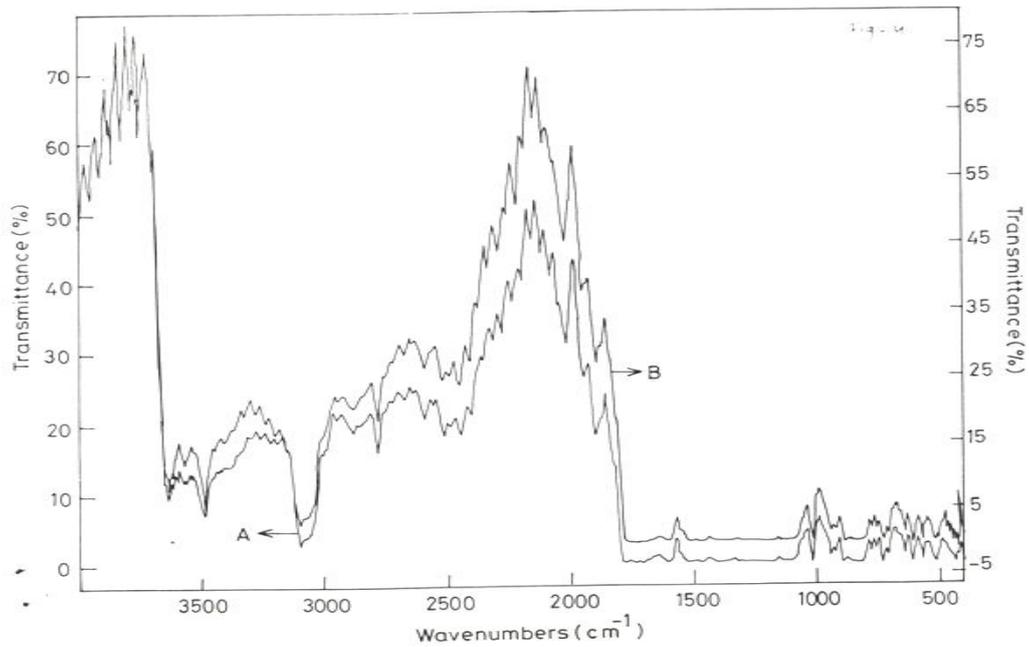


Fig 4- FTIR spectra of (A) virgin sample and (B) the irradiated sample at the fluence of  $9 \times 10^{13}$  ions cm<sup>-3</sup>.

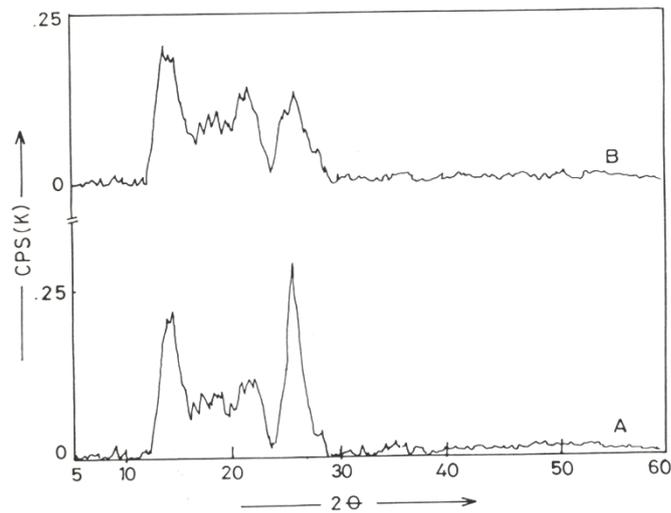


Fig-5 X-ray diffraction pattern of (A) virgin sample and, (B) irradiated once at the fluence of  $9 \times 10^{13}$  ions cm<sup>-2</sup>.