Thin films of polypropylene and polyimide were irradiated by 100 MeV Ag$^{7+}$ ions in the fluence range of $1.0 \times 10^{11}$ to $5.0 \times 10^{12}$ ions/cm$^2$. The surface and bulk properties of pre and post irradiated samples were characterized by various techniques such as FTIR, UV-Visible, EDS spectroscopy, XRD, SEM and contact angle method. It is observed that physicochemical changes induced by 100 MeV Ag$^{7+}$ ions are qualitatively and quantitatively different than the Co-60 gamma rays and 6 MeV electron irradiation. In case of polypropylene, FTIR analysis shows that the C-H and C-C bonds are rigorously damaged due to SHI irradiation. However, though EDS analysis shows a significant increase in oxygen contents, FTIR shows no signatures of carbonyl groups. This indicates that oxygen diffuses due to radiation induced tracks and pores, but does not form the bonds with rigorously damaged network. UV-Visible analysis shows quite a significant decrease in the band gap from 5.37 to 3.39 eV ascribing to heavy carbonization. Interestingly, XRD shows a noticeable enhancement in the crystallinity indicating SHI induced local relief on crystallites due to breaking of tie molecules. Contact angle in the present case is found to increase from 78° to 97° which is due to excessive surface roughening and graphitization of the surface. Polyimide irradiated by the same heavy ions and at the same fluences continues to show a different behavior. FTIR shows scissioning of various bonds in PMDA and ODA, but the imide groups and C=C bonds are found to be less rigorously scissioned than C-H, OH, NH and C=O bonds. UV-Visible spectra show a decrease in the band gap, but only by 6 %. XRD shows decrease in crystalinity indicating amorphisation. Contact angle shows a decrease from 82° to 43° indicating surface roughening and presence of polar groups on the surface.
4.1 Background and Purpose: In chapter 2 and 3, the effects of 1.17 MeV and 1.33 MeV Co-60 gamma radiation and 6 MeV electron radiation on the physicochemical properties of polypropylene and polyimide were presented. Though, these radiations have some advantages, they are considered as ‘classical’ radiations, in the sense that their energies and stopping powers are quite lower than that of Swift Heavy Ion radiation. The effects of Swift Heavy Ion irradiation on the polymers are of special interest from basic as well as application point of view. This is due to some distinct features of SHI radiation. For example Swift Heavy Ions have high energy, highest possible stopping power (LET’s) and hence can deposit largest energy densities along their track. Further, the range of Swift Heavy Ions in solids is lower than that of electrons and gamma rays. As a result it is possible to modify surface properties by keeping the bulk intact. SHI irradiation with high fluences can be used for ion implantation. This enables to dope foreign species in materials. The presence of traces of foreign atoms dominates the mechanical, chemical, electrical, optical, magnetic as well as superconducting properties of materials. Due to high stopping power, SHI with even low fluence can be used to deliver significantly large amount of doses, due to which several physicochemical changes with substantial magnitude can be induced in polymers. A few of physicochemical changes in polymers that can be typically induced by SHI irradiation are... crosslinking, scissioning, formation of free radicals, radiochemical alterations such as unsaturation or formation of double bonds, evolution of gases, formation of carbonaceous clusters, chemically etchable latent tracks, change in intrinsic free volume, creation of defects (free radicals or impurities), amorphisation, phase transitions etc. Thus the polymers, which are difficult to process by chemical means, can be easily modified by SHI irradiation. As a result, SHI irradiation on polymers is showing great potential for applications in the fields such as radiation enhanced diffusion, sputtering, Ion Beam Mixing (IBM), Ion Assisted Deposition (IBD), Tribology, microelectronics, biomedical, nanotechnology, device technology and materials science [1-6].

In view of the above discussion, in this chapter the effects of 100 MeV Ag\textsuperscript{7+} ions on the physicochemical properties of polypropylene and polyimide in the fluence range $1.0 \times 10^{11}$ to $5.0 \times 10^{12}$ ions/cm\textsuperscript{2} are presented. Whereas, in the chapters 2 and 3, the effects of Co-60 gamma and 6 MeV radiations have been studied in the dose ranges from 57.6 to
230.4 kGy and 294 to 1176 kGy, in the present case the doses have been extended in the range 1462 to 73119 kGy. These high values of doses are due to large stopping powers of SHI in the polymers. The physicochemical changes induced by 100 MeV Ag\textsuperscript{7+} ions have been analyzed using techniques such as FTIR, UV-Visible, EDS spectroscopy, XRD, SEM and contact angle methods.

4.2 15 UD Pelletron Accelerator: The 100 MeV Ag\textsuperscript{7+} ions for the irradiation of polypropylene and polyimide were obtained from the ‘Pelletron’ facility at Inter-University Accelerator Centre, New Delhi, India. A schematic of the Pelletron and its photograph is shown in figure 4.1 and 4.2 respectively. The availability of different types of ions with narrow energy resolution makes this accelerator extensively versatile. This accelerator is capable of accelerating any ion, covering from hydrogen to uranium, with energies from few tens of MeV to two hundred of MeV. This accelerator is a vertical tandem accelerator of ~ 26.5 m in height. As shown in figure 4.1, the main ‘terminal’ of the accelerator is a high voltage dome of 1.52 m in diameter and of 3.61 m of height. This dome is fixed at the center of the tank filled with sulfur hexafluoride. The dome can be charged to high voltage, which can be varied from 4 MV to 16 MV. The 15 UD Pelletron accelerator consists of a source which can provide different types of negative ions. The ions after extraction from the source pass through a mass analyzer and enter into the accelerating column. The ion source is kept at ground potential. The vacuum in the Pelletron beam line is maintained around 10\textsuperscript{-8} Torr. Initially negative ions are produced and pre-accelerated to a few hundreds of keV and mass analyzed before injecting into the high accelerating column. The negative ions get accelerated while traveling through the accelerating tube from the column top up to the positively charged dome. While passing through the positive terminal dome these negative ions also pass through a stripper, which removes some electrons from the negative ions, thus transforming them into positive ions. When these positive ions reach the other end of the positively charged dome, they get repelled and accelerated while reaching the ground potential, at the bottom end of the tank. In this manner the same terminal voltage is used twice for accelerating the ions. After leaving the accelerating column, the ions of particular energy are analyzed by a magnet and guided into a horizontal plane magnet known as switching magnet. This magnet can deflect the ions into any of the beam lines for experiments in
Figure 4.1 Schematic Diagram Showing the Principle of Acceleration of Ions in "Pelletron".

Figure 4.2: Photograph of the 15 UD Pelletron Accelerator, at IUAC New Delhi
the beam hall. This entire accelerator is computer controlled and operated from the control room. The energy ‘E (MeV)’ of the accelerated ion at the end of the second accelerating column depends on the charge state ‘q’ of the ion and the terminal potential ‘V₁’

\[ E = E_{\text{inj}} + (q + 1) V_t \text{ MeV} \]  

...(4.1)

where, \( V_t \) = the terminal voltage in MV, \( q \) = charge state of the positive ion and \( E_{\text{inj}} \) = energy of the injected ion. The ion current is normally measured by a Faraday cup and the magnitude of the current in terms of particle per second is decided by the charge state.

4.3 Interactions of Energetic Ions with Matter: When an energetic ion passes through the matter, it loses its kinetic energy through electromagnetic interactions with electrons in the vicinity which are raised to excited states or torn away from the atoms. These changes of state are caused by Coulomb’s force, which can give a sharp impulse to an electron as the ion passes by. The energy transferred to the electrons represents loss of kinetic energy of the moving ion, which therefore will slow down and eventually stop.

The radii of atomic nuclei are so small compared to atomic dimensions that in the initial stages nuclear scattering and interactions are rare compared to interactions with electrons; therefore nuclear reactions may be neglected to first approximation. The energy transferred to the ions (or nucleus) is therefore negligible. The slow down process or stopping process is mainly an atomic process. Based on classical, quantum as well as relativistic treatments given to interaction of heavy ions with electrons in the matter by Bohr, Bethe and Block, the energy loss (or stopping power or linear stopping coefficient) of heavy ion through matter can be shown to be equal to

\[ \frac{dE}{dx} = n\sigma dx = n\sigma = \frac{z^2 Z n e^4}{4\pi \varepsilon_o m V^2} \left[ \ln \frac{2mV^2}{l} - \ln \left(1 - \frac{V^2}{c^2}\right) - \frac{V^2}{c^2} \right] \]  

...(4.2)

Where \( \sigma \) is the stopping cross-section for ion per atom given by
\[
\sigma = \frac{z^2Ze^4}{4\pi e^2 m V^2} \left[ \ln \frac{2mV^2}{I} - \ln \left( 1 - \frac{V^2}{c^2} \right) - \frac{V^2}{c^2} \right] \quad \ldots (4.3)
\]

Where \( z_e \) is the charge of ion, \( e \) is the charge on electron, \( n \) is number of target atoms per unit volume, \( m \) is the mass of electron, \( V \) is velocity of ion and \( c \) is the speed of light and \( I \) is the average excitation energy (ionization potential) of electron. Roughly \( I \) in electron volts is \( 13Z \), where \( Z \) is the atomic number of stopping atoms. For relatively low speeds, last two terms in the square bracket of equation 4.2 almost cancel each other. Since the term \( \ln(2mV^2/I) \) is reasonably slowly varying with \( V \), the main variation of the stopping power is due to the terms outside the square bracket. Equation (4.2) thus shows that the energy loss of heavy ion through matter is (i) proportional to number of electrons per unit volume in the stopping material (ii) proportional to square of the charge of the ion and (iii) inversely proportional to the square of the velocity of the incident particle. Since \( dE/dx \) increases as \( V \) decreases, slower particles produce more ion pairs per unit length than faster ones. Due to inverse square dependence on the velocity, the stopping power decreases rapidly with the energy in the energy range 1 to 10 MeV. The stopping power increases slowly thereafter as \( V \) increases because the second and third terms in the square bracket become important. It can also be observed that, the energy loss depends upon charge and speed but not on the mass of ion. The electrons released due to ionization by ion carry substantial energy and therefore can take part in further ionization process. This causes the multiplication in the number of ionization events. Further, the deexcitations which follow after initial excitations result in emission of photons. The energy loss process of ion through the matter is thus statistical. The statistical nature of the slowing down process is also responsible for another phenomenon called as straggling. Straggling is due to the fact that identical particles of identical energies do not suffer the same energy loss in passing through the matter of given thickness. The energy distribution of the ions in simple cases is Gaussian. The radiative (Bremsstrahlung) energy loss which is dominant for electrons is very less significant in case of heavy ions, as ions due to their heavy mass are deflected to a negligible extent. The energy loss of heavy ions is stronger than that of electrons due to two reasons (i) The energy loss of ions varies directly with \( z^2 \), where \( z_e \) represents the charge on ion (ii) the energy loss of ions
as well as electrons varies inversely with the square of the velocity and the velocity of ions is considerably smaller than that of electrons. At a comparable energy, since electron moves much faster than a heavy ion, it has a lower probability of interaction and hence a lower specific ionization.

As mentioned earlier, in the initial stages of passage of ion through the matter, the **electronic energy loss** \( (S_e) \) is dominant, where the ion passes through the cloud of electrons and looses its energy by inelastic collisions which results in ionization-excitation of the electrons. In this process, the ion itself looses its electrons. When ion becomes slow due to this energy loss process, it starts acquiring the electrons from the surrounding atoms and then finally approaches towards neutrality. Such neutral atom suffers hardbound elastic collisions with the surrounding atoms. This energy loss which occurs in the final stages of the range of ion through the matter is called as **nuclear energy loss** \( (S_n) \). Such hardbound collisions may also result in the displacement cascade of atoms in the path, which creates various types of defects in the material. It may be noted that electronic energy loss is dominant in the initial stages of ion while the nuclear energy loss is dominant at the end of trajectory of the ion. Further, electronic energy loss is stronger than nuclear energy loss [7-10].

**4.4 Defects produced by Heavy Ions:** The process of atomic displacement produced by heavy ions is different than that of gamma rays and electrons. As discussed earlier, the ions are ionized in the beginning of their range and then start gaining the electrons in the later part as they slow down. Therefore, it is necessary to consider energy loss in the different regions separately. At the higher energy when the ion enters in the medium, it looses some of its electrons and gets multiply ionized. At this stage the mechanism of energy loss of the moving ion is through electronic excitation. At higher energies the electrons of the moving ion can be neglected and the collisions are of Rutherford type that is due to Coulomb interaction. As the kinetic energy of the atom decreases the degree of ionization also decreases. As the degree of ionization decreases the energy loss in electronic excitation also decreases. As the moving atom now becomes neutral, the energy is lost in the collision with the target atom which is of hard sphere type.
At higher energies of the order of tens of MeV, the moving ion nucleus directly interacts with the nucleus of the target atom, and this interaction is via Coulomb potential and thus the scattering is of Rutherford type.

Consider a moving atom/ion/particle of mass $M_2$ and charge $Z_2e$ interacts with stationery particle of mass $M_1$ with charge $Z_1e$. Then the Rutherford cross-section is given by; $(d \rightarrow \text{displacement})$

$$
\sigma_d = \pi M_2 Z_2^2 Z_1^2 \frac{e^4}{M_1 E E_d} \tag{4.4}
$$

The mean energy transferred to the struck atom for the case in which the atom is displaced is given as:

$$
E_{ad} = E_d \ln \left( \frac{E_{adm}}{E_d} \right) \tag{4.5}
$$

Where $E_{adm} = \frac{4M_1 M_2 E}{(M_1 + M_2)^2}$ (This is the maximum energy transferred to the struck atom when it is displaced). In general $E_{adm}/E_d$ is if the order of 10 and thus $E_{adm}$ is of the order of few hundreds of eV. The relation 4.5 is valid only when the ratio of $E_{adm}$ to $E_d$ is greater than 1. The mean free path between collisions in which displacements are produced is given by $L_d = 1/N_0 \sigma_d$ where $N_0$ is the number of atoms in unit volume. The local energy deposition which is less than $E_d$ results in thermal spikes, that is local temperature of the target increases. This may not be the major source of energy loss in this energy range. The knocks on atoms produced by Rutherford collisions are sufficiently energetic to produce further displacements. Assuming that a knock on atom with energy $E_d$ will produce $E_d/2E_d$ further displacements for $E_d > 2E_d$ and will produce only one displacement for $E_d < E_{adm} < 2E_d$, the average total number of displacements $n_d$ produced in Rutherford collision is

$$
n_d = \frac{1}{2} \left\{ 1 + \ln \left( \frac{E_{adm}}{E_d} \right) \right\} \tag{4.6}
$$

The major source of energy loss of moving ions at higher energies is electronic excitation. In this higher energy range the moving atom is stripped off all its electrons,
and the energy loss is due to Rutherford collisions of electrons of the solid with the nucleus and the rate of energy loss is given by

\[
\frac{dE}{dR} = \frac{4N_e \pi e^2 Z_1 Z_2^2 M_2}{2E} \ln \frac{4m_e E}{M_2 I}
\]

Where \( I \) is the ionization potential of the target atom with atomic number \( Z_1 \), the moving atomic number \( Z_2 \) and mass \( M \), If the ion is the same as those of the atoms of the solid, then

\[
\frac{dE}{dR} = \frac{4N_e \pi e^2 Z_1^3 M}{2E} \ln \frac{4m_e E}{M_2 I}
\]

As the energy of the ion reduces it starts gaining electrons from the solid and hence the effective charge of the ion changes (decreases) and is denoted by \( Z_{\text{effective}} \). This effective charge is given by

\[
Z_{\text{effective}} = 0.9 \times 10^{-3} \left( \frac{E}{A} \right)^{1/2} Z_2^{3/3}
\]

Where \( E \) is in eV and \( A \) is the atomic mass number of the ion. As the energy of the ion further decreases it approaches towards charge neutrality and then experiences collision with the atoms of the lattice which is of hard sphere type. This interaction is dominated now by electrons of the moving atoms. The energy at which atom becomes neutral can be calculated. If the velocity of the ion is \( v \) then electrons of the lattice with velocity much less than \( v \) can at most transfer energy \( \sim m_e v^2 \) to the electrons of the moving atom, if this energy is less that the atom’s ionization potential then the atom remains neutral.

Assuming minimum ionization energy of the atom as 2 eV, the value of \( E_n \) at which atom becomes neutral is

\[
E_n = \frac{1}{2} Mv^2 = \frac{1}{2} M \frac{1}{m_e}
\]

\[
E_n = \frac{1840}{2} \text{A, eV} = \text{A, keV}
\]

Where \( A \) is the atomic mass number of the ion

The hard sphere collision basically gives rise to the atomic displacements. MeV energy ions can penetrate a few microns in the target before coming to rest. The property of ions
to produce displacements at the end of range is utilized to introduce defects in specific areas [11].

4.5 Coulomb Explosion Model: It is well known that energetic ion beams form chemically etchable tracks and spurs of micron size while passing through the insulators. These tracks can alter the property of materials. Such tracks or spurs are not formed in case of metals. This indicates that electronic processes play an important role in ion-target interaction. Numerous models have been developed to explain the track formation and sputtering process. The models based on collision cascade of ions with the target atoms can not explain why tracks are not formed in metals, while the thermal spike model, in which the energy of ions is assumed to be converted in to phonons which then melt the lattice, has also been found inadequate, as no correlations have been found between the track formation and the thermal properties of materials.

Coulomb explosion or ion explosion model can adequately explain the track formation process in insulators. It also explains the difference in the damage processes of metals and insulators. It is known that the ion looses most of its energy in electronic energy loss regime. While passing through the lattice it looses its orbital electrons. Such ion with lost electrons excites and ionizes the atoms of the target along its track. This forms a narrow cylinder of material with net positive charge. Thus there occurs a mutual coulomb repulsion between the ion and the ionized target atom, due to which target atoms are recoiled. Further, the ionized target atoms in the track also strongly repel each other. This strong mutual repulsion of the ionized target atoms is called as Coulomb explosion and is responsible for formation the ionized track containing intense charge. This Coulomb repulsion and the corresponding recoil is sufficiently large to displace the target atoms, as it can be shown that the two electron charges separated by 1 atom have potential energy of 3.5 eV and the potential energy due to coulomb repulsion of cluster of even five ions can reach up to 30 eV which is quite greater than the binding energy per atom of the of target. This destroys the lattice order along the track as target atoms are recoiled and repelled. Thus the ionized track contains dense cloud of interstitial atoms and vacancies along the original ion trajectory. The motion of the target atoms due to their recoil and repulsion is mainly opposed by neighboring atoms. However, as the ion interaction causes ionization of target atoms, they loose electrons and their effective
radius decreases. This provides considerable volume for the motion of recoiled atoms. Now even though these target atoms deionize due to electrons surrounding the ionized track, they are permanently trapped out of their lattice positions. This is because of high energy deposited by ion, due to which the track is highly charged. This intensely ionized track is transient because neutralization and screening by electrons can quench the repulsive energy in an ionization track. However, the charge in the track generates an intense electric field responsible for exerting an accelerating force on the target atoms, which causes their motions before they get neutralized due to electrons outside the track. In polymeric materials less energy is required to break the bonds than to ionize the atoms and the high density of broken bonds along the trajectory of a particle effectively decreases the molecular weight of the region and results in increased chemical reactivity. The ion-solid interaction also results in the ejection of the atoms from the surface due to electronic excitations. This is called as electronic sputtering [12, 13].

4.6 100 MeV Ag\(^{7+}\) Ion Induced Physicochemical Changes in Isotactic Polypropylene:

4.6.1 Introduction and Literature Survey: There are number of reports available on the effects of low as well as high-energy radiations on polypropylene, out of which, the gamma irradiation [14, 15] and high energy electron irradiation [16-18] shows significant chemical and morphological changes. A literature survey indicates that SHI irradiation of polypropylene shows a significant decrease in band gap, loss in crystallinity and formation of carbonyl and hydroxyl groups for 86 MeV Ni\(^{7+}\) ion irradiation in the fluence range 1.0×10\(^{11}\) to 1.0×10\(^{13}\) ions/cm\(^2\) [19]. Polypropylene irradiated with 3.6 MeV and 5.4 MeV C\(^+\) ions in the fluence range 5×10\(^{13}\) to 5×10\(^{14}\) ions/cm\(^2\) also shows decrease in the band gap. This has been ascribed to formation of conjugated double bonds, which has been confirmed by appearance of peak at 1650 cm\(^{-1}\) in FTIR. These results are found consistent with RGA, which shows evolution of gases [20]. Differential Scanning Calorimetric (DSC) analysis of 80 MeV Si\(^{7+}\) and 120 MeV Ag\(^{9+}\) irradiated polypropylene in the fluence range 10\(^{10}\) to 10\(^{13}\) ions/cm\(^2\) shows decrease in melting and crystallization temperature. UV-Visible analysis shows formation of double bonds while FTIR shows oxidation and distortion of isotacticity [21]. However, to modify the polymer, energy loss of SHI is very important and specific to its nature, energy and environment. The effects
of such parameters of SHI irradiation on surface properties of polypropylene have not been paid much attention. Therefore, in this part, the effects of 100 MeV Ag$^{7+}$ ions on chemical, optical, structural and surface properties of polypropylene are presented in order to confirm the relative contributions of carbonization, conjugation and oxidation.

4.6.2 Experimental: Thin films of isotactic polypropylene having approximately 500-micron thickness were obtained by compression molding technique. Samples having dimension 1 cm × 1 cm × 500 μm were cut from these films. These samples were then irradiated by 100 MeV Ag$^{7+}$ ions from 15 UD pelletron accelerator at Interuniversity Accelerator Center, New Delhi, India. The fluence was varied from sample to sample in the range of 1.0×10$^{11}$ to 5.0×10$^{12}$ ions/cm$^2$. Relatively low fluence was selected to avoid the overheating of the polymer. The irradiation was carried out in high vacuum (= 10⁻⁸ torr) and at room temperature. The energy loss (LET) of 100 MeV Ag$^{7+}$ ions in polypropylene as calculated from SRIM, TRIM software is 8.226 MeV/micron (Electronic energy loss, $S_e = 8.193$ MeV/micron, Nuclear energy loss, $S_n = 0.03302$ MeV/micron) and the range is estimated to be 22.27 micron. The corresponding doses and energy densities were calculated by substituting these values and the fluences in formulae 3.10 and 3.11 in chapter 3 respectively. These are shown in table 4.1.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Fluence (ions/cm$^2$)</th>
<th>Dose (kGy)</th>
<th>Energy Density (MeV/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pristine</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>1.0×10$^{11}$</td>
<td>1462</td>
<td>8.23×10$^{15}$</td>
</tr>
<tr>
<td>3</td>
<td>5.0×10$^{11}$</td>
<td>7312</td>
<td>4.11×10$^{16}$</td>
</tr>
<tr>
<td>4</td>
<td>1.0×10$^{12}$</td>
<td>14624</td>
<td>8.23×10$^{16}$</td>
</tr>
<tr>
<td>5</td>
<td>5.0×10$^{12}$</td>
<td>73119</td>
<td>4.11×10$^{17}$</td>
</tr>
</tbody>
</table>

Table 4.1: Fluence, Dose and Energy Density of 100 MeV Ag$^{7+}$ Ion Irradiated Polypropylene
Figure 4.3 (a, b, c and d) show the electronic and nuclear energy loss, collision events, straggling and range of 100 MeV Ag$^{7+}$ Ions in polypropylene respectively as calculated from TRIM software.

The pre and post-irradiated samples were then subjected to various characterizations. FTIR spectroscopy was used to investigate the effects of radiation on scissioning and/or crosslinking of various bonds and to verify the possibility of formation of various irradiation induced functional groups, especially the carbonyl and hydroxyl ones. UV-Visible spectroscopy was used to study the changes in typical optical properties such as
band gap and absorbance in UV-Visible region. Photoluminescence spectroscopy (PL: Perkin Elmer LS-55 Luminescence spectrometer) in emission as well as excitation mode was carried out to investigate the changes in luminescent properties of polypropylene, particularly as regards to SHI irradiation induced oxidation, unsaturation and defects. The peaks recorded in emission spectra were further confirmed in excitation spectra. XRD was used to investigate the irradiation-induced changes in various crystalline properties such as relative crystallinity, crystal symmetry and size of crystallites. The surface morphology was investigated using SEM analysis. Finally, the effects of SHI irradiation on surface texture and chemistry of polypropylene were studied using contact angle method.

4.6.3 Results and Discussion:

(i) FTIR Analysis:

Figure 4.4 shows the typical FTIR spectra of pristine and ion-irradiated polypropylene at different fluences. Y scale in the figure is appended for comparison.

![FTIR Spectra](image)

Figure 4.4: FTIR Spectra of Pristine and 100 MeV Ag$^{7+}$ Ion Irradiated Polypropylene at Different Fluences: Spectra Recorded a Few Days after Irradiation
As discussed in chapter 2 and 3, absorbance in the region 2850-2950 cm\(^{-1}\) corresponds to \(\text{CH}_3\), \(\text{CH}_2\), \(\text{CH}\) stretching, while the peaks in the region 1450-1480 cm\(^{-1}\) are due to \(\text{CH}_3\) and \(\text{CH}_2\) bending. Various weak, medium and strong peaks in the region 809 to 1377 cm\(^{-1}\) correspond to \(\text{CH}_3\), \(\text{CH}_2\), \(\text{CH}\) bending, wagging, twisting and C-C stretching. The peaks observed near 1170 cm\(^{-1}\), 999-977 cm\(^{-1}\) confirm the isotactic category of polypropylene used in this study [15, 22]. It can be observed that the absorbance at various positions rapidly decreases with the fluence and it clearly indicates the scissioning of various C-H and C-C bonds due to 100 MeV Ag\(^{7+}\) ion irradiation. The scissioning of bonds is observed to become apparent at the minimum fluence of \(1\times10^{11}\) itself and the bond structure is found to be successively and rigorously damaged in the fluence range from \(5\times10^{11}\) to \(5\times10^{12}\) ions/cm\(^2\). Moreover, the peaks near 1170 cm\(^{-1}\), 999-977 cm\(^{-1}\) are also found to be decreased in intensity with the ion fluence. This indicates that the isotactic arrangements of polymer chains are distorted after irradiation. However, the typical peaks around 1725 cm\(^{-1}\) and 3400 cm\(^{-1}\) which correspond to carbonyl (C=O) and hydroxyl (OH) groups respectively, are not noticeably observed in the FTIR spectra. This shows that polypropylene irradiated by 100 MeV Ag\(^{7+}\) in high vacuum has not undergone on carboxylation process. This attributes to the presence of high vacuum during irradiation and insignificant concentration of free radicals. As the energy loss of 100 MeV Ag\(^{7+}\) ions in polypropylene is considerably high, the possibility of partial scissioning of bonds (that is required for production of free radicals involving unpaired electrons) seems to be insignificant. A comparison of FTIR analysis of gamma irradiated and 6 MeV electron irradiated polypropylene (chapter 2: figure 2.11 and Chapter 3: figure 3.3 respectively) with the present case shows that the breaking of bonds is more severe and this attributes to extremely high doses of energy deposited by 100 MeV Ag\(^{7+}\) ions. However, the concentration of the carbonyl and hydroxyl groups which signify oxidation is almost unnoticeable in the present case. Further, EDS spectra in figure 4.5 show that a significant proportion of oxygen is diffused after irradiation. The diffusion is due to track and pores created by SHI irradiation. But the diffused oxygen has not formed bonds with the rigorously damaged network of polypropylene. The severe destruction of the molecules under SHI is a consequence of the multiple hits of the energetic ions on the same molecule which completely destroys the molecule in to
small fragments. The energy deposition in case of SHI occurs at high densities, resulting in multiple bond scissions.

The FTIR analysis of same irradiated samples was repeated after four months, in order to investigate the post irradiation effects as regards to carbonylation of polypropylene. These spectra are shown in Figure 4.6. It is found that, particularly at low fluences, the C-H bonds are partially recovered and peak corresponding to carbonyl groups are also marginally observed at 1705 cm⁻¹. This indicates the possibility of crosslinking and oxidation at low fluences in the post irradiation period.

(ii) UV-Visible Spectroscopy: Figure 4.7 shows UV-Visible spectra of pristine and Ag⁺⁺⁺ ion irradiated polypropylene at different fluences. It can be observed that the absorption edge rapidly shifts with the fluence towards higher wavelength. The maximum red shift is from pristine value of 218 nm to 367 nm at the highest fluence of 5×10¹² ions/cm². This corresponds to decrease in the optical band gap from 5.37 to 3.39 eV, which is almost 37%. Moreover, the absorbance at all the wavelengths is observed to be increased with the ion fluence. As discussed in chapter 2 and 3, the large reduction of optical band gap
Figure 4.6: FTIR Spectra of Pristine and 100 MeV Ag\(^{7+}\) Ion Irradiated Polypropylene at Different Fluences: Spectra Recorded Four Months after Irradiation

Figure 4.7: UV-Visible Spectra of Pristine and 100 MeV Ag\(^{7+}\) Ion Irradiated Polypropylene at Different Fluences
can be attributed to formation of carbon enriched clusters due to partial evolution of hydrogen after irradiation. The residual carbon left after the evolution of hydrogen, may have graphite like form which results in to the decrease in optical band gap. Further, the increase in absorbance at all the wavelengths in UV-Visible regime for different fluences can be attributed to change in color of the films after irradiation. It was observed (figure 4.8) that the pristine polypropylene film was colorless and after irradiation it successively became yellowish, reddish and finally brownish with increase in fluence.

![Figure 4.8: Photograph of the Pristine and 100 MeV Ag\textsuperscript{7+} Ion Irradiated Polypropylene Films](image)

This strongly attributes to carbonization, irradiation-induced defects and chromophoric groups behaving as color centers [19, 23, 24].

(iii) XRD Analysis: Figure 4.9 shows the XRD spectra of pristine and ion irradiated polypropylene at various fluences. The spectra are appended for comparison. As discussed in chapter 2 and 3 the XRD spectra confirm the known \(\alpha\)-monoclinic form of polypropylene and the prominent peaks observed at \(2\theta = 14^\circ, 17^\circ, 18.5^\circ\) and \(22^\circ\) correspond to (110), (040), (030) and (041) planes respectively [25]. It is observed from the figure that there is a notable and successive growth in the intensity of crystalline peaks with the ion fluence. In particular, the height of (110) peak markedly increases with the fluence. In chapter 2 and 3, the XRD analysis of gamma and electron irradiated polypropylene has indicated only minor changes in the crystalline structure, however in present case the crystallinity is found to be enhanced with the fluence. The energy deposited in the present case is very high. The enhancement in the crystallinity mainly
attributes to local relief in the strain on the crystallites due to breaking of tie molecules existing in amorphous zones [18]. Secondly, the molecules that acquire extra mobility due to scissioning, may displace from amorphous to the crystalline zones [26]. As a result, the crystalline zones may enrich in atoms while the amorphous zones may deplete. Moreover, the significant increase in overall crystallinity may also indicate that the relative fraction of crosslinked network contributes to amorphous content of the polypropylene, and it decreases due to scissioning. Further, the molecules shortened due to scissioning are less constrained in the amorphous regions and are better able to reorient into crystal lattice. It is known that high energy irradiation increases the temperature of polymers. Thus polypropylene network may have annealed to some extent resulting in increase in crystallinity.

(iv) Photoluminescence Spectra: An idealized polypropylene is not known to be luminescent, however the presence of impurities, additives, defects, unsaturation and chromophores may cause photoluminescence [27, 28]. Figure 4.10 shows the photoluminescence spectra of pristine and Ag$^{7+}$ ion irradiated polypropylene at different
fluences. The excitation wavelength used in this case was 236 nm. The emission spectra show a strong peak at 443 nm i.e. 2.81 eV and a weak peak at 484 nm i.e. 2.57 eV. These peaks were further confirmed by recording the excitation spectra by taking emission wavelength as 443 nm. Figure 4.11 shows the corresponding excitation spectra which confirms the excitation peak at 236 nm. It is observed that, the

![Figure 4.10: Photoluminescence (Emission) Spectra of Pristine and 100 MeV Ag\textsuperscript{7+} Ion Irradiated Polypropylene at Different Fluences](image)

intensity of both the peaks in emission spectra decrease with the increase in ion fluence. This shows that polypropylene becomes successively less luminescent after ion irradiation. This attributes to the disappearance of luminescent centers such as impurities, defects, unsaturation and chromophores in the polypropylene [27, 28]. As SHI leads to scissioning of various bonds and evolution of gases, the luminescent centers may discompose and then released during irradiation, which results in to the decrease in intensity of the emission peaks. Further,
the absence of carbonylation effects, conjugation and the decrease in optical band gap also seems to be responsible for decrease in the PL intensity.

(v) Contact Angle Measurements: As discussed in previous chapters, wettability of the polymer surface is governed by its roughness and surface chemistry. In general, surfaces involving polar groups such as carbonyl or hydroxyl are known to be hydrophilic. Thus, the contact angle measurements can clarify the changes in the surface texture and chemistry after SHI irradiation. Figure 4.12 shows the contact angles of a 10 microliter drop of distilled water on the surface of pristine and 100 MeV Ag$^{7+}$ ion irradiated polypropylene at the maximum fluence of $5\times10^{12}$ ions/cm$^2$. The contact angles and various related parameters shown in table 4.2 do not reveal specific trend with the fluence, which may be due to presence of polar groups on the surface at lower fluences and their absence at higher fluences and also the excessive surface roughness at higher fluences. However, it is observed that the contact angle increases from pristine value of
Figure 4.12: Photographs of a 10 Micro-Liter Water Drop on the Surface of Pristine and 100 MeV Ag$^{7+}$ Ion Irradiated Polypropylene at the Fluence of $5\times10^{12}$ ions/cm$^2$

Table 4.2: Contact angle, Work of Adhesion, Roughness and Area Fraction of the Liquid Solid Interface of Pristine and 100 MeV Ag$^{7+}$ Ion Irradiated Polypropylene at Different Fluences

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Fluence (ions/cm$^2$)</th>
<th>Contact angle (Deg.)</th>
<th>Roughness “r” $\cos\theta = r \cos\theta$</th>
<th>Work of Adhesion (mJ/m$^2$)</th>
<th>Area fraction (f) of the liquid solid interface $\cos\theta = f \cos\theta + f - 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pristine</td>
<td>78</td>
<td>1.0</td>
<td>88</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>$1.0\times10^{11}$</td>
<td>76</td>
<td>1.16</td>
<td>90.41</td>
<td>1.03</td>
</tr>
<tr>
<td>3</td>
<td>$5.0\times10^{11}$</td>
<td>74</td>
<td>1.33</td>
<td>92.9</td>
<td>1.06</td>
</tr>
<tr>
<td>4</td>
<td>$1.0\times10^{12}$</td>
<td>71</td>
<td>1.56</td>
<td>96.5</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>$5.0\times10^{12}$</td>
<td>97</td>
<td>-0.58</td>
<td>63.9</td>
<td>0.73</td>
</tr>
</tbody>
</table>

$\gamma_{lg} = \text{Surface tension of liquid gas interface} = 72.8 \text{ mJ/m}^2$

$\theta = \text{Contact angle of the flat pristine sample}$

$\theta' = \text{Contact angle of the rough sample after irradiation}$

$78^\circ$ to $97^\circ$ at the maximum fluence of $5\times10^{12}$ ions/cm$^2$. This overall increase in the contact angle is almost 24% and it clearly shows that polypropylene surface has become significantly hydrophobic after irradiation at higher fluences. This attributes to the
absence of carbonyl and hydroxyl groups which are known to be polar, excessive surface roughening and carbonization (graphite is non polar) [29-32]. Moreover, the trapped air between water droplet and the surface due to increased surface roughness may reduce the liquid-solid contact area resulting in increased hydrophobicity [33]. If the water droplet does not entirely wet the surface and leaves pockets of air between the droplet and the substrate, then the observed contact angle is influenced by the fraction $f$ of the droplet that is actually in contact with the surface. This heterogeneous contact angle in such case is given by Cassie-Baxter equation $\{ \cos \theta_y = f \cos \theta_w + (f - 1) \}$ [34] instead of Wenzel equation $\left( \cos \theta_w = r \cos \theta_y \right)$. Figure 4.13 schematically illustrates the difference in homogeneous (Wenzel) and heterogeneous (Cassie Baxter) wetting regimes.

Figure 4.13: A Schematic Illustration of the Difference Between (a) Homogenous (Wenzel) and (b) Heterogeneous (Cassie-Baxter) Wetting Regimes

(vi) SEM Analysis: The surface roughening as mentioned in previous section is supported by SEM analysis. Figure 4.14 shows the SEM images of pristine and 100 MeV Ag$^{7+}$ ion irradiated polypropylene at different fluences. The magnification used was $\times2000$ in the present case. It can be observed that the degree of roughness/imperfection increases with the ion fluence. The surface of ion irradiated polypropylene is observed to be consisting of defects in the form of voids, blisters and tracks of varying sizes. As discussed in chapter 2 and 3 this can be mainly attributed to uneven evolution of gases/sputtering and from the surface of polypropylene the corresponding change in surface free volume during ion irradiation [35, 36]. Particularly, the SEM image at the maximum fluence of $5\times10^{12}$ ions/cm$^2$ shows several cavities which must have allowed the trapping of air. The trapped air must have made the surface consistent with heterogeneous (Cassie Baxter) wetting regimes, thus reducing the effective area fraction.
Figure 4.14: SEM Images of Pristine 100 MeV Ag\textsuperscript{7+} Ion Irradiated Polypropylene at Different Fluences

of the liquid solid contact. This may be one of the reasons why the surface appears hydrophobic at the maximum fluence.

4.7 Surface and Structural Changes in Polyimide by 100 MeV Ag\textsuperscript{7+} Ion Irradiation

4.7.1 Introduction and Literature Survey: In chapter 2, it is observed that polyimide has shown remarkable stability in its physicochemical properties against gamma radiation up to the dose levels of 230.4 kGy. Whereas in chapter 3, polyimide irradiated with 6 MeV electrons in the dose range 294 to 1176 kGy is found to be enhanced in mechanical properties and acquired hydrophilic properties. In this part the effects of 100 MeV Ag\textsuperscript{7+} ions on the surface and bulk properties of polyimide have been studied in the dose range 1065 to 53250 kGy. A literature survey indicates that the effects of ions with energies ranging from keV to GeV on polyimide are being extensively studied. In a few reports, an exponential decrease in the intensities of various bonds such as C-H, C=O, N-H, C-N, C-O-C and the imide groups with increasing fluence is observed [37-39]. The decrease in optical band gap and the increase in the absorbance in UV-Visible regime have been correlated with graphitization and the conjugation [38, 40] and has been confirmed by Micro-Raman and XRD studies [41]. Specifically, SHI irradiation with extremely high energies in GeV range has shown formation of new bonds such as C-N-C along with the destruction of existing bonds [40]. Whereas, XPS studies of SHI irradiated polyimide have shown the sputtering of the atoms such as C, N and O [42]. The surface roughening and formation of nanosized latent tracks and pores due to SHI irradiation has been revealed using AFM and SEM analysis [43-45]. From this literature survey, it also appears that the effects of SHI irradiation on polymers are extremely specific to the ion species, with their energy, the type of polymer and the irradiation environment. Thus, each SHI
and its irradiation on a particular polymer becomes a specific case for investigation. Further, the effects of UV, laser and plasma processing on polymer surfaces as regards to their wettability are reported [29-32]. In a few cases, superhydrophobic polymer surfaces have been tailored using pulsed laser deposition technique [33]. It appears that, irradiation induced hydrophilic or hydrophobic properties strongly depend upon oxidation, carbonization and roughening. However, such studies are not yet reported as regards to the SHI irradiation induced changes in wettability of polyimide surfaces. As SHI irradiation on polyimide leads to roughening, carbonization and oxidation depending upon ion energy and fluence, the contact angles and consequently the polymer wettability are expected to change significantly. Therefore, in the present part, we report the 100 MeV Ag\textsuperscript{7+} ion induced changes in the surface as well as bulk properties of polyimide in the fluence range $1.0 \times 10^{11}$ to $5.0 \times 10^{12}$ ions/cm\textsuperscript{2}. The ion irradiation induced scissioning/crosslinking, carbonization and amorphisation have been investigated using FTIR, UV-Visible and XRD spectroscopy respectively, while the corresponding changes in the wettability and the surface roughening has been analyzed using contact angle measurements and SEM analysis.

4.7.2 Experimental: Thin samples having dimensions $1 \text{ cm} \times 1 \text{ cm} \times 50 \mu\text{m}$ were cut from as-received polyimide (PMDA-ODA, Kapton, density 1.42 g/cm\textsuperscript{3}) sheets. The irradiation of these samples was carried out with 100 MeV Ag\textsuperscript{7+} ion beam in Interuniversity Accelerator Center, New Delhi, India. The irradiation was carried out in high vacuum ($\sim 10^{-8}$ torr) and at room temperature. The fluence was varied from sample to sample in the range from $1.0 \times 10^{11}$ to $5.0 \times 10^{12}$ ions/cm\textsuperscript{2}. The energy loss and the range of 100 MeV Ag\textsuperscript{7+} ions in polyimide as calculated from SRIM/TRIM software are 9.451 MeV/micron (Electronic energy loss, $S_e = 9.41034$ MeV/micron, Nuclear energy loss, $S_n = 0.040342$ MeV/micron) and 18.51 micron respectively. The corresponding doses and energy densities were calculated by substituting these values and the fluences in formulae 3.10 and 3.11 in chapter 3 respectively. These are shown in table 4.3. Figure 4.15 (a, b, c and d) show the electronic and nuclear energy loss, collision events, straggling and range of 100 MeV Ag\textsuperscript{7+} Ions in polyimide respectively as calculated from TRIM software. The pre and post-irradiated samples were then subjected to various characterizations to investigate the SHI induced changes in bulk and surface properties.
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Fluence (ions/cm²)</th>
<th>Dose (kGy)</th>
<th>Energy Density (MeV/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pristine</td>
<td>00</td>
<td>00</td>
</tr>
<tr>
<td>2</td>
<td>1.0×10¹¹</td>
<td>1065</td>
<td>9.45×10¹⁵</td>
</tr>
<tr>
<td>3</td>
<td>5.0×10¹¹</td>
<td>5324</td>
<td>4.73×10¹⁶</td>
</tr>
<tr>
<td>4</td>
<td>1.0×10¹²</td>
<td>10649</td>
<td>9.45×10¹⁶</td>
</tr>
<tr>
<td>5</td>
<td>5.0×10¹²</td>
<td>53243</td>
<td>4.73×10¹⁷</td>
</tr>
</tbody>
</table>

Table 4.3: Fluence, Dose and Energy Density of 100 MeV Ag⁺⁺ Ion Irradiated Polyimide

FTIR spectroscopy was carried out to monitor scissioning of various bonds and formation of new functional groups, especially as regards to oxidation. UV-Visible spectroscopy was carried out to measure the changes in absorbance in UV-Visible regime and the optical band gap. XRD spectra were recorded to examine the SHI induced changes in the crystalline properties. Finally, the changes in wettability after SHI irradiation was studied using contact angle measurements and surface morphology were analyzed using SEM.

**4.7.3 Results and Discussion:**

(i) **FTIR Analysis:** Figure 4.16 shows the FTIR spectra of pristine and 100 MeV Ag⁺⁺ ion irradiated polyimide at different fluences. The figure is appended for comparison. As mentioned in earlier chapters, the peak at 3085 cm⁻¹ corresponds to C-H stretching. The carbonyl groups (C=O, stretching) in PMDA are found at 1725-1781 cm⁻¹ and the hydroxyl groups (OH) at 3630 cm⁻¹ while 1260-1289 cm⁻¹ represent C-O-C stretch in ODA. The peaks at 3486 cm⁻¹ and 1602 cm⁻¹ represent N-H stretching and bending respectively. The cyclic imide (CO-N-CO) group can be monitored by peaks at 1376-1390 (=C-N stretch), 1725-1781 (C=O stretch). The stretching in imide is observed at peaks near 1380 and 1117 cm⁻¹ and its deformation is observed at 725 cm⁻¹ [38-40, 46]. It can be observed that, the overall bond structure involving almost all above-mentioned bonds is intact at the fluence of 1.0×10¹¹ ions/cm², and then these bonds are gradually scissioned after the fluence of 5×10¹¹ ions/cm². This can be confirmed by observing the
Figure 4.15: (a) Electronic (red) and Nuclear (blue) Energy loss, (b) Collision events (c) Straggling and (d) Range of 100 MeV Ag$^{7+}$ Ions in Polyimide as Calculated from TRIM software

decrease in the intensities of almost all the peaks after the fluence of $5\times10^{11}$ ions/cm$^2$. A comparison of these FTIR spectra of SHI irradiated polyimide with those in case of gamma and electron irradiated polyimide (figures 2.12 and 3.15 in chapters 2 and 3 respectively) shows that there is no scissioning of bonds in case of gamma and electron irradiated polyimide, but there is a notable scissioning of bonds in the present case. This attributes to the substantial energy and dose deposited by SHI irradiation. The relative absorbance $A/A_0$ (where $A_0$ and $A$ is the absorbance of the pristine and ion irradiated samples respectively), of some characteristic bonds has been plotted against ion fluence and it is shown in Figure 4.17. It can be seen that, though there is an overall decrease in
the relative absorbance of all the characteristic bonds, the C-H, C=O and OH bonds are scissioned at almost the same rate, while the scissioning of N-H bonds is comparatively rigorous, whereas the imide group and the C=C bonds, though scissioned, are relatively stable as compared to N-H, C-H and C=O bonds. The decrease in the absorbance of C=O groups with the ion fluence indicates decarbonylation of polyimide, however, it may be noted that the SHI induced loss of C=O bonds must have been compensated to some extent by simultaneous oxidation due to ion induced free radicals. Further, the C=O groups in the pristine polyimide are restricted to PMDA, however after SHI irradiation; these may be distributed randomly over entire monomer including PMDA and ODA.

Furthermore, the decrease in the aromatic C=C bonds may have been compensated by SHI irradiation induced conjugation. A glance at the FTIR analysis of gamma, electron and ion irradiated polypropylene and polyimide shows that depending upon the radiation, its dose and the dose rate of gamma electron and ion irradiation, polypropylene is oxidized/carbonylized to less or more extent, however such oxidation/carbonylation effects are not observed for polyimide irradiated with any of these radiations in any dose.

Figure 4.16: FTIR Spectra of Pristine and 100 MeV Ag\textsuperscript{7+} Ion Irradiated Polyimide at Different Fluences
range. This may be due to two reasons...one may be that polyimide, due to its aromatic and complex monomer and CTC based extraordinarily strong inter and intramolecular interactions, may have acquired relatively lesser concentration of free radicals that are not sufficient for oxidation/carbonylation and second reason may be the presence of substantial concentration of carbonyl groups in the monomer, which imparts high oxidation state, may have prevented the oxidation.

(ii) UV-Visible Spectroscopy: The UV-Visible spectra of pristine and 100 MeV Ag^{7+} ion irradiated polyimide are shown in Figure 4.18. It is observed from the figure that the absorption edge shows a red shift from 505 to 538 nm. This corresponds to decrease in optical band gap from 2.45 to 2.30 eV and it is almost 6%. Further, it can also be seen that, the spectral features of polyimide are partially lost at the maximum fluence of 5x10^{12} ion/cm^2. Thus the optical properties of polyimide which remain unaffected after gamma and electron irradiation up to the dose range of 1176 kGy are found to show a change in the present case, where the energy deposited is very high. This indicates degradation or destruction of CTC complexes, which are responsible for the amber color of polyimide and its characteristic absorption below 505 nm. The loss in spectral features
Figure 4.18: UV-Visible Spectra of Pristine and 100 MeV Ag\textsuperscript{7+} Ion Irradiated Polyimide at Different Fluences

at the higher fluences may also be due to higher degree of conjugation or formation of complex functional groups at higher fluences [45]. Moreover, the absorbance at almost all the wavelengths in the UV-Visible regime is found to be increasing with the fluence. The decrease in the optical band gap and increase in the absorbance in UV-Visible regime can be attributed to conjugation (formation of conjugated double bonds) and carbonization (formation of hydrogenated amorphous graphite clusters whose size increases with the fluence). This was further confirmed by the change in color of polyimide, which turned from amber to black with metallic luster with increase in ion fluence. This can be observed in the photographs of the pristine and ion irradiated polyimide films as shown in figure 4.19 [37-39].

Figure 4.19: Coloration of Ion Irradiated Polyimide Films with Different Fluences
(iii) XRD Analysis: As noted in chapter 2, XRD of polyimide does not give sharp peaks in 10-60° region. This may be due to its bulky and aromatic monomer and crosslinked arrangements of polymer chains. The XRD spectra of pristine and 100 MeV Ag⁺ ion irradiated polyimide at different fluences are shown in figure 4.20.

![XRD Spectra](image)

Figure 4.20: XRD Spectra of Pristine and 100 MeV Ag⁺ Ion Irradiated Polyimide at Different Fluences

It is observed from the figure that particularly at the maximum fluence of $5 \times 10^{12}$ ions/cm², the intensity of the broad and diffused XRD peak decreases by almost 21%, and this indicates some sort of amorphisation. This may be either due to distortion in the arrangements of polymers chains or formation of amorphous/disordered graphite clusters due to SHI irradiation [41, 43, 47].

(iv) Contact Angle Measurements: The SHI irradiation induced changes in the surface chemistry and morphology may lead to changes in the wettability of polyimide surface. Thus, contact angle measurements can clarify and give the information of the changes in the surface texture and chemistry of polyimide. Figure 4.21 shows the typical images of a 10 micro-liter drop of distilled water over the surface of pristine and ion irradiated polyimide.
polyimide at the maximum fluence of $5 \times 10^{12}$ ions/cm$^2$. Table 4.4 shows the contact angles of the pristine and ion irradiated polyimide at different fluences.

Figure 4.21: Photographs of a 10 Micro-Liter Water Drop on the Surface of Pristine and 100 MeV Ag$^{7+}$ Ion Irradiated Polyimide at the Fluence of $5 \times 10^{12}$ Ions/cm$^2$

It is observed that, contact angle decrease from its pristine value of 82° to 43°. This decrease is almost 48% and this clearly indicates that 100 MeV Ag$^{7+}$ ion irradiation has induced significant changes in the surface texture and chemistry of polyimide. The decrease in the contact angle i.e. the increase in wettability can mainly be attributed to the introduction of polar groups such as carbonyl, hydroxyl and hydroperoxide on the surface of polyimide [29, 30] and the increased roughness [48, 49]. Although, the FTIR analysis shows decrease in carbonyl groups (decarbonylation), it may be noted that though the carbonyl groups in PMDA are decomposed and released after ion irradiation, the possibility of overall side-by-side oxidation due to radiation induced free radicals can not be ignored. The newly introduced polar carbonyl (or hydroxyl and hydroperoxide) groups after the surface oxidation may have spread more or less uniformly over the entire surface. On the contrary, the carbonyl groups in the pristine polyimide are only restricted to PMDA. Thus, it can be said that after irradiation the polar groups occupy greater surface fraction of polyimide making it successively hydrophilic. This is indicated by increasing values of work of adhesion as shown in table 4.4. Further, as discussed in chapter 3, another reason for decrease in the contact angle is the surface roughening of polyimide, which avails greater effective area of contact between solid and liquid. The SHI irradiation is also known to create latent tracks in the polymers [44]. Therefore, the increased porosity/surface cavities in the polyimide may be responsible for allowing the
water to spread to a greater extent on the irradiated surface. This is indicated by the increasing

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Fluence Ions/cm²</th>
<th>Contact angle (Deg.)</th>
<th>Roughness “r” (r \cos \theta = \cos \theta')</th>
<th>Work of Adhesion (mJ/m²)</th>
<th>Area fraction ((f)) of the liquid solid interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>00</td>
<td>82</td>
<td>1.0</td>
<td>82.9</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>(1 \times 10^{11})</td>
<td>78</td>
<td>1.49</td>
<td>87.94</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>(5 \times 10^{11})</td>
<td>76</td>
<td>1.74</td>
<td>90.41</td>
<td>1.09</td>
</tr>
<tr>
<td>4</td>
<td>(1 \times 10^{12})</td>
<td>73</td>
<td>2.1</td>
<td>94.1</td>
<td>1.14</td>
</tr>
<tr>
<td>5</td>
<td>(5 \times 10^{12})</td>
<td>43</td>
<td>5.25</td>
<td>126</td>
<td>1.52</td>
</tr>
</tbody>
</table>

Table 4.4: Contact angle, Work of Adhesion, Roughness and Area Fraction of the Liquid Solid Interface of Pristine and 100 MeV Ag⁺ Ion Irradiated Polyimide at Different Fluences

\[W_a = \gamma_{lg}(1 + \cos \theta)\]

\[\cos \theta' = f \cos \theta + f - 1\]

\(\gamma_{lg}\) = Surface tension of liquid gas interface = 72.8 mJ/m²

\(\theta\) = Contact angle of the flat pristine sample

\(\theta'\) = Contact angle of the rough sample after irradiation

values of the area fractions of the liquid solid interface with the ion fluence, which is shown in table 4.4.

(v) SEM Analysis: Figure 4.22 shows the SEM images of pristine and 100 MeV Ag⁺ ion-irradiated polyimide at different fluences. The magnification is \(\times 5000\). It can be clearly observed that the degree of surface roughening/imperfection increases with the fluence. The surface of ion-irradiated polyimide is observed to consist of globules, cavities, blisters and voids of various sizes. As discussed in chapter 2 and 3, this attributes to SHI induced scissioning and cross linking on the surface of polyimide, which is responsible for sputtering on the surface (uneven evolution of gases) and corresponding molecular rearrangements as well as change in surface free volume.
Another reason behind surface roughening may be thermal effects induced by SHI irradiation [35-37].

**4.8 Conclusion:** Both polypropylene and polyimide have shown significant modifications in the surface and bulk properties after 100 MeV Ag$^{7+}$ ion irradiation. However, though both the polymers are subjected to similar radiation with similar fluence under the same conditions, the changes in physicochemical properties are found to be qualitatively and quantitatively different for polypropylene and polyimide. For polypropylene, the FTIR spectra show rigorous scissioning of C-H and C-C bonds, however, oxidation/carbonylation effects are not noticeably observed. Whereas, UV-Visible spectra have shown 37% reduction in the band gap and also increase in the absorbance. This mainly attributes to the carbonization. XRD spectra show significant increase in overall crystallinity which indicates the increase in the fraction of crystalline zones at the expense of amorphous ones. The PL spectra show decrease in the intensity of emission as well as excitation peaks which reveal the disappearance of luminescent centers due to SHI irradiation. Contact angle is found to be increased at the maximum fluence which indicates the increase in hydrophobic properties, due to absence of carbonylation effects, excessive increase in surface roughening and carbon enrichment on the surface. The surface roughening is confirmed in SEM analysis. Thus 100 MeV Ag$^{7+}$ ion irradiation can induce several desirable changes in the structure and properties of polypropylene namely, prominent increase in overall crystallinity, significant decrease in optical band gap and increase in the hydrophobicity of the surface.

Further, polyimide, which is generally known to be radiation resistant polymer, has also shown significant modifications in the surface as well as bulk properties after
100 MeV Ag\textsuperscript{7+} ion irradiation up to fluence of 5×10\textsuperscript{12} ions/cm\textsuperscript{2}. FTIR analysis clearly shows overall decrease in the intensities of C-H, C-N, N-H, O-H, C=O, C=C and C-O-C bonds but with different rates. UV-Visible spectra shows 6% decrease in optical band gap and overall increase in the absorbance in the UV-Visible regime. This is attributed to carbonization and conjugation, which is confirmed by darkening of polyimide films with the ion fluence. XRD spectra signify overall amorphisation due to formation of disordered graphite clusters. Contact angle decreases by 48% at the maximum fluence, and this ascribes to formation of polar groups on the surface and increased porosity. The increased roughness is confirmed in SEM analysis. It appears that a few properties, particularly the band gap and hydrophilicity of polyimide could be tailored by using 100 MeV Ag\textsuperscript{7+} ion irradiation.

References


D. C. Tayal, “Nuclear Physics”, Himalaya Publishing House, India, 2005


B. T. Kelly, Irradiation Damage to Solids, Pergamon, New York


Methods in Physics Research B, 236, (2005), 456-460


47 M. Guenther, G. Gerlach, G. Suchaneck, K. Sahre, K. -J. Eichhorn, B. Wolf, A. Deineka, L. Jastrabik, “Ion-Beam Induced Chemical and Structural Modifications of
Polymers” Surface Coating and Technology, 158-159, (2002), 108-113
