Chapter 3

MeV Electron Irradiation Induced Physicochemical Changes in Isotactic Polypropylene and Polyimide

Thin films of polypropylene and polyimide were irradiated with 6 MeV pulsed electron beam in the fluence range varying from $0.5 \times 10^{15}$ to $2.0 \times 10^{15}$ electrons/cm$^2$ and $1.0 \times 10^{15}$ to $4.0 \times 10^{15}$ electrons/cm$^2$ respectively. The pre and post irradiated samples were characterized using various techniques such as FTIR, UV-Visible, EDS spectroscopy, XRD, SEM, contact angle measurements and stress-strain analysis. In case of polypropylene, the FTIR analysis shows scissioning of C-H and C-C bonds at lower fluences and crosslinking at higher fluences. The typical carbonyl groups appear at 1725 cm$^{-1}$ and this signifies oxidation, which is confirmed in EDS analysis. The UV-Visible analysis shows a decrease in band gap signifying carbonization. In surface properties, the contact angle is found to decrease from 83° to 63°. This is due to surface oxidation and surface roughening which is also confirmed in SEM and FTIR. The surface hardness shows 20% increase which is due to graphitization on the surface. Interestingly, polyimide irradiated with the same radiation under identical conditions, but at higher fluences shows a different behavior, particularly in bulk mechanical properties. Whereas, the stress-strain based bulk mechanical properties of polypropylene show a degradation, these properties are found to be noticeably improved in case of polyimide. This attributes to aromatic nature of polyimide, which may have favored crosslinking. In the surface properties, the contact angle decreases from 59° to 32°. This is due to surface roughening which is confirmed in AFM and profilometry. This study leads to a definite conclusion that the polypropylene and polyimide, which are aliphatic and aromatic polymers respectively show remarkably different responses under 6 MeV electron irradiation.
3.1 **Background and Purpose:** One of the aims of this thesis is to investigate the effects of radiations having increasing energies and increasing energy losses on the structure and properties of polypropylene and polyimide which represent polymers of aliphatic and aromatic categories respectively. The radiations which are chosen for this purpose are Co-60 gamma rays, 6 MeV electrons and 100 MeV Ag\(^{7+}\) ions. This chapter reports investigations on the 6 MeV electron beam induced physicochemical changes in isotactic polypropylene and polyimide. The energy deposition mechanism of high electron radiation is distinctly different from those of non-particulate radiations such as gamma rays and x-rays and particulate radiations such as protons, alpha rays and heavy ions. Though high energy electrons have lesser penetration depth than gamma rays, their stopping power (dE/dx) is fairly large as compared to gamma rays. This is due to three reasons... (i) The energy of 6 MeV electrons is fairly larger than Co-60 gamma rays (which have energies 1.17 MeV and 1.33 MeV) (ii) Whereas gamma rays can sometimes pass through the matter without interacting with atoms, the electrons due to their charge must interact with the atoms. The electrons have their own electric field and hence can interact with the atoms through Coulombic potential. High energy electrons can thus produce more uniform and densely distributed defects while passing through the matter. (iii) In addition to ionization-excitation, electrons lose their energy by one additional radiative mechanism called as Bremsstrahlung. In radiation processing, high energy electron radiation has a few distinct advantages over gamma radiation, a few of which are... (a) Due to stronger interaction, high electron radiation has higher dose rates than gamma radiation. Due to this, large energy can be deposited over small time intervals ranging from fraction of a second to a few minutes. This increases the possibility of crosslinking, as oxidation effects are relatively weak at high dose rates. Whereas, in case of gamma radiation longer treatment times allow continuous diffusion of oxygen and thus more oxidative reactions (b) The dose rate of electron radiation remains constant over the period of time (c) The machine parameters of electron beam sources can be controlled. (d) electron beam machines have the facilities of on-off control (e) electron beam can be focussed [1-3].

3.2 **High Energy Electron Beam Facility: The Race Track Microtron:** The 6 MeV electron beam used for irradiation of polypropylene and polyimide was obtained from
Race Track Microtron at Department of Physics, University of Pune, India. Microtron is a re-circulating electron accelerator in which an electron beam is passed repeatedly through RF accelerating cavity by using magnetic field. The energy gain depends upon the electric field in the accelerating cavity and number of orbits. The advantage of Microtron over LINACs is superior beam current with good energy resolution. Figures 3.1 and 3.2 (a and b) show the schematic diagram and photographs of Race Track Microtron. The various parts, typical operating parameters and overall working of the Race Track Microtron in the Department of Physics, University of Pune is described below

(i) **Electron Gun:** The electrons are generated by using the filament, by indirect heating and then pulled by intense electric field. The anode energizes the electrons; these electrons are then drawn in the RF cavity by using pole pieces. The typical operating potential of the electron gun is 25 KV.

(ii) **RF Cavity:** The electrons are accelerated in the cavity due to RF power obtained by using a 1 MW pulsed Magnetron. The electrons are accelerated when the RF power reaches peak. The energy gained in each passage is 1 MeV. The magnetron and the electron are pulsed, due to which the electron beam occurs in pulses of approximately 1.6 μSec to 2 μSec duration with repetition rate of 50 pps. The operating RF frequency of pulsed magnetron is 2.76 GHz.

(iii) **Sector Magnets:** The magnetic field is applied using four sector electromagnets having a pole gap of 0.7 cm. The magnetic field in the pole gaps is 0.15 T. The RF cavity is placed in field free region. The magnetic field by the sector magnets makes the electrons to travel in elongated circular paths i.e. circular in magnetic field and straight in field free region. Due to circular paths, the electrons are repeatedly passed through the cavity, which is on one side of all orbits. The RF power supplied by the magnetron accelerates i.e. energizes the electrons to approximately 1 MeV in each passage. Thus electrons in magnetic field will cover the trajectory with ever increasing radius, which are all tangent to RF cavity. In every orbit the
Figure 3.1: The schematic Diagram of Race Track Microtron

![Schematic Diagram of Race Track Microtron](image)

Figure 3.2 a: The Photograph of Race Track Microtron

![Photograph of Race Track Microtron](image)
electron gains the energy as all orbits pass through the cavity. The electrons are extracted at the end of sixth orbit due to which the effective electron energy of the electron beam in the Race Track Microtron is 6 MeV. The peak beam current is 10 mA. The beam diameter can be varied from 1 to 6 mm.

(iv) **Extraction Port and Faraday Cup:** Faraday cup is used to analyze the electron beam. It can intercept any orbit.

(v) **Control Panel:** All operating parameters are optimized together to achieve resonance conditions so that electrons acquire maximum energy in every orbit and successively extracted in the final orbit without loss. The entire operation of Race Track Microtron can be controlled and monitored using Control Panel. The machine is operated under high vacuum (10^-6 torr) and has proper radiation shielding.

[4, 5]

### 3.3 Interaction of High Energy Electrons with Matter:

As discussed earlier, the interactions of all non-particulate as well as particulate radiations with matter mainly results in energy transfer to the absorber, and this energy transfer is fundamentally due to their interactions with the target atoms. The energy transferred by a given radiation
depends upon the dE/dx i.e. LET (Linear Energy Transfer) and the penetration power i.e. range of the radiation in the target. The interaction of electrons with matter is different from those of other non-particulate radiation such as gamma rays as well as heavy particulate radiation such as protons or alpha particles or neutrons. In case of gamma rays and x rays the energy loss (attenuation or absorption) occurs by either photoelectric effect, Compton scattering or pair production depending upon the radiation energy and the target. Whereas, electron being a charged particle has its own electric field and therefore interacts with the atoms through Coulombic potential. There are four different mechanisms by which an energetic electron can interact with the matter.

3.3.1 Inelastic Collisions with Electrons: This is the most important mechanism by which electrons lose their energy. During such inelastic collisions, incident electron transfers part of its energy to a bound atomic electron taking it to excited state (excitation) or unbound state (ionization). This process is predominant when electrons have relatively low energies (E < m_0c^2 ~ 1 MeV). The energy loss (LET) due to ionization-excitation (inelastic collisions) is given by Bethe’s formula

\[
\left(-\frac{dE}{dx}\right)_{\text{ion}} = \frac{ne^4Z}{8\pi(e_0)^2}mV^2 \left[ \ln\frac{mV^2K}{2I^2(1-\beta^2)} - \frac{2\sqrt{1-\beta^2}}{1+\beta^2}\ln2 + 1 - \beta^2 + \cdots \right].
\]

Where I is the average excitation energy of electron, K is the kinetic energy, V is the speed of electron, \( \beta = \frac{V}{c} \) and n is the number of electrons per unit volume. The secondary electrons produced in this process further interact with the matter.

3.3.2 Radiative Collisions of Electrons with Atomic Nucleus: Incident electron passing through the field of atomic nucleus experiences a deflection with resultant emission of electromagnetic radiation. This process is known as Bremsstrahlung. This process is dominant at higher energies (E > m_0c^2 ~ 1 MeV i.e. relativistic energies). This leads to a loss of kinetic energy of the incident electron. This can be considered as a radiative type of inelastic collision between the electron and the nucleus. In addition there is also a probability that the electrons can excite the nuclei in a similar inelastic collision. However the cross section of this process is low. Bethe has shown that when K >> mc^2 (relativistic energies), the differential energy loss due to Bremsstrahlung (continuous x-
radiation primarily from acceleration of the electrons in the electric field of nuclei) is
given by

\[ \left( -\frac{dE}{dx} \right)_{\text{rad}} \approx \frac{4Ze^6nK(Z+1.3) \ln\left(183Z^{-1/3}\right)+\frac{1}{8}}{[4\pi(e_0^2)]^4\hbar^2c^5} \]

\[ \text{... (3.2)} \]

Where \( n \) is the number of atoms per unit volume of atomic number \( Z \). The radiation loss
is proportional to the kinetic energy \( K \) of the electron, whereas the ionization loss is
proportional to \( \ln K \) and inversely proportional to square of the velocity. Thus the
radiation loss increases very much more rapidly with \( K \) than the ionization loss. It can
be seen that for light elements and low electron energies the collisional energy loss
predominates and radiative losses, which varies with \( Z^2 \), start becoming comparable only
at high electron energies and heavy targets. The Bremsstrahlung energy loss is less
dominant for polymers. The radiative energy loss is negligible for heavy charged
particles like protons, alpha particles etc. as it is inversely proportional to square of the
mass of the incident charged particle.

3.3.3 Elastic Collisions with Atomic Electrons and Nucleus: The incident electrons can
have an elastic collision with a nucleus resulting in a deflection of electron without any
radiative loss or excitation of the nucleus. Here the electron is just scattered at 45° due to
cloud of atomic electrons. The elastic scattering due to nucleus results in to
backscattering i.e. the scattering angle is 90°. The elastic scattering from electrons or
nucleus does not result in energy loss. However these collisions have very small
crosssection.

Electrons being lighter particles suffer deflections at considerably large angles
due to collisions and scattering. Therefore the path of electrons is not straight. Further,
because of their extensive straggling and the large statistical fluctuations in the results of
their collisions with the absorber, it is not possible to determine a range of high energy
electrons in the precise way possible with the heavier charged particles. Moreover, the
energy loss straggling results in a wide distribution for the quantity \( R \), even for the
monoenergetic incident electrons. Because of the large deflections the range \( R \) along the
trajectory of an electron of a given energy exceeds appreciably the average thickness of absorber, which it can penetrate [6-9].

3.3.4 Defects Produced by the Electrons: As discussed earlier the interaction of electrons with atoms results in ionization. During ionization rest of the atom gets recoil and is displaced from its position. The displacement of an atom requires a threshold energy $E_d$ for its displacement, if impinging particle possesses this much energy, the atom is displaced. This displaced atom acts as interstitial atom and is located between lattice sites, and the empty lattice site forms the vacancy. Introduction of vacancies and interstitials change the band structure of the material due to change in bond length and the distance between the atoms. Interstitial atoms, vacancies, the change in band structure results in defects. Energetic electrons with energies around 1 MeV are able to produce displacements by direct interaction through coulomb potential with the nuclei of the target. Electrons with energy in the range of MeV should be treated using relativistic mechanics. The mass of the nucleus is very much greater than that of electron therefore collision with the nucleus only alters the direction of electron. If the electron with kinetic energy $E$, is deflected through angle $\theta$, then the energy transferred to the nucleus of mass $M$ is

$$E_{nuc} = \frac{2m_e}{Mm_c^2} \left( E + 2m_e c^2 \right) E \sin^2 \left( \frac{\theta}{2} \right)$$ \hspace{1cm} \text{...(3.3)}$$

Where $m_e$ is the mass of electron and $c$ is the speed of light. The above equation can also be expressed as

$$E_{nuc} = E_{nucm} \sin^2 \left( \frac{\theta}{2} \right)$$ \hspace{1cm} \text{...(3.4)}$$

Where $E_{nucm}$ is the maximum possible energy that could be transferred. For practical purpose $E_{nucm}$ is taken as

$$A E_{nucm} = 560.8 \times (x+2)$$ \hspace{1cm} \text{...(3.5)}$$
Where is $A$ is the atomic mass number of the target and $x = E/m_e c^2$. Let $E_{em}$ be the minimum electron energy to produce displacements then

$$E_d = 2\times \frac{m_e}{M} \times \frac{E_{em}}{m_e c^2} \times (E_{em} + 2m_e c^2)$$

... (3.6)

Or in terms of practical units

$$E_d = \frac{E_{em}(E_{em} + 1.022 \times 10^6)}{470 \times 10^6}$$

...(3.7)

The electron nucleus interaction is through Coulomb potential as; at high electron energies the atomic electrons can be neglected. The Coulomb interaction gives rise to the Rutherford scattering of electrons. If $E_{nuc}$ is only slightly greater than $E_d$ each collision displacing an atom produces only primary displacement and hence the damage is also simplest. In this case the displacement cross-section is given by

$$\sigma_d = \frac{\pi b^2}{4} \left( \frac{E_{nuc}}{E_d} \right)$$

$$\sigma_d = 5.55 \left( \frac{Z^2}{A} \right) \times 10^{-24} \text{cm}^2$$

...(3.8)

Where, $b = \frac{2Ze^2}{m_e v^2 \left( 1 - \frac{v^2}{c^2} \right)}$

The impinging electrons are slowed down rapidly in the solid as they lose their energy to the electrons of the solid. Therefore, the irradiation damage can be produced only in very thin samples of the order of few millimeters, through which these electrons can pass. Now if the ratio $E_{nuc}/E_d$ is greater than 1 then the primary knock on may produce further displacements.

As the electrons pass through the medium they loose their energy in ionizing atoms and radiative collisions. During the interaction with the material, the electron gets deflected many a times and therefore it is really difficult to calculate its range in the material. The empirical relation for the range of electrons in a material is
\[ R \left( \frac{mg}{cm^2} \right) = (530 \times E)^{-106} \quad \cdots (3.9) \]

Where \( E \) is the energy of electrons in MeV. This relation holds good for electron energies from 1 MeV to 20 MeV. The irradiation damage is produced uniformly by the electrons if the sample thickness is chosen in such a way that \( \sigma_d \) does not vary much throughout the sample [10].

**3.4 6 MeV Electron Beam Induced Physicochemical Changes in Polypropylene.**

**3.4.1 Introduction and Literature Survey.** A literature survey indicates that there are a few reports on investigations on effects of gamma, electron and ion radiations on polypropylene [11-16]. For example, in reference [11] Svorcik et al have reported the effects of 14.89 MeV electron irradiation on polyethylene and polystyrene in the dose range of 57.6 kGy to 576 kGy, where polyethylene has shown greater red shift in absorption edge of the UV-Visible spectra as compared to polystyrene. Misra et al have reported enhancement in the thermal properties of 2 MeV electron irradiated polypropylene at the dose of 23 kGy, which has been attributed to crosslinking [12]. An increase in dielectric constant and dielectric loss has been observed for polypropylene irradiated by 1.5 MeV electron beam at the dose levels of 295 and 1080 kGy [13]. In report [14] polypropylene has been irradiated by 1.5 MeV electrons in the dose range from 5 to 120 kGy, and it has shown slight improvement in crystallinity and 10% decrease in the optical band gap. Polypropylene irradiated by gamma rays and ions have also shown considerable modifications in properties [15, 16]. However, the radiation effects on polymers are extremely specific to type of radiation with it’s energy, dose rate and deposited dose and therefore, more investigations are needed as far as the radiation energy, mode of energy deposition and energy densities are concerned. In particular, the effects of high energy pulsed electron irradiation on mechanical properties such as surface hardness and surface roughness of polypropylene need more attention. Therefore, in this part the effects of 6 MeV pulsed electron irradiation on optical, mechanical and structural properties and bulk as well as surface morphology of isotactic polypropylene
have been systematically studied and discussed in the fluence range from \(0.5 \times 10^{15}\) to \(2.0 \times 10^{15}\) electrons/cm\(^2\).

### 3.4.2 Experimental Details:
Thin films of isotactic polypropylene having approximately 400-micron thickness were obtained using compression moulding technique as described in chapter 1. These films were cut in to the strips having size 100 mm\(\times\)15 mm\(\times\)400 \(\mu\)m for stress strain measurements. For all other characterizations the films having size 15 mm\(\times\)15 mm\(\times\)400 \(\mu\)m were used. These samples were irradiated with 6 MeV electron beam from Race Track Microtron in Department of Physics, University of Pune, India. The diameter of the beam was approximately 15 mm. The strips for mechanical measurements were irradiated at the centre, while the other samples having size 15 mm\(\times\)15 mm\(\times\)400 \(\mu\)m were uniformly exposed to the electron beam. The average beam current was 0.1 \(\mu\)A, while the pulse duration and pulse rate were 2 \(\mu\)Sec and 100 pps respectively. The irradiation was carried out in air and at room temperature. The electron fluence was varied from sample to sample from \(0.5 \times 10^{15}\) to \(2.0 \times 10^{15}\) electrons/cm\(^2\). ESTAR programme was used to estimate the stopping power and range of 6 MeV electrons in polypropylene and accordingly the stopping power is 2.065 MeV-cm\(^2\)/g and the respective range is estimated to be 3.27 cm. From these values, the doses and deposited energy densities (MeV/cm\(^3\)) were calculated by using formulae as given in eqns (3.10) and (3.11) and are as shown in table 3.1.

\[
\text{Dose (Rad)} = \text{fluence} \times 1.6 \times 10^{-8} \times \text{Stopping power} \quad \ldots (3.10)
\]
\[
\text{Energy density} = \text{fluence} \times \text{stopping power} \quad \ldots (3.11)
\]

The pristine and electron irradiated polypropylene films were characterized using various techniques such as FTIR, UV-Visible, XRD, SEM, contact angle, hardness (IRHD) and stress-strain measurements. The methodology and the specifications of the instruments used in various characterizations is same as given in chapter 1.

### 3.4.3 Results and Discussion:

(i) **FTIR Analysis:** Figure 3.3 shows the FTIR spectra of pristine and electron irradiated
<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Fluence (electrons/cm²)</th>
<th>Dose (kGy)</th>
<th>Energy density (MeV/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pristine (00)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.5×10¹⁵</td>
<td>165.2</td>
<td>0.93×10¹⁵</td>
</tr>
<tr>
<td>3</td>
<td>1.0×10¹⁵</td>
<td>330.4</td>
<td>1.86×10¹⁵</td>
</tr>
<tr>
<td>4</td>
<td>1.5×10¹⁵</td>
<td>495.6</td>
<td>2.79×10¹⁵</td>
</tr>
<tr>
<td>5</td>
<td>2.0×10¹⁵</td>
<td>660.8</td>
<td>3.72×10¹⁵</td>
</tr>
</tbody>
</table>

Table 3.1: Fluence, Doses and Energy Densities Deposited by 6 MeV Electron Radiation in Polypropylene

Polypropylene. The Y scale in the figure is appended for the comparison.

![FTIR Spectra](image)

**Figure 3.3: FTIR Spectra of Pristine and 6 MeV Energy Electron Irradiated Polypropylene**

As mentioned in chapter 2, the absorbance in the region 2850-2950 cm⁻¹ corresponds to CH₃, CH₂, CH stretching, while the peaks in the region 1450-1480 cm⁻¹ are due to CH₃ and CH₂ bending. Various weak, medium and strong peaks in the region 809 to 1377 cm⁻¹.
correspond to CH₃, CH₂, 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 [17, 18]. A precise comparison of pristine and electron irradiated polypropylene reveals that the absorbance corresponding to both C-H stretching and bending vibrations in the regions 2800-3000 cm⁻¹ and 1450-1480 cm⁻¹ finds a gradual decrease with the fluence. The various small as well as medium peaks in the region 809-1369 cm⁻¹ are also observed to be successively decreased in the intensity. This indicates that high-energy electrons deposit enough energy to scission the C-H and C-C bonds in the polypropylene network. However, a small recovery is also seen at the highest fluence of 2×10¹⁵ electrons/cm², and it may be because of the dominating nature of crosslinking over the scissioning. In general, during irradiation of polymer, the scissioning and crosslinking take place side by side. Depending upon the type of radiation, dose rate and environment, either crosslinking or scissioning may dominate at higher fluences. If the dose rate of electron irradiation is comparatively high then the large dose can be delivered within very short time intervals. As a result, during irradiation process itself, the highly reactive products such as free radicals, can react with themselves to a greater extent than the oxygen. Consequently, at higher electron fluence, crosslinking may dominate over the oxidation. Another prominent and clear observation is the peak appeared at 1725 cm⁻¹, which is found to be present in the spectra at all the fluences, and observed to be marginally increasing with the fluence. This particular fact indicates that a fraction of the free radicals generated due to electron irradiation have also reacted with oxygen [18, 19]. The oxidation effects were further confirmed in energy dispersive spectroscopy, the results of which are shown in figure 3.4. In this figure, the oxygen contents in polypropylene are found to be increased steadily with the fluence and the net increase is from pristine value of 2.13 % to 5.84 %. However, in our case the specific absorption corresponding to hydroxyl (3400 cm⁻¹) group was not recorded and this may be due their less concentration, which could therefore not be detected. It may also be noted that the gas evolution during irradiation has always a higher yield for hydrogen as compared to carbon. A comparison of FTIR and EDS spectra of gamma irradiated polypropylene (figures 2.11 and 2.15 in chapter 2) and electron irradiated polypropylene
Figure 3.4: EDS Spectra of Pristine and 6 MeV Energy Electron Irradiated Polypropylene

indicates that electron irradiation has deposited higher doses as compared to gamma irradiation, however the oxidation effects are comparatively lower in case of electron irradiation than gamma irradiation. This is due to the fact that electron irradiation in this case has a high dose rate. As a result large doses can be deposited in smaller time intervals. In such cases the continuous diffusion of oxygen during irradiation process (which results in strong oxidation effects) is comparatively lower than that in case of slow dose rate/longer irradiation period cases.

(ii) UV-Visible Spectroscopy: Figure 3.5 shows the UV-Visible spectra of pristine and electron irradiated polypropylene. The Y scale in the figure is appended for the comparison. A significant red shift is observed in the absorption edge from the pristine value of 240 nm to 380 nm at the maximum fluence of $2 \times 10^{15}$ electrons/cm$^2$. This corresponds to the decrease in optical band gap from 5.17 to 3.27 eV. The absorption of radiation in UV-Visible region is mainly due to the promotion of electrons from $\sigma$, $\pi$, and $\pi$ bonds to their own excited states. The high energy electron irradiation induced ionization and excitation of polymer molecules leads to the several possible reaction events between the excited and ionized species and creates more unsaturated sites.
involving conjugation or double bonds [11]. Moreover, the irradiated polymer matrix also contains several non-bonding electrons and favors low energy level transitions such as $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ etc. to a greater extent [20]. Apart from this, scissioning of bonds due to electron irradiation also results in to the evolution of gases from the surface of polypropylene. In such a case of aliphatic polymers, which contain most of the hydrogen and carbon, the evolution of hydrogen should occur predominantly as compared to carbon, as C-H bonds are scissioned more readily than the C-C bonds. This leads to increase in C:H ratio and generates several carbon-enriched clusters in the polymer matrix. The residual carbon left in polypropylene acquires graphite like form. Therefore, conjugation and carbonization seem to be main processes responsible for decrease in the band gap of polypropylene [14, 21]. A comparison of UV-Visible spectra of gamma irradiated polypropylene (figure 2.13, chapter 2) and electron irradiated polypropylene indicates that the decrease in band gap in case of gamma radiation is 26% while in the present case it is 37%. This indicates that electron irradiation, which has deposited comparatively higher energy in terms of bond breaking , has been responsible for a comparatively greater decrease in the band gap. Thus the carbonization and conjugation occurs to a greater extent in case of high energy electron irradiation.
(iii) XRD Analysis: The XRD spectra for pristine and electron irradiated polypropylene are shown in Figure 3.6. The Y scale in the figure is appended for comparison. The XRD pattern confirms the established α-monoclinic form of the polypropylene. The crystalline peaks observed at 2θ values of 14.3°, 17.3°, 19° and 22° are due to (110), (040), (130) and (041) planes respectively [22, 23].

![Figure 3.6: XRD Spectra of Pristine and 6 MeV Electron Irradiated Polypropylene](image)

The comparison of spectra indicates that, there is no major change observed in the height, width and positions of XRD peaks after electron irradiation. This shows that overall crystallinity of polypropylene is not affected to a large extent. However, the XRD spectrum of polypropylene irradiated at the maximum fluence of $2 \times 10^{15}$ electrons/cm$^2$ reveals that, the height of (110) peak at $2\theta = 14.5^\circ$ has marginally decreased and a new peak at $2\theta = 16.36^\circ$ has appeared with sufficient intensity. This attributes to the reorganization of polymer chains, due to scissioning and crosslinking. Moreover, electron irradiation does not affect all the regions of the polymers to the same extent, but the amorphous zones of the polymers, which contain mostly the tie molecules, are more vulnerable to high energy electrons. When these tie molecules are scissioned under the...
electron irradiation, the strain on the crystallites may be relieved, then it may facilitate the reorganization of crystalline and amorphous zones. Furthermore, the scissioning of these bonds and the local mobility of free radicals thus being generated can cause their displacement amongst the crystalline planes. As a result, some of the crystalline planes may deplete in the atoms and others may get enriched. This fact explains the decrease in the intensity of (110) peak and the increase in the intensity of newly appeared peak at $2\theta = 16.36^\circ$ [24].

(iv) Surface Morphology: (SEM analysis): Figure 3.7 shows the SEM images of the surface of pristine and electron irradiated polypropylene. It can clearly be seen from

![SEM Images of Pristine and Electron Irradiated Polypropylene](image)

Pristine 5x10$^{14}$ el/cm$^2$ 1.0x10$^{15}$ el/cm$^2$ 1.5x10$^{15}$ el/cm$^2$ 2.0x10$^{15}$ el/cm$^2$

**Figure 3.7: SEM Images of Pristine and 6 MeV Energy Electron Irradiated Polypropylene (Magnification ×5000)**

the images that the degree of roughness/imperfection of the surface of polypropylene increases with the electron fluence. Especially, the surface of irradiated polypropylene is observed to be consisting of defects in the form of voids, blisters globules and cracks of varying sizes. This indicates that high-energy electron irradiation has induced scissioning and crosslinking on the surface within the thickness of a few micron. The scissioning of bonds is mainly responsible for evolution of gases i.e. sputtering of surface particles/erosion from the surface of polypropylene. The evolution of gases or erosion rate may have different yields at different positions on the surface of polypropylene. Moreover, the high electron induced free radicals on the surface of polypropylene can react with themselves and the oxygen. Therefore, this uneven evolution of gases from the surface, crosslinking and oxidative embrittlement on the surface results in to the surface-defects and corresponding change in the free volume. Overall, these facts are responsible for increase in the surface roughness of the irradiated polypropylene [25, 26].
(v) **Contact Angle:** Figure 3.8 shows typical images of liquid drop of 10 micro-liter volume on the surface of pristine and electron irradiated polypropylene at the maximum fluence of $2 \times 10^{15}$ electrons/cm$^2$.

![Pristine](image1) ![2.0×10^{15} el/cm^2](image2)

*Figure 3.8: Photographs of a 10 Micro-litre Water Drop on the Surface of Pristine and Electron Irradiated Polypropylene*

The contact angle is found to decrease from pristine value of 83° to 63° at the maximum fluence of $2 \times 10^{15}$ electrons/cm$^2$. This further confirms the surface roughening as observed in SEM and oxidation in FTIR analysis. The decrease in contact angle from the pristine value is almost 24% which indicates the hydrophobic nature of polypropylene turned in to hydrophilic after electron irradiation. This mainly attributes to oxidation of the polypropylene surface, which involves formation of carbonyl groups (C=O). Carbonyl groups are known to be polar. This results in the decrease in the contact angle with electron irradiation [27]. Moreover, SEM images have clearly shown considerable surface roughening of polypropylene after irradiation. In general, roughening is known to decrease the contact angle, because water spreads to a greater extent due to tiny cavities and pores on the surface [28]. The increase in roughness avails greater area of contact between the water and the substrate. The formation of polar groups and increased area fraction of the liquid solid interface increases the work of adhesion. The decrease in the contact angle and the corresponding increase in roughness, area fraction of the liquid solid interface and the work of adhesion are shown in table 3.2

(vi) **Hardness:** Figure 3.9 shows the hardness (expressed in terms of IRHD number) of polypropylene irradiated at different electron fluences. (IRHD: International Rubber Hardness Degrees hardness number is a measure of the indentation resistance of
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Fluence (electrons/cm²)</th>
<th>Contact angle (Deg.)</th>
<th>Work of Adhesion (mJ/m²)</th>
<th>Roughness “r”</th>
<th>Area fraction (f) of the liquid solid interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>00</td>
<td>83</td>
<td>81.7</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.5×10¹⁵</td>
<td>77</td>
<td>89.2</td>
<td>1.85</td>
<td>1.09</td>
</tr>
<tr>
<td>3</td>
<td>1.0×10¹⁵</td>
<td>74</td>
<td>92.9</td>
<td>2.26</td>
<td>1.13</td>
</tr>
<tr>
<td>4</td>
<td>1.5×10¹⁵</td>
<td>63</td>
<td>105.6</td>
<td>3.73</td>
<td>1.30</td>
</tr>
<tr>
<td>5</td>
<td>2.0×10¹⁵</td>
<td>63</td>
<td>105.6</td>
<td>3.73</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Table 3.2: Contact angles, Work of Adhesion and Area Fraction of the Liquid Solid Interface of Pristine and 6 MeV Electron Irradiated Polypropylene

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

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

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

Figure 3.9: Variation in Hardness (IRHD) With Different Fluences for Polypropylene Irradiated at 6 MeV Electron Energy
elastomeric or rubber materials based on the depth of penetration of a ball indenter. While measuring IRHD number, an initial contact force is applied to an indenter and the penetration is set to zero. The force is increased to a specified total load and the depth of penetration is measured. The IRHD value is related to the depth of indenter penetration. In many cases, IRHD and Shore A hardness are equivalent. It is observed from the figure that hardness increases with the fluence and increases by almost 20% up to the maximum fluence of $2 \times 10^{15}$ electrons/cm$^2$. Polypropylene is usually considered a polymer, which degrades under irradiation; however, the surface hardness is seen to be increasing with the fluence. This may be due to the fact that high energy electron irradiation induces evolution of gases from the surface of polypropylene due to which the regions near surface may enrich in hydrogenated amorphous carbon clusters (aC:H). This carbonization has been confirmed and supported by the results of UV-Visible spectra where considerable reduction in the band gap of irradiated polypropylene is observed. FTIR has also shown decrease in the intensity of C-H bonds, which has indicated dehydrogenation. Thus, increase in the hardness of polypropylene with electron fluence can be ascribed to the graphitization over the surface [29]. The increase in the hardness may also be because of the total energy density of electrons varying from $0.93 \times 10^{15}$ to $3.72 \times 10^{15}$ MeV/cm$^3$, which is quite high enough. In such a case, density of spurs (zones enriched with highly reactive free radicals), may be sufficient to allow the crosslinking over the surface. Since the electron beam in the present case offers a very high dose rate and can deposit a high energy density in a small time interval during irradiation, it may dominate crosslinking on the surface at the higher fluences.

(vii) Bulk Mechanical Properties: Stress-Strain Measurements: Figure 3.10 shows the stress-strain curves of pristine and electron irradiated polypropylene. The curves for higher doses could not be measured, as the samples became too fragile to handle. Figures 3.11 (a, b, c and d) show that the bulk mechanical properties based on stress-strain curves such as tensile strength, percentage elongation, Young’s modulus and strain energy per unit volume respectively are degraded due to electron irradiation. This is due to the
Figure 3.10: Stress-strain Curves of Pristine and Electron Irradiated Polypropylene

Figure (3.11): (a) Tensile strength and (b) Percentage Elongation (c) Young’s Modulus and (d) Strain Energy per Unit Volume of Pristine and Electron Irradiated Polypropylene
scissioning of bonds and the oxidation as observed in FTIR and EDS spectra. Though the bulk mechanical properties show degradation, the surface hardness is found to be enhanced. As discussed in previous section, the enhancement in the surface hardness is due to carbonization on the surface. The evolution of hydrogen gas has higher yield on the surface due to which carbonization takes place to a greater extent on the surface than in the bulk.

3.5 6 MeV Electron Beam Induced Physicochemical Changes in Polyimide:

3.5.1 Introduction and Literature Survey: Polyimide differs from polypropylene in three main respects…(i) the monomer of polyimide is aromatic imide which contains three benzene rings, whereas polypropylene is an aliphatic polymer without benzene rings (ii) The CTC based inter and intra-molecular interaction in polyimide is extraordinarily strong in polyimide and (iii) The presence of four carbonyl groups in the PMDA part of its monomer impart considerable oxidation resistance to polyimide. In previous chapter it is observed that polyimide has shown remarkable stability against gamma radiation up to the dose levels of 230.4 kGy. In this part, an attempt has been made to evaluate the effects of 6 MeV electron radiation on physicochemical properties of polyimide. A literature survey indicates that there are a few attempts to evaluate the effects of high energy radiation on mechanical and the structural properties of polyimide. For example the effects of 3 MeV proton radiation on the mechanical properties of polyimide have been studied in the dose range 0-75 MGy, where the tensile strength and percentage elongation show a degradation [30]. The degradation in the thermal properties of 2 MeV electron irradiated polyimide has been observed at the dose levels of 23 kGy [31]. The effects of 2 MeV electron radiation on the mechanical properties of ten aromatic polymers including polyimide have been studied up to the dose level of 120 MGy, where polyimide has shown maximum radiation stability amongst these ten polymers. [32]. Effects of 4 MeV light ions (\(^{1}\text{H}, {^{4}}\text{He}, {^{12}}\text{C}\)) on hardness and Young’s modulus have shown enhancement up to the fluence of \(10^{16}\) ions/cm\(^2\), which has been attributed to crosslinking [33]. Mechanical properties of four optically transparent polyimides subjected to 1 MeV electron radiation at the dose levels of 18.5 MGy and up to the temperatures of 523 K have been reported, where these polyimides maintained the properties up to the temperature of 450 K and then showed a deterioration [34]. However,
more investigations are needed as far as the radiation energy, mode of energy deposition and energy densities are concerned. In particular, the effects of high energy pulsed electron irradiation on mechanical properties and surface roughness of polyimide needs more attention. To the best of our knowledge there are no reports available on the effects of 6 MeV electron radiation on the bulk and surface properties of polyimide. Therefore, in the present work, the effects of 6 MeV electron irradiation on bulk and surface properties of polyimide are investigated.

3.5.2 Experimental Details: A sheet of polyimide (PMDA-ODA, Kapton, C_{22}H_{10}N_{2}O_{5}, density =1.43 gm/cm^3) having thickness 50 μm was cut into the strips having size 100 mm×15 mm×50 μm for stress strain measurements. For all other characterizations the films having size 15 mm×15 mm×50 μm were used. These samples were irradiated with 6 MeV electron beam from Race Track Microtron. The diameter of the beam was approximately 15 mm. The strips for mechanical measurements were irradiated at the centre, while the other samples having size 15 mm×15 mm×50 μm were uniformly exposed to the electron beam. The electron fluence was varied from sample to sample and was in the range of 1×10^{15} to 4×10^{15} electrons/cm^2. The stopping power and the range of 6 MeV electrons in polyimide, as calculated from ESTAR programme are 1.836 MeV-cm^2/gm and 2.36 cm respectively. From these values, the doses and deposited energy densities (MeV/cm^3) were calculated by using formulae as given in eqns 3.10 and 3.11 and are as shown in Table 3.3.

<table>
<thead>
<tr>
<th>Sr No.</th>
<th>Fluence (el/cm^2)</th>
<th>Dose (kGy)</th>
<th>Energy Density (MeV/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>00</td>
<td>00</td>
<td>00</td>
</tr>
<tr>
<td>2</td>
<td>1.0×10^{15}</td>
<td>294</td>
<td>2.61×10^{15}</td>
</tr>
<tr>
<td>3</td>
<td>2.0×10^{15}</td>
<td>588</td>
<td>5.21×10^{15}</td>
</tr>
<tr>
<td>4</td>
<td>3.0×10^{15}</td>
<td>882</td>
<td>7.83×10^{15}</td>
</tr>
<tr>
<td>5</td>
<td>4.0×10^{15}</td>
<td>1176</td>
<td>10.44×10^{15}</td>
</tr>
</tbody>
</table>

Table 3.3: Fluence, Doses and Energy Densities Deposited by 6 MeV Electron Radiation in Polyimide
Pre and post irradiated samples were then characterized by various techniques. The strips of irradiated polyimide were used for stress-strain measurements, which were performed on tensile testing machine. In this case the load cell was 100 kg, while strain rate and the gauge length was kept 20 mm/min and 50 mm respectively. For pristine as well as irradiated samples, an average of measurements on four samples was taken. From the stress-strain curves various parameters such as tensile strength, percentage elongation, strain energy and Young’s modulus were calculated using the procedures as mentioned in chapter 1. The FTIR measurements were performed for investigating the effects of irradiation on the bond structure. The UV-Visible spectroscopy was carried out for studying the high energy electron beam induced changes in optical properties, especially the band gap. The effects of electron irradiation on the surface properties were studied using three techniques namely contact angle, AFM and profilometry.

3.5.3 Results and Discussion:

(i) Mechanical Measurements: Figure 3.12 shows the stress-strain curves of pristine and 6 MeV electron irradiated polyimide. It is clearly observed that the stress-strain curve become successively large as the electron fluence increases. This indicates that the mechanical properties of polyimide are enhanced after electron irradiation. The various parameters such as tensile strength, percentage elongation, strain energy and Young’s modulus as calculated from the stress-strain curves are shown in Figures 3.13 a, b, c and d respectively. It is observed that the tensile strength, percentage elongation and strain energy increase from the pristine value of 73 MPa to 89 Mpa, 10 % to 22 % and 4.75 MJ/m$^3$ to 14.2 MJ/m$^3$ respectively at the maximum fluence of $4 \times 10^{15}$ electrons/cm$^2$. The relative percentage increments in these parameters are 22 %, 120 % and 199 % respectively. This significant enhancement in the mechanical properties may be attributed to crosslinking. When a polymer is irradiated, both scissioning as well as crosslinking take place side by side. Depending upon the type of polymer, the radiation and the dose rate either scissioning or crosslinking may dominate. In general the aromatic polymers have higher yields for crosslinking than the scissioning [35]. Moreover, the dose rate of 6 MeV electrons was considerably high. In such case the density of radiation induced spurs (zones enriched with highly reactive free radicals) may be high enough to allow the
Figure 3.12: Stress-Strain Curves of Pristine and Electron Irradiated Polyimide

Figure 3.13 Variation in (a) Tensile Strength (b) Percentage Elongation (c) Strain Energy and (d) Young's Modulus with Fluence for 6 MeV Electron Irradiated Polyimide
overlapping of spurs. As a result the free radicals may crosslink with each other [29]. One possible mechanism of electron beam induced crosslinking in polyimide is shown in figure 3.14.

![Possible Mechanism of Electron Beam Induced Crosslinking in Polyimide](image)

Figure 3.14: Possible Mechanism of Electron Beam Induced Crosslinking in Polyimide

Further, the dominance of scissioning or crosslinking depends upon the dose rate and the extent of radiation induced oxidation. If dose rates are high and oxidation effects are weak then crosslinking may dominate over scissioning. Usually, the oxidation effects are weak if the dose rates are high [35]. In addition, due to presence of large concentration of carbonyl groups in the monomer, polyimide has high oxidation resistance [36]. This indicates that the oxidation effects are extremely low due to high dose rate of electron irradiation as well as the oxidation resistance of polyimide. This is another reason why crosslinking has dominated over scissioning, because crosslinking is strong if oxidation effects are low. However, as against the enhancement of tensile strength, percentage elongation and strain energy, the Young’s modulus is found to marginally decrease from its pristine value of 1700 Mpa to 1160 Mpa at the fluence of $3 \times 10^{15}$ electrons/cm$^2$ and then increase up to 1600 MPa at the fluence of $4 \times 10^{15}$ electrons/cm$^2$. The overall decrease is 6 % and can be attributed to the fact that the increase in the percentage elongation is considerably greater than the increase in tensile strength. This may indicate
that the 6 MeV electron irradiation has increased the chain flexibility in polyimide. A comparison between the effects of 6 MeV electron irradiation on the mechanical properties of polypropylene (Figure 3.10 and 3.11) and polyimide show that under the same irradiation and same conditions, polypropylene exhibits a degradation in the bulk mechanical properties, while polyimide shows a gradual and significant improvement in the mechanical properties up to the fluence of $4.0 \times 10^{15}$ electrons/cm$^2$. This difference in the responses is due to the typical structures of these polymers. As explained earlier, the degradation of polypropylene is due to its simple aliphatic structure which favors chain scissioning and oxidation, while, the enhancement in the mechanical properties of polyimide under the same irradiation, but at higher doses is due to its aromatic structure, oxidation resistance and high dose rate of electron radiation which favor crosslinking.

(ii) FTIR, EDS and UV-Visible Spectroscopy: Figure 3.15 shows the FTIR spectra of pristine and electron irradiated polyimide at different fluences. The spectra are appended for comparison.

![FTIR Spectra of Pristine and Electron Irradiated Polyimide](image)

**Figure 3.15:** FTIR Spectra of Pristine and Electron Irradiated Polyimide
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\(^{-1}\), 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 (\(=\text{C}-\text{N}\) stretch). The stretching in imide is observed at peaks near 1380 and 1117 cm\(^{-1}\) and its deformation is observed at 725 cm\(^{-1}\) [26, 37]. It is observed that the absorbance of almost all the bonds remains intact up to the maximum fluence of \(4 \times 10^{15}\) electrons/cm\(^2\). More importantly, the absorbance in the region 1725-1781 cm\(^{-1}\), which corresponds to carbonyl groups, remains unchanged up to the maximum fluence. This mainly indicates that polyimide is not oxidized after irradiation. The absence of oxidation effects are confirmed in EDS analysis as shown in Figure 3.16, where only marginal variations in the oxygen contents are observed.

![Figure 3.16: EDS Spectra of Pristine and Electron Irradiated Polyimide](image)

Figure 3.16 shows the UV-Visible spectra of pristine and electron irradiated polyimide. It is observed that there is no noticeable change in the absorption edge and in the overall absorbance in 700-200 nm region. In general, after high energy radiation the polymers show a red shift in the absorbance edge and overall increase in
the absorbance due to carbonization and oxidation. Thus it is confirmed that the polyimide has retained its bond structure and has not undergone oxidation after high energy electron irradiation.

(iii) Contact Angle: Figure 3.18 shows the images of 10 micro liter drop of distilled water on the surface of pristine and electron irradiated polyimide at the maximum fluence of $4 \times 10^{15}$ electrons/cm$^2$. The contact angles, roughness, work of adhesion and the area fraction of the liquid-solid interface of pristine and electron irradiated polyimide at different fluences are shown in table 3.4. It is observed that the contact angle decreases from its pristine value of $59^\circ$ to $32^\circ$ at the maximum fluence of $4 \times 10^{15}$ electrons/cm$^2$. This decrease is almost 46% and indicates that the 6 MeV electron irradiation has considerably affected the surface properties of the polyimide. The roughness, area fraction of the liquid solid interface and the work of adhesion as calculated using the procedures discussed earlier (section 3.4.3, v). The work of adhesion and the area fraction of the liquid-solid interface are found to be increased with the fluence. The significant decrease in the contact angle, increase in the work of adhesion and the area fraction of the liquid-solid interface mainly attribute to the electron beam induced surface roughening. According to
Figure 3.18: Contact Angle of a 10 Micro-Liter Drop of Distilled Water on The Surfaces of (A) Pristine and (B) Electron Irradiated Polyimide at The Fluence of $4 \times 10^{15}$ e/Cm$^2$

| Sr. No. | Fluence el/cm$^2$ | Contact angle (Deg.) | Work of Adhesion (mJ/m$^2$) | Roughness “r” $\cos\theta' = r \cos\theta$ | Area fraction ($f$) of the liquid solid interface $\cos\theta' = f \cos\theta + f - 1$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>00</td>
<td>59</td>
<td>1</td>
<td>1.0</td>
<td>110.3</td>
</tr>
<tr>
<td>2</td>
<td>$1.0 \times 10^{15}$</td>
<td>51</td>
<td>1.2</td>
<td>1.075</td>
<td>118.6</td>
</tr>
<tr>
<td>3</td>
<td>$2.0 \times 10^{15}$</td>
<td>49</td>
<td>1.27</td>
<td>1.093</td>
<td>120.6</td>
</tr>
<tr>
<td>4</td>
<td>$3.0 \times 10^{15}$</td>
<td>35</td>
<td>1.59</td>
<td>1.201</td>
<td>132.4</td>
</tr>
<tr>
<td>5</td>
<td>$4.0 \times 10^{15}$</td>
<td>32</td>
<td>1.65</td>
<td>1.210</td>
<td>134.5</td>
</tr>
</tbody>
</table>

Table 3.4: Contact angles, Work of Adhesion and Area Fraction of the Liquid Solid Interface of Pristine and 6 MeV Electron Irradiated Polyimide

- $\gamma_{lg}$ = Surface tension of liquid gas interface = 72.8 mJ/m$^2$
- $\theta$ = Contact angle of the flat pristine sample
- $\theta'$ = Contact angle of the rough sample after irradiation

Wenzel equation ($\cos\theta' = r \cos\theta$), if the surface is hydrophilic ($\theta < 90^\circ$) then the contact angle decreases with increase in surface roughness. The increased roughness avails a greater area fraction for the contact between the solid and liquid [28, 38]. This results in
decrease in the contact angle. A significant decrease in the contact angle indicates that polyimide surface can be made significantly hydrophilic by using high energy electron irradiation. The polyimide surface with increased hydrophilicity can be used for applications such as grafting, adsorption or adhesion of organic or inorganic species on the surface.

iv. AFM and Profilometry: The electron irradiation induced surface roughening which is responsible for decrease in contact angle, is confirmed in AFM and profilometry. Figures 3.18 and 3.19 show the AFM images and surface profilograms of pristine and electron irradiated polyimide at the fluence of $4 \times 10^{15}$ electrons/cm$^2$.

![AFM Images](image1.png)

**Figure 3.19:** AFM Images (a) Pristine and (b) Electron Irradiated Polyimide at the Fluence of $4 \times 10^{15}$ el/cm$^2$

![Surface Profilograms](image2.png)

**Figure 3.20:** Surface Profilograms of (a) Pristine and (b) Electron Irradiated Polyimide at the Fluence of $4 \times 10^{15}$ el/cm$^2$

In both the figures it is observed that the surface roughness increases after electron irradiation. The roughness average $R_a$ as calculated from the profilograms in Figure 3.19
is found to increase from 0.06 μm to 0.1 μm. This surface roughening is attributed to radiation induced sputtering/erosion of molecules i.e. evolution of gases from the surface. The erosion takes place to different extent in different regions. Further, the scissioning and crosslinking on the surface causes the molecular rearrangements on the surface. This follows the change in free volume and induces surface defects, which increases the surface roughening [25, 26].

3.6 Conclusion: The physicochemical properties of 6 MeV electron irradiated polypropylene and polyimide have been studied in the fluence range of $0.5 \times 10^{15}$ to $2.0 \times 10^{15}$ electrons/cm$^2$ and $1.0 \times 10^{15}$ to $4.0 \times 10^{15}$ electrons/cm$^2$ respectively. Both these polymers have shown considerable modifications after high energy electron irradiation, however the modification is found to depend upon the chemical structure and morphology of these polymers.

The FTIR analysis of electron irradiated polypropylene shows scissioning of bonds and the oxidation effects. The UV-visible spectra show 37% decrease in band gap, which is ascribed to conjugation and carbonization. Both the surface properties show improvement upon electron irradiation. The contact angle decreases from 83° to 63°, and this is due to formation of oxidation based polar groups on the surface and the roughening which is confirmed in FTIR, EDS and SEM. The hardness is found to increase by 20%, which is due to graphitization and crosslinking on the surface. Interestingly, polyimide irradiated with the same radiation under same conditions, but at considerably higher doses shows a different behavior, particularly in mechanical properties. As against the degradation in the bulk mechanical properties of polypropylene, these properties are found to be significantly enhanced in case of polyimide. This indicates that radiation induced scissioning is the dominant effect in case of polypropylene due to its simple aliphatic structure and sensitivity to oxidation effects, while in case of polyimide the crosslinking is dominant due to its aromatic monomer and oxidation resistance. Further, polyimide also shows a decrease in the contact angle due to electron beam induced surface roughening which is confirmed in AFM and profilometry. Thus aliphatic and aromatic polymers can show different behaviours under 6 MeV electron irradiation at normal and identical conditions.
References:


36 D. Wilson, H.D. Stenzenberger, P.M. Hergenrother, Polyimides, Blackie (Glasgow and London) 1990
