Modification of Optical Bandgap and Formation of Carbonaceous Clusters Due to 1.75 MeV N\textsuperscript{5+} Ion Irradiation in PET Polymers and Search for Chemical Reaction Mechanisms

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Abstract: The effects of 1.75 MeV N\textsuperscript{5+} ion beams of varying fluences, ranging from 1\times10\textsuperscript{11} to 5\times10\textsuperscript{14} ions/cm\textsuperscript{2} on structural, optical, and chemical properties of polyethylene terephthalate (PET) polymer, have been investigated by x-ray diffraction (XRD), UV–Visible spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. The XRD patterns of PET samples show that the crystallinity increases with ion irradiation of fluences 4\times10\textsuperscript{11} and 5\times10\textsuperscript{12} ions/cm\textsuperscript{2}. Optical bandgap energy decreases more at the ion fluences of 5\times10\textsuperscript{14} ions/cm\textsuperscript{2}. Absorption maxima shifted towards a higher wavelength value due to the formation of extended conjugation. Acetylenic (-C≡C-) group formation and free CO\textsubscript{2} group are confirmed by FTIR spectroscopy. The reaction mechanism of the degradation product formation chemistry is discussed.

Keywords: FTIR; UV-Vis spectroscopy; PET; XRD; polymer; ion beam; reaction mechanism; radiation chemistry.

1. Introduction

Polyethylene terephthalate (PET) is an essential polymer with a high melting point, good mechanical properties, and resistance to moisture and heat. Its crystallinity can vary from amorphous to moderately high. Application of PET in optoelectronics, thin-film processing, polymer membranes, cable insulation, textile, space technology, and nuclear engineering attracted more global attention [1–14]. This polymer is suitable for medical applications [15–21] due to its high biocompatibility, low toxicity, and a range of beneficial mechanical properties[22, 23]. Polymer membranes or thin polymer films with discrete pores, formed by a bombardment of heavy ions and chemical etching [24, 25], have applications in creating different microfluid diodes and biosensors [26, 27].

A significant modification in the few properties of a polymer material by using a chosen ion beam irradiation in a controlled way is an egregious tool. Irradiation can create a chemical
and structural change in polymer materials with specific and desirable optical properties. For this, a theoretical understanding of the fundamental processes behind such ion beam interaction with polymers is required. The damage resulting from the ion irradiation of polymer is complex [4,25]. It brings irreversible chemical and physical modifications into play that strongly influence the macroscopic properties of the material. In particular, the ionizing radiations induce active chemical species (like anions, cations, electrons, and free radicals) by ionization and excitation mechanism. These chemical “species” interactions lead to three main processes: cross-linking, chain scission, and oxidation [28].

There are numerous published papers on ion radiation damage of polymers [29–39]. However, the reaction mechanism of the product formation, to be discussed here, has seldom been covered. Some of the recent works in PET are reported here. Silver doped PET containers can reduce the growth of E.Coli bacteria and be useful for beverage applications [40, 41]. Exposure to 100 keV N⁵⁺ irradiation on PET membrane affects the intensities of typical bands and a decrease in bandgap energy [24]. The reduction of optical bandgap energy under UV-irradiation is associated with the augmented conjugation in the PET polymer samples, resulting from the formation of many ion pairs and the breakage of the covalent bonds [42]. Gamma and ion beam irradiation up to 10 kGy doses have no significant effect on the migration level of polymer additives and radiolysis products [43]. The induced crystallization in the PET polymer under irradiation is due to the transfer of stresses from the amorphous region to the crystalline regions [44]. PET flexible film with high gas barrier performance with heat resistance properties was developed [45]. The optimization of ion-track membrane formation in PET and the correlation between their parameters and processing modes was studied by [46]. The damage mechanism of PET is not yet well understood. An energetic charged projectile (here N⁵⁺) impinging on the target (here PET sheet) is quickly stripped of some of its electrons. It modifies its charge state by further interaction with the target solid. It is convenient to divide the energy loss of a fast ion into two parts, one due to Electronic Stopping (Sₐ) and the other due to Nuclear Stopping (Sₙ). Nuclear Stopping, prominent toward the end region of the ion range, involves energy loss to the atomic cores or nuclei of the solid. The relative contribution of Se and Sn depends on the projectile mass, velocity, charge state, and on the target itself [47]. The range (projected range) of 1.75 MeV N⁵⁺ has thus been calculated by the SRIM program to be ~2.85 µm, small compared to our sample thickness of 1mm. Electronic energy loss (Sₐ = 7.102×10⁰⁰) predominates over nuclear energy loss (Sₙ= 4.601×10⁻⁰²) in the higher ion energy region, which means that most of the ion is within the initial range of energy is used to excite and ionize target atoms. The resulting signatures show up in spectroscopic results. The energy transfer through Sn can repel the target atoms from their lattice positions to generate stable vacancy clusters towards the end of the range.

Here, we have measured physical and chemical changes in the PET polymer sheet produced by the N⁵⁺ ion beam. The damages have been estimated with the help of a UV-visible spectrophotometer, Fourier Transform Infrared (FTIR) Spectrometer, and X-rays diffractometer. The bandgap energy (Eₐ) or Highest occupied molecular orbital (HOMO)-Lowest unoccupied molecular orbital (LUMO) gap energy for different ion fluences has been derived from observed optical absorption spectra.
2. Materials and Methods

1mm thick sheet of the thermoplastic polymer polyethylene terephthalate (PET) has been procured from Goodfellow Cambridge Limited. Samples of size (1 cm × 1 cm) have been used in original form without any intervention for the present study. The chemical structure of PET polymer is shown in Figure 1.

![Chemical structure of PET polymer](https://biointerfaceresearch.com/)

**Figure 1.** Chemical structure of PET polymer.

2.1. Ion-irradiation.

The PET samples have been mounted on a vertical vacuum-shielded sliding ladder and irradiated with a 1.75 MeV N\(^{5+}\) ion beam at the Low Energy Ion Beam (LEIB) Facility, Inter-University Accelerator Centre (IUAC), New Delhi. The ion beam fluence was measured by integrating the ion charge on the sample ladder. The ladder has been insulated from the rest part of the irradiation chamber. In order to expose the whole target area uniformly, the beam was scanned in x and y directions.

2.2.1. X-ray diffraction.

The XRD measurements have been done with PROTO, AXRD Benchtop Powder Diffraction system using monochromatic CuK\(\alpha\) (\(\lambda=1.541\) Å) line over 2\(\theta\) =10º to 75º. For XRD, each sample has been mounted on the spinning sample-holder, using clay to maintain the height of the polymer sheet tightly. The instrument software-generated XRD profiles from measured XRD data points for virgin or unirradiated and different irradiated samples are shown in Figure 2.

![X-ray diffraction patterns](https://biointerfaceresearch.com/)

**Figure 2.** X-ray diffraction patterns of virgin PET samples and samples irradiated by 1.75 MeV N\(^{5+}\) ions to different ion fluences.
2.2.2. UV-visible spectrometry.

UV–Visible spectrophotometer (Lamda 360, India) has been used in absorption mode with a bandwidth of 0.5 nm, in the range of wavelength 200–1100 nm at room temperature. UV-visible absorption spectra originate from electronic transition within a molecule. The absorption of radiation energy involves the promotion of an electron from the lower energy (ground state) to the higher energy state (excited state) called electronic excitation, and it is quantized [48]. Chromophores are covalently unsaturated molecular groups responsible for the color development of the molecule. These may be C=C, C≡C, C=O, C≡N, C=N-, NO2, etc. If the compound absorbs radiation in the visible region (380–750 nm), it appears colored [49]. UV-Visible absorption spectra of virgin and differently N5+ irradiated PET samples are shown in Figure 3.

![UV-Visible absorption spectra of virgin and 1.75 MeV N5+ irradiated PET polymer for different ion fluences.](https://doi.org/10.33263/BRIAC131.035)

Figure 3. UV-Visible absorption spectra of virgin and 1.75 MeV N5+ irradiated PET polymer for different ion fluences.

2.2.3. Fourier transforms infrared (FTIR) spectroscopy.

FTIR spectroscopy is a versatile tool for studying molecular bonding, structure, and functional group analysis. The band peaks in FTIR spectra give dual information, (i) the functional group existing in the IR-active region and any shift in the band peak position in a spectrum is directly related to a change in bond strength or bond angle, and (ii) variation in the intensity of particular band peak in a spectrum correlates to the changes in the proportion of that functional group. FTIR spectra of virgin and different ion fluence irradiated samples were recorded by Bruker-Alpha spectrometer in the wavenumber range 600 to 4000 cm⁻¹. Figure 4 illustrates the FTIR spectra.
3. Results and Discussion

3.1. XRD.

Inter planar spacing (d) has been calculated from the XRD scattering angle, 2θ, using the equation: 
\[ d = \frac{\lambda}{2 \sin \theta} \]
where \( \lambda \) is the wavelength and 2θ is the diffraction angle. The full-width at half maximum (FWHM = β) of a diffraction peak has been calculated. Crystallite size (L) was estimated using the Scherrer equation: 
\[ L = \frac{K \lambda}{\beta \cos \theta} \]
where K, the Scherrer constant, depends on lattice direction and crystallite morphology.

Table 1. Total Crystallinity value (in %) of 1.75 MeV N\(^{5+}\) ion irradiated and virgin PET polymers.

| Sample No. | Ion Fluences (ions/cm\(^2\)) | Current (nA) | Crystallinity (%) | Amorphous (%) |
|------------|-------------------------------|--------------|-------------------|---------------|
| Unirradiated | 0                             | 0            | 48.39             | 51.61         |
| PET1       | 1×10\(^{11}\) ions/cm\(^2\) | 5            | 49.36             | 50.64         |
| PET2       | 4×10\(^{11}\) ions/cm\(^2\) | 5            | 55.80             | 44.20         |
| PET3       | 7×10\(^{11}\) ions/cm\(^2\) | 5            | 51.83             | 48.17         |
| PET4       | 10×10\(^{11}\) ions/cm\(^2\) | 5            | 51.85             | 48.15         |
| PET5       | 10×10\(^{11}\) ions/cm\(^2\) | 20           | 47.11             | 52.89         |
| PET6       | 5×10\(^{12}\) ions/cm\(^2\) | 20           | 55.12             | 44.88         |
| PET7       | 10×10\(^{12}\) ions/cm\(^2\) | 20           | 51.80             | 48.20         |
| PET8       | 5×10\(^{13}\) ions/cm\(^2\) | 20           | 53.38             | 46.62         |
| PET9       | 10×10\(^{13}\) ions/cm\(^2\) | 20           | 49.12             | 50.88         |
| PET10      | 5×10\(^{14}\) ions/cm\(^2\) | 20           | 50.11             | 49.89         |
| PET11      | 3×10\(^{14}\) ions/cm\(^2\) | 20           | 48.41             | 51.59         |

It is seen from Table 1, a significant increase in the crystallinity of the irradiated polymer. The increase in crystallinity is more pronounced for ion fluences 4×10\(^{11}\) and 5×10\(^{12}\) relating to the virgin polymer. This enhancement in crystallinity seems to be due to the generation and rearrangements of vacancy clusters, ion-track membranes, and free radicals upon irradiation in the amorphous region. The rearranged amorphous region is converted into a crystalline zone through stress transfer by the covalent bond acting in the polymer backbone.

Figure 4. FTIR spectra of virgin and 1.75 MeV N\(^{5+}\) ions/cm\(^2\) irradiated PET polymer for different ion fluences.
There is a report [44] that the amorphous region of PET polymer under stress changes into the crystalline zone.

![Graph](image)

**Figure 5.** Variation of crystallinity for various ion fluences exposure of PET sample.

### 3.2. UV-Vis spectroscopy.

Figure 3 clearly shows that the absorption maxima shifted from lower towards a higher wavelength (bathochromic shift) with the increasing ion fluences.

![Camera photo view](image)

**Figure 6.** Camera photo view of different ion fluences irradiated PET polymer.

| Sample No. | Ion Fluences (ions/cm²) | Current (nA) | \( \lambda_{\text{max}} \) (nm) | Absorption value at a particular wavelength |
|------------|-------------------------|--------------|----------------------------------|---------------------------------|
|            |                         |              | 340 nm                          | 373 nm | 431 nm | 527 nm | 585 nm | 627 nm | 768 nm |
| Unirrad.   | 0                       | 0            | 343                             | 0.3102 | 0.1279 | 0.0981 | 0.0946 | 0.0973 | 0.1025 | 0.1007 |
| PET1       | 1×10¹¹                  | 5            | 376                             | 0.4216 | 0.2099 | 0.1581 | 0.1425 | 0.144  | 0.1481 | 0.1429 |
| PET2       | 4×10¹¹                  | 5            | 344                             | 0.3888 | 0.1819 | 0.1222 | 0.1061 | 0.106  | 0.11   | 0.1064 |
| PET3       | 7×10¹¹                  | 5            | 346                             | 0.4579 | 0.2384 | 0.1837 | 0.177  | 0.1847 | 0.1941 | 0.2019 |
| PET4       | 10×10¹¹                 | 5            | 348                             | 0.5041 | 0.2626 | 0.1848 | 0.1574 | 0.1582 | 0.1619 | 0.1556 |
| PET5       | 10×10¹²                 | 20           | 376                             | 0.9754 | 0.6402 | 0.4977 | 0.4432 | 0.4426 | 0.4355 | 0.4222 |
| PET6       | 5×10¹²                  | 20           | 376                             | 0.9754 | 0.6402 | 0.4977 | 0.4432 | 0.4426 | 0.4355 | 0.4222 |
| PET7       | 10×10¹²                 | 20           | 431                             | 2.6021 | 2.2061 | 1.728  | 1.3483 | 1.2641 | 1.1856 | 1.0606 |
| PET8       | 5×10¹³                  | 20           | 482                             | 3.0946 | 2.262  | 1.1207 | 0.3696 | 0.2333 | 0.1867 | 0.1304 |
| PET9       | 10×10¹³                 | 20           | 527                             | 3.3333 | 2.9588 | 1.754  | 0.606  | 0.3595 | 0.2626 | 0.1415 |
| PET11      | 3×10¹⁴                  | 20           | 627                             | 2.8954 | 3.3634 | 3.4663 | 1.6749 | 1.0724 | 0.7813 | 0.3601 |
| PET10      | 5×10¹⁴                  | 20           | 768                             | 3.1192 | 3.5599 | 4.5084 | 3.5435 | 2.6467 | 2.0183 | 0.9934 |
This shift in absorption may be due to the creation of free radicals, ions, and hot molecules by ion irradiation. The color of PET polymer after ion irradiation has been changed. It is transparent for the virgin sheet. The color changes from colorless to cream (shown in Figure 6) at $\sim 10^{11}$ ions/cm$^2$, yellowish at $\sim 10^{12}$ ions/cm$^2$, and goes to dark brown irradiated above $\sim 3\times10^{14}$ ions/cm$^2$. This change in color of irradiated films can be co-related to spectra (Figure 3). The absorption maxima of irradiated films get shifted towards the higher wavelength or redshift from the pristine one. The absorbance value at a particular wavelength for different ion fluences is shown in Table 2, which shows that for higher fluence ($5\times10^{14}$ ions/cm$^2$), the absorbance peak is more pronounced than the lower one ($1\times10^{11}$ ions/cm$^2$). The shift in absorption maxima towards a higher wavelength (redshift) is shown in Figure 7.

**Optical bandgap energy:** The optical bandgap energy has been calculated using Tauc’s equation: $\alpha h\nu = \beta (h\nu - E_g)^n$, where $\alpha$ is the optical absorption coefficient, $E_g$ is the bandgap energy, $h\nu$ is the photon energy. $\beta$ is the band tailing parameter, depending on the electron-hole mobility. The constant $n$ has different values for different transitions, direct allowed transition ($n = 1/2$ and $3/2$), and indirect allowed and forbidden transitions ($n = 2$ and $3$), respectively.

**The number of carbon atoms (N):** The number of carbon atoms (N) per conjugation length in a cluster is correlated with the optical bandgap ($E_g$). The number of carbon atoms per each conjugated length (N) was calculated by modified Tauc’s equation [50]: $N = (2\beta)/E_g$, where $2\beta$ is the band structure energy of a pair of adjacent $\pi$ sites. Here, $\beta \approx 2.9$ eV is associated with $\pi \rightarrow \pi^*$ optical transitions in -C=C- structure [51].

The shift in absorption maxima from pristine towards a higher wavelength is attributed to forming a conjugated system of carbon bonds due to bond breaking and reconstruction by irradiation or the possible development of carbon clusters [28,52,53]. XRD result supports the rearrangement in the molecule due to enhancement in the crystallinity.
Table 3. Bandgap ($E_g$) calculation for different ion fluences irradiated PET polymer. Analysis of $E_g$ and $N$ of PET samples assuming ($n = 2$ and $1/2$). $N$ = number of C-atoms per conjugation length has been explained already in the text.

| Dose (ions/cm$^2$) | Bandgap Energy ($E_g$ in eV); $n = 2$ | $N=2\pi\beta/E_g$ | Bandgap Energy ($E_g$ in eV); $n = 1/2$ | $N=2\pi\beta/E_g$ |
|--------------------|--------------------------------------|-------------------|----------------------------------------|-------------------|
| $0 \times 10^{11}$ | 3.629                                | $\sim 5$          | 3.825                                  | $\sim 5$          |
| $1 \times 10^{11}$ | 3.629                                | $\sim 5$          | 3.818                                  | $\sim 5$          |
| $4 \times 10^{11}$ | 3.635                                | $\sim 5$          | 3.813                                  | $\sim 5$          |
| $7 \times 10^{11}$ | 3.629                                | $\sim 5$          | 3.813                                  | $\sim 5$          |
| $1 \times 10^{12}$ | 3.603                                | $\sim 5$          | 3.766                                  | $\sim 5$          |
| $5 \times 10^{12}$ | 3.501                                | $\sim 5$          | 3.338                                  | $\sim 5$          |
| $5 \times 10^{13}$ | 1.918                                | $\sim 10$         | 2.997                                  | $\sim 6$          |
| $1 \times 10^{14}$ | 1.853                                | $\sim 10$         | 2.764                                  | $\sim 7$          |
| $3 \times 10^{14}$ | 1.461                                | $\sim 12$         | 2.369                                  | $\sim 8$          |
| $5 \times 10^{14}$ | 1.086                                | $\sim 17$         | 1.956                                  | $\sim 9$          |

Figure 8. Variation of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ graph of PET polymer irradiated by 1.75 MeV N$^+$ ions in different doses.

Figure 9. Variation of $(\alpha h\nu)^2$ vs. $h\nu$ graph of PET polymer irradiated by 1.75 MeV N$^+$ ions in different doses.
Bandgap measurement is shown in Table 3, and variation of \((ahv)^{0.5}\) vs \(hν\) is shown in Figure 8, and interpretation of \((ahv)^2\) vs \(hν\) is shown in Figure 9, and bandgap \((E_g)\) dependency concerning different ions irradiation is shown in Figure 10. The decrease in bandgap energy and increase in the number of C-atoms per conjugation length (N) favors the formation of unsaturation centers [54]. The change in the bandgap is more in the case of ion fluences \(5x10^{14}\) compared to the pristine polymer. This seems to be due to rich centers of electron density as created by ion irradiation. There is a report of the deep trap of ion or electrets in irradiated PET polymer suitable for electrical application [25,55,56].

![Figure 10. Bandgap \((E_g)\) change of PET sample versus \(N^5+\) ion irradiation to different fluences.](https://biointerfaceresearch.com/)

### 3.3. FTIR spectroscopy.

The FTIR spectra of the 1.75 MeV \(N^5+\) ions/cm\(^2\) irradiated PET polymer with different ion fluences ranging from \(1x10^{11}\) to \(5x10^{14}\) ions/cm\(^2\) in Figure 4. The result shown in Table 4 shows the decrease in the intensity of the absorption in the range of the wavenumbers 600–1760 cm\(^{-1}\) and increase in the 1768–4000 cm\(^{-1}\) The development of broad-spectrum in the 2904–3639 cm\(^{-1}\) is more pronounced. The peak range 1012–630 cm\(^{-1}\) represents wagging vibrations for aliphatic, alkene, aromatic, and alkyne C-H groups [4]. The shift in the peak towards a higher wavenumber with broadening suggests that after irradiation, the environment of the carbonyl group attached to the para position of the phenyl group is changed. The shift in peak from 1715 cm\(^{-1}\) to a lower value of 1697 cm\(^{-1}\) suggests that the carbonyl group is in a higher density zone. This is due to the formation of the acetylene (unsaturated) group extending conjugation; as a result, the shift in peaks towards a lower value. This seems to be since the energy deposition damaged the PET polymer from the ion beam. This deposited energy is responsible for many processes, like oxidation, amorphization of the crystalline region, crosslinking in the adjacent radicals, and scission of the chains [25]. This increase in the intensity of the peaks at 2358cm\(^{-1}\) is due to the formation of the free CO\(_2\) molecule. This intensity increases with the addition of ion fluences. This seems to be due to the generation of a free CO\(_2\) group as suggested in the schematic reaction mechanism using the Norrish Type-1 reaction. The broad spectrum in the wavenumber range 2450–3690 cm\(^{-1}\) is due to the formation of
unsaturated alkynes (unsaturation or olefinic) group and oxidation of PET polymer with atmospheric oxygen under ion irradiation. The formation of C–H and O–H stretching vibration of deferent types of H-bonds and alkyne group (C≡C-) at (3294 cm\(^{-1}\)) in the region 3600–2500 cm\(^{-1}\) with the irradiation of Mo ions is reported [4]. The formation of the hydroxyl group (O-H) and extended conjugation is represented in the schematic reaction mechanism.

| Table 4. Assignment of peaks of FTIR spectra (cm\(^{-1}\)) of virgin and achieved by 5 nA & 20 nA beam currents of 1.75 MeV N\(^{5+}\) irradiated PET polymer for different ion fluences. |
|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Current (nA) | 5nA | 20nA |
| Zero | 1x10\(^{11}\) | 4x10\(^{11}\) | 7x10\(^{11}\) | 10x10\(^{11}\) | 1x10\(^{12}\) | 5x10\(^{12}\) | 1x10\(^{13}\) | 5x10\(^{13}\) | 1x10\(^{14}\) | 5x10\(^{14}\) | 3x10\(^{14}\) |
| 3750 | 3750 | 3750 | 3750 | 3751 | 3750 | 3747 | 3752 | 3750 | 3750 | 3753 |
| 3649 | 3649 | 3652 | 3645 | 3649 | 3647 | 3648 | 3646 | 3650 | 3649 | 3658 |
| 2960 | -- | -- | 2957 | -- | 2961 | 2961 | 2958 | -- | -- | -- |
| 2365 | 2350 | 2360 | 2365 | 2363 | 2365 | 2371 | 2366 | 2363 | 2363 | 2363 |
| 1951 | 1950 | 2321 | 2323 | 2321 | 2321 | 2321 | 2321 | 2321 | 2321 | 2321 |
| 1713 | 1713 | 1715 | 1714 | 1715 | 1715 | 1715 | 1715 | 1715 | 1716 | 1705 |
| -- | -- | -- | 1650 | 1650 | 1650 | 1649 | 1647 | 1648 | 1650 | 1697 |
| -- | -- | -- | 1635 | 1520 | 1635 | 1635 | 1636 | 1651 | 1541 | 1541 |
| 1408 | 1408 | -- | 1408 | -- | 1408 | 1408 | 1408 | 1408 | -- | 1456 |
| 1235 | 1234 | 1234 | 1234 | 1235 | 1236 | 1237 | 1234 | 1233 | |
| 1087 | 1085 | 1085 | 1085 | 1085 | 1087 | 1089 | 1089 | 1085 | 1085 |
| 1014 | 1014 | 1014 | 1014 | 1014 | 1014 | 1014 | 1014 | 1014 | 1014 |
| 871 | 871 | 871 | 871 | 871 | 871 | 871 | 871 | 871 | |
| 792 | 792 | 792 | 792 | 792 | 792 | 792 | 792 | 792 | |
| 721 | 721 | 721 | 721 | 721 | 721 | 722 | 722 | 722 |

The change in the environment of the carbonyl group is related to the reduction in bandgap energy (Table 3) after irradiation. Earlier researchers [25,40,55–57] reported that the decrease in bandgap energy with the increase of ions irradiation (depends on its energy & types of ions) dose, consequently the conductivity of PET polymer increases. This energy dissipation in the form of ion implantation leads to changes in the structure and composition of the PET sample. The formation of new peaks 2365 cm\(^{-1}\) confirms the generation of the free CO\(_2\) molecule; peak 1650 cm\(^{-1}\) endorses an unsaturated group in the irradiated polymer; 3649 cm\(^{-1}\) is due to the development of the hydroxyl group. The change in the peak from 1715 to 1706 cm\(^{-1}\) for the carbonyl (\(>\text{C}=\text{O}\)) group suggests the carboxylic group’s developed in the irradiated polymer. Since the ion beam treatment of PET samples with different ion fluences, free radical, ionic species, neutral atoms are generated [58]. The polarity and the surface property being changed [59] due to irradiated polymer interact with the atmospheric oxygen as a result –OH and COOH groups are formed. The schematic reaction mechanism equation (4) explains the hydroxyl and the carboxylic group formation.

3.4. Schematic reaction mechanism of product formation.

When any ionizing electromagnetic radiation interacts with a polymer, ionization and excitation phenomena can occur in the polymer. This absorption of energy can result in bond cleavages and the formation of non-saturated fragments called free radicals. Adolf Chapiro (1988) had shown that these free radicals are responsible for most of the chemical transformations detected in the polymers.
3.4.1. Generation of free radical, formation of alkene, alkyne, and carboxylic group using (Norrish Type-II) reaction.

The formation of the acetylene group is due to sudden bombardment. High energy deposition may remove hydrogen radicals and form acetylene linkage in the group, as depicted in the following reaction mechanism equation (1).

$$\text{PET} \xrightarrow{1.75 \text{ MeV } N^+ \text{ ion irradiation}} \text{Formation of alkene group}$$

$$\text{PET} \xrightarrow{\text{Norrish Type-II}} \text{Formation of alkyne group}$$

$$\text{PET} \xrightarrow{\text{Norrish Type-II}} \text{Formation of carboxylic group}$$

$$\text{PET} \xrightarrow{\text{Norrish Type-II}} \text{Carboxylic group formation and elimination of volatile molecule acetylene}$$

3.4.2. Formation of unsaturation center.

The formation of low molecular weight products acetylene group (HC≡CH) and H₂ gas evolution is due to sudden bombardment with high energy deposition, and this may remove
hydrogen radical from unsaturated alkene center to form an alkyne group as shown in equation (2) and (3). A diagram follows.

\[
\text{Alkene form} \xrightarrow{\text{(ion irradiation)}} \text{Alkyne form} + \text{H}_2
\]

Formation of unsaturation, hydroxyl group, free CO and with disappearance of carbonyl group

\[
\text{PET} \xrightarrow{\text{1.75 MeV N}^{5+} \text{ ion irradiation}}
\]

Formation of free CO
Formation of the acetylene group in the irradiated PET film is supported by the FTIR broad peak at 3294 cm$^{-1}$ as observed by Steckenreiter et al. 1997 [4] and shift in carbonyl broad peak towards lower value from 1714 to 1705 and 1697 cm$^{-1}$, supporting the electron density increase around the carbonyl group.

3.4.3. Loss of carbonyl functional group and formation of degradation (scission) products:

The schematic reaction mechanism equation (4) explains chain scission and generation of free carbon monoxide molecule, hydroxyl group formation, and carbonyl groups loss in irradiated PET polymer.

The enhanced polarity at the surface of the irradiated polymer [33] is due to the formation of the hydroxyl group (-OH) and carboxylic group (-COOH). This is in support of the result reported by [4,59]. The FTIR peak at 3649 cm$^{-1}$ supports the formation of the hydroxyl group, and the broad peak at 1715 cm$^{-1}$ supports the change in environment for the carbonyl (>C=O) group.

3.4.4. Formation of free CO and CO$_2$ molecules using (Norrish Type-I) reaction:

The free CO$_2$ and CO molecule formation are explained using the Norrish Type-I reaction mechanism in equation (5).

The formation of CO molecules appearing at FTIR peak 2169 cm$^{-1}$ is reported [60]. The broadening of the 2169 cm$^{-1}$ peak supports the formation of CO and is hindered by CO$_2$ molecule formation. The formation of alkyne groups agrees with the result reported [59] by simultaneous observation of the R-C≡C-H stretching vibration band at 2102 cm$^{-1}$, which is too weak to be evaluated quantitatively.

4. Conclusions

We have investigated the effects of 1.75 MeV N$^{5+}$ ion irradiation on PET polymer with varying ion fluences. The enhancement in the crystallinity is observed for ion fluences 4x10$^{11}$ and 5x10$^{12}$ ions/cm$^2$ in the irradiated polymer. This enhancement is due to the conversion of the amorphous regions to the crystalline zone; as a result, crystallinity increases. The ion irradiation transfers energy and stress through the covalent bond, and hence the amorphous area is converted into the crystalline zone. The bandgap energy or HOMO-LUMO gap energy becomes lower for the dose 5x10$^{14}$ ions/cm$^2$. FTIR result shows a modification in the chemical structure of polymer by the impact of N$^{5+}$ ion irradiation. The carbonyl peaks shift towards lower values results from forming an electron-rich zone around the carbonyl group. The peak at 2365 cm$^{-1}$ supports the formation of a free CO$_2$ molecule; at 3650 cm$^{-1}$ due to the development of hydroxyl group formation in the form of benzoic acid substitute. The shift in absorption maxima towards a higher wavelength (redshift) is due to the generation of extended conjugation resulting from forming an acetylenic group. The reaction mechanism of product formation chemistry of degradation products like the formation of conjugation, acetylenic (-C≡C-), hydroxyl, free CO$_2$, carbonyl group, with the use of Norrish type-I and type-II reaction have been explained.

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Conflicts of Interest

The authors declare no conflict of interest.

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