

Physical and chemical response of 70 MeV carbon ion irradiated Kapton-H polymer

H S VIRK*, P S CHANDI and A K SRIVASTAVA

Department of Physics, Guru Nanak Dev University, Amritsar 143 005, India

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Abstract. Physical and chemical responses of 70 MeV carbon ion irradiated Kapton-H polymer were studied by using UV-visible, FTIR and XRD techniques. The ion fluences ranging from 9.3×10^{11} – 9×10^{13} ions cm^{-2} were used. Recorded UV-visible spectra clearly showed a decrease in absorption initially with fluence, but for the higher fluences it showed a recovery characteristic. A decrease in band-gap energy of 0.07 eV was observed. The FTIR analysis indicated the high resistance to radiation induced degradation of polymer. The diffraction pattern of Kapton-H indicates that this polymer is semi-crystalline in its nature. In case of irradiated one, there was an average increase of crystallite size by 20%, but diffuse pattern indicates that there was a 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.

1. Introduction

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

Polyimides are used extensively in situations requiring high-performance plastic materials because of their unique combination of superior mechanical, electrical, chemical and thermal properties (Lee 1996). Kapton, a popular polyimide, is able to operate in the temperature range of as low as -269°C and as high as 400°C (Du Pont 1988). In particular the radiation resistance, and fire resistance, have made this polyimide one of the favourite choices for applications in wire and cable insulation, electrical component seal assemblies, in nuclear power plants, military aircraft and space shuttles (Thomas and Lindsay 1991; Young and Slempe 1993).

When a 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 smaller than the range of the projectile ion, then the energy deposition is mainly due to the 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), defects (unsaturations, scissions, crosslinks) and heat (Chailley *et al* 1995).

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 (Picq *et al* 1998). These radicals are responsible for most of the chemical transformations observed in the polymer films. The very high value of energy transferred induces an unusual density of electron-hole pairs close to the ion path and consequently the polymer modifications differ from those observed with low ionizing projectiles (Balanzat *et al* 1995, 1996; Steckenreiter *et al* 1997).

Analysis of the structure of polymers has been a problem of continuing interest for over four decades. Even to this day, the concept that has recently gained wide recognition is that the main physical properties of polymers depend not only on the chemical structure but also on the supermolecular organization (Perepechko 1981).

This paper reports on the investigation of physical and chemical response of 70 MeV carbon ion bombarded polyimide (Kapton-H) polymer, with special reference to properties like optical, chemical and structural. In order to study the effect of the 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.

2. Experimental

The self-supporting polyimide (Kapton-H) commercial specimen in the form of a flat polished film of thickness

*Author for correspondence

75 μm was obtained from Du Pont (UK). The samples of size ($1 \times 1 \text{ cm}^2$) were prepared for irradiation. They were used in as received condition without any further treatment. The irradiations were performed on five identical samples. Polymer samples were mounted on a vacuum-shielded vertical sliding ladder and irradiated in the general purpose scattering chamber under high vacuum of the order of 4×10^{-6} Torr by using the 70 MeV $^{12}\text{C}^{+5}$ ion beam with a beam current of 4 particle nano Ampere, available from the 15 UD Pelletron accelerator at the Nuclear Science Centre, New Delhi (Mehta and Patro 1988; Kanjilal *et al* 1993). 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 9.3×10^{11} – 9×10^{13} ions cm^{-2} . In order to expose the whole target area, the beam was scanned in the x - y plane. The range of the incident ion, as estimated by SRIM (Ziegler 1997), was more than the thickness of the polymer film. The ion beam energy and the thickness of the target were so chosen that only the modification due to electronic energy loss affected the exposed sample.

The nature of the ion beam induced changes has been analysed by using the UV-visible spectrophotometer (UV-160-Shimadzu) in the range 200–800 nm. The Fourier transform infrared (FTIR) spectroscopy was performed in the absorption mode using Nicolet–Avatar 320 FT-IR in the range 4000 – 400 cm^{-1} . The preliminary structural studies were carried out by a X-ray powder diffractometer (Rigaku D Max IIC) with CuK_α radiation (1.5418 \AA for a wide range of Bragg angles 2θ ($5^\circ \leq 2\theta \leq 60^\circ$)) at the scanning rate of $5^\circ/\text{min}$. All the physical and chemical measurements were carried out at room temperature of 24 – 26°C .

3. Results and discussion

All our experiments can be divided into three types of measurements: UV-visible spectrophotometry, FT-IR spectroscopy and X-ray diffraction of the virgin and irradiated samples. The projected range of 70 MeV $^{12}\text{C}^{+5}$ ion beam in polyimide (Kapton) was calculated to be around $133 \mu\text{m}$, using SRIM code (Ziegler 1997), 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. Collisional processes produce lattice vibration and displacement of the target atoms. Displacement damage is usually considered to be the most important cause of material modification in solids; however, in polymers, ionization processes are also highly important (Du Pont 1988). The SRIM calculation (Ziegler 1997) indicates that 99.95% of energy lost by 70 MeV $^{12}\text{C}^{+5}$ ion in $75 \mu\text{m}$ thick polyimide is electronic in nature. The electronic stopping power of

the beam, $(dE/dx)_e$, is 32.62 eV/\AA . The irradiation doses deposited in the Kapton-H at five different fluences, 9.3×10^{11} , 9.3×10^{12} , 1.53×10^{13} , 4.53×10^{13} and 9×10^{13} ions cm^{-2} are 3.6, 36.3, 59.8, 177.2 and 352.0 Joules, respectively.

3.1 Optical response

Ultraviolet-visible spectroscopy, which gives us an idea about the value of optical band-gap energy (E_g), 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 s , π and n -orbitals from the ground state to higher energy states which are described by molecular orbitals (Dyer 1994). The electronic transitions (\rightarrow) that are involved in the ultraviolet and visible regions are of the following types $s \rightarrow s^*$, $n \rightarrow s^*$, $n \rightarrow p^*$, and $p \rightarrow p^*$. 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 colour centres (Srivastava and Virk 2000). Ion beam interaction with polymers generates damage which leads to the formation of new defects and new charge states.

The results of optical absorption studies with UV-visible spectrophotometer carried out on virgin and irradiated samples are illustrated in figure 1. For the sake of comparison between the virgin and irradiated samples, the

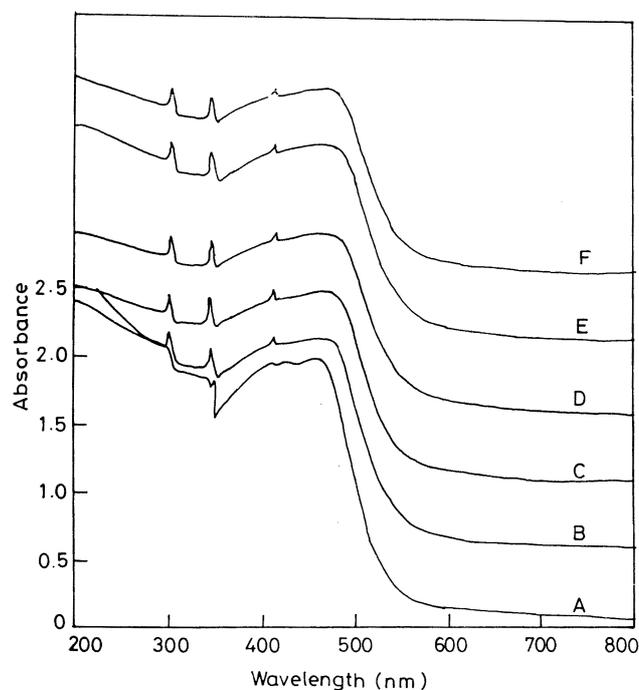


Figure 1. The optical absorption spectra of polyimide (Kapton-H) irradiated with a 70 MeV $^{12}\text{C}^{+5}$ ion beam: (A) virgin, (B) 9.3×10^{11} , (C) 9.3×10^{12} , (D) 1.53×10^{13} , (E) 4.53×10^{13} and (F) 9×10^{13} ions cm^{-2} .

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

Irradiation fluence (ions/cm ²)	Absorbed dose (Joules)	Absorption edge (I_g) (nm)	Band-gap energy (eV)
0	0	536.8	2.31
9.30×10^{11}	3.6	546.6	2.27
9.30×10^{12}	36.3	552.4	2.25
1.53×10^{13}	59.8	557.7	2.23
4.53×10^{13}	177.2	555.4	2.24
9.00×10^{13}	352.0	557.8	2.23

actual spectra for high fluences (figure 1, D–F) are shifted along y-axis by regular displacement. The optical absorption spectra of the irradiated samples in figure 1(B–F) show three characteristic peaks at around 302 nm, 351 nm and 419 nm, respectively. The three characteristic absorption peaks may be correlated with the electronic transition occurring in imide group (NC = O). It is well known that the compounds with oxygen and nitrogen, containing non-bonding electrons, are capable of showing these types of characteristic absorptions (Virk *et al* 2001).

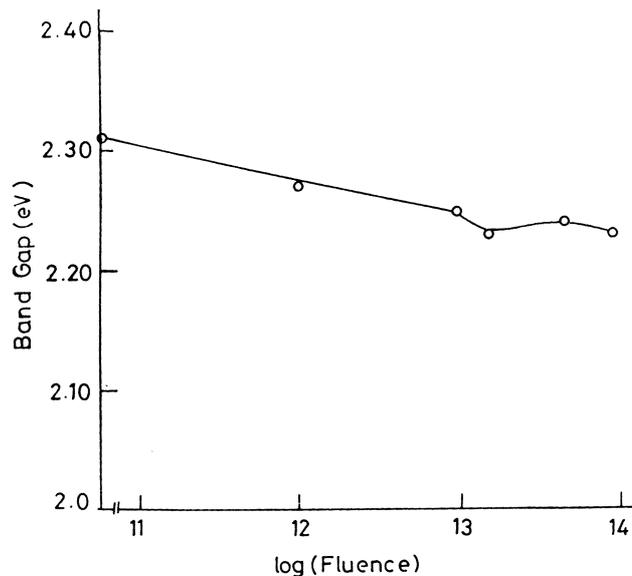
The spectrum of the virgin sample (figure 1A) differs appreciably from the spectra of the irradiated samples as the first peak at 302 nm and the third peak at 419 nm are absent and only the second peak at 351 nm exists in the form of a dip. The absorbance of virgin sample is maximum at 200 nm and decreases sharply after 470 nm. For irradiated samples, absorbance decreases at low fluences around 200 nm but shows recovery and enhancement for high fluences. Between 300 and 800 nm, the absorbance increases successively with fluence for irradiated samples.

Figure 1 also shows that the absorption decreases very sharply and comes to the minimum absorption defined by absorption-edge (I_g). The values of I_g for virgin and irradiated samples are estimated to be 536.8, 546.6, 552.4, 557.7, 555.4 and 557.8 nm, respectively. The optical band gap energy for the virgin as well as irradiated samples has been calculated from the respective values of I_g using the formula, $E_g = hc/I_g$, where h is Planck constant. A shift in the absorption edge (I_g) towards higher wave length by 21 nm indicates the decrease in band gap energy of the irradiated polymer sample. The quantitative value of the irradiation dose (estimated by SRIM-97) deposited in Kapton-H at five different fluences and the band gap energy for the virgin and irradiated samples are given in table 1.

Figure 2 shows the variation in band gap energy 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 fluences, it shows a slight recovery characteristic which may be due to cross-linking of the polymeric chains.

3.2 Chemical response (FTIR spectroscopy)

The nature of chemical bonds of polymers can be studied through the characterization of the vibration modes

**Figure 2.** The variation in band gap energy with irradiation fluence.

determined by infrared spectroscopy (Davenas *et al* 1989). Figure 3 (A, B) shows the FTIR spectra of the virgin (A), and one of the irradiated samples (B) at the fluence of 9×10^{13} ions cm⁻². There is only a slight change in the intensity of the irradiated sample as compared to the virgin sample. This is due to high resistance of the polyimide sample to ionic radiation. The presence of ladder structure is responsible for such a high resistance. The minor changes in the peaks of irradiated sample may be due to the breakage of one or two bonds in the ladder structure, but this will not change the overall structure of the polymer. From these observations, it may be concluded that the polyimide (Kapton-H) is highly resistant to radiation degradation.

3.3 Structural response

Figure 4 (A, B) represents the diffraction pattern of the virgin and one of the irradiated Kapton polymer at the highest fluence of 9×10^{13} ions cm⁻². The diffraction pattern of virgin polymer clearly indicates that this

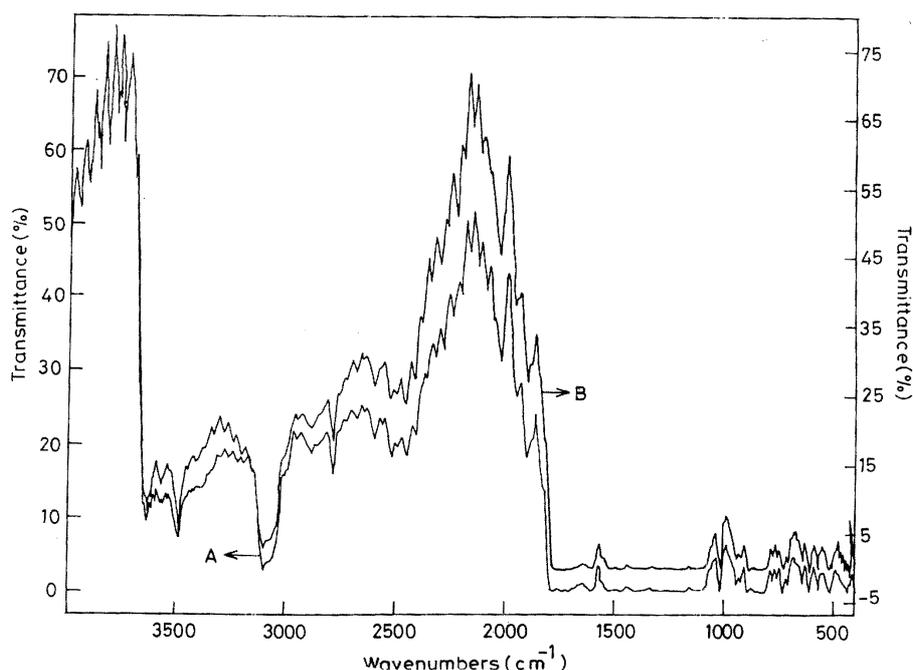


Figure 3. FTIR spectra of (A) virgin sample and (B) irradiated sample at the fluence of 9×10^{13} ions cm^{-2} .

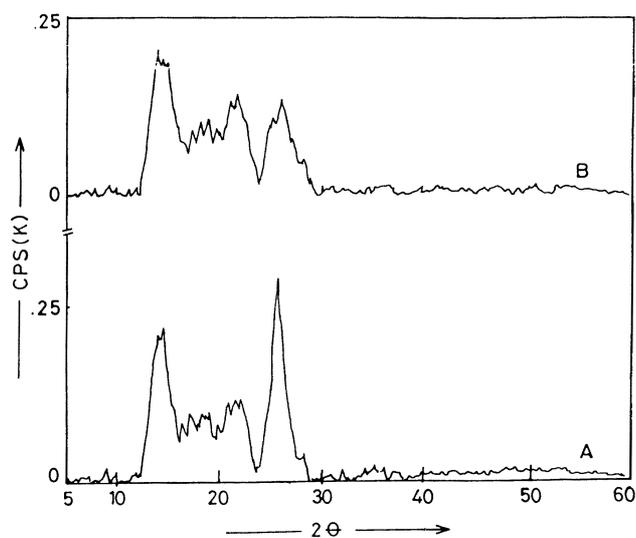


Figure 4. X-ray diffraction pattern of (A) virgin sample and (B) irradiated one at the fluence of 9×10^{13} ions cm^{-2} .

polymer is semi-crystalline in nature. The X-ray diffraction data of the virgin sample (table 2) show three peaks at $2q = 13.76^\circ$, 14.80° and 25.66° with lattice spacing $d = 6.430 \text{ \AA}$, 5.980 \AA and 3.460 \AA and the corresponding full widths at half maxima (FWHM) are 1.26° , 1.05° and 1.26° , respectively. The diffraction pattern of virgin sample shows partial crystallinity and the most intense peak at $2q = 25.66^\circ$. However, in case of irradiated one, a significant change in the diffraction pattern has been observed (table 3). The X-ray diffraction data show six peaks

Table 2. X-ray diffraction analysis of the virgin Kapton-H polymer.

Sl. no.	$2q$	Intensity	d (\AA)	Width	I/I_0
1.	13.76	178	6.430	1.26	61
2.	14.80	201	5.980	1.05	69
3.	25.66	289	3.468	1.26	100

Table 3. X-ray diffraction analysis of the irradiated Kapton-H polymer at a fluence of 9×10^{13} ions cm^{-2} .

Sl. no.	$2q$	Intensity	d (\AA)	Width	I/I_0
1.	13.98	204	6.329	1.170	99
2.	15.04	185	5.885	0.870	90
3.	21.02	133	4.222	0.690	65
4.	21.74	145	4.084	0.720	71
5.	25.10	111	3.545	0.750	54
6.	26.08	129	3.413	0.870	63

instead of three recorded in the virgin sample, with the most intense peak at $2q = 13.98^\circ$. The diffraction patterns of virgin and irradiated ones are quite different and the three original peaks are found at slightly higher angular positions at $2q = 13.98^\circ$, 15.04° and 26.08° with $d = 6.329 \text{ \AA}$, 5.885 \AA and 3.413 \AA respectively. It is evident that the diffraction pattern of the irradiated Kapton is more broader (diffused) than the virgin one, which indicates a decrease in crystallinity.

Table 4. Crystallite size of virgin and irradiated Kapton-H polymer.

Kapton-H virgin sample				Kapton-H irradiated sample			
$2q$	$\text{Cos}q$	Width, b (radians)	Crystallite size, L (Å)	$2q$	$\text{Cos}q$	Width, b (radians)	Crystallite size, L (Å)
13.76	0.9928	0.022	70.5	13.98	0.9925	0.020	77.6
14.80	0.9917	0.018	86.3	15.04	0.9914	0.015	103.5
25.66	0.9750	0.022	71.8	26.08	0.9742	0.015	105.3

The concept of crystallinity in the case of polymers is quite different than that of other solids (Srivastava and Virk 1999). However, the decrease in intensity and the shift in angular position towards the higher angle can be explained by a decrease in lattice spacing (Guzman *et al* 1985). The broadening of peaks suggests an evolution of the polymer toward a more disordered state and also a change in crystallite size on irradiation by carbon beam.

The crystallite sizes of the virgin and irradiated Kapton-H polymer have been calculated using Scherrer's (1918) equation:

$$b = KI/L \cos q, \quad (1)$$

where b is full width at half maxima (FWHM) in radians, λ the wavelength of X-ray beam (1.5418 Å), L the crystallite size in Å and K a constant which varies from 0.89 to 1.39, but for most cases it is close to 1 (Azaroff 1968). Assuming $K = 1$ in (1), the crystallite sizes corresponding to three peaks of the virgin and irradiated polymer are calculated and given in table 4. In the case of virgin sample, the average crystallite size is estimated to be 76.2 Å. But in the case of irradiated one, the average value is found to be 95.5 Å indicating an average increase in crystallite size of the order of 20% due to heavy ion irradiation. However, particularly in case of solid polymeric materials, the exact nature of the interrelation between spacing, crystallite size and the degree of disorder is yet to be understood in proper perspective.

4. Conclusions

UV-vis spectroscopic analysis of irradiated Kapton-H polymer reveals a change in optical density of polymer and creation of defects, which may be due to both degradation and cross-linking of polymer chains simultaneously. FTIR analysis reveals that ring or ladder-structured polymers 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. Kapton-H has a partial crystallinity as evidenced by X-ray

diffraction pattern. Heavy ion irradiation induces an average increase of 20% in crystallite size.

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