Chapter 3

Results and Discussions

3.8 General

The aim of present work is to study the effect of low energy ion implantation on the surface characteristics of CR-39, polycarbonate (PC) and polypropylene (PP) polymers. In the present work, we have studied the modifications in the structural, optical, dielectric, and electrical properties of these polymers as an effect of 100 keV nitrogen and 130 keV argon ion implantation. The changes in the surface morphology and structure of the pre-and post-implanted specimens have been studied using Rutherford Backscattering spectrometry (RBS), X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and UV-Visible Spectroscopy techniques. Using Rutherford backscattering spectroscopy the composition and depth profiling of the specimens have been investigated. The spatial distribution of ion implantation induced modification in the form of carbonization, oxygen redistribution, dehydrogenation etc. in the implanted polymeric layers have also been studied using RBS. The chemical states of the elements in the implanted surfaces have been studied using XPS. The surface morphology has been investigated using AFM. The structural modifications in the implanted polymeric matrices have been examined using UV-Visible Spectroscopy. The dielectric spectroscopic behaviour like dielectric constant, dielectric loss tangent, spreading factor (α), average relaxation time (τ₀) and molecular relaxation time (τ) of the pre- and post- implanted specimens have been studied at room temperature. The changes produced in the electrical properties have been investigated using I-V characteristics measurements. The possible conduction mechanism in virgin and implanted surfaces has also been assessed by applying appropriate model (Poole Frankel, Schottky, SCLC and Hopping) to I-V characteristics. Finally, the modification in the structural, dielectric and electrical behaviour has been correlated with the implantation induced changes on the cross-linked
and linear structure of these polymeric matrices. All these studies are discussed in the sections 3.2 to 3.7 in this chapter.

3.9 Effect of Argon Ion Implantation on CR-39

The CR-39 specimens were implanted by 130 keV Ar⁺ ions with various fluences of 5×10¹⁴, 1×10¹⁵ and 1×10¹⁶ Ar⁺ cm⁻². The effects of argon ion implantation on the structure, optical, dielectric and electrical properties of CR-39 specimens have been investigated and the results are discussed in the following sections.

3.9.1 Rutherford Backscattering Spectroscopy

RBS measurements have been used to analyze the composition and structure of the Ar⁺ implanted modified surface layers of CR-39. From the RBS spectra of pre- and post-implanted CR-39 specimens, the various elements present in the implanted layer and their differential cross-sections have been calculated using the kinematic factors. Also, the projected range, retained dose and atomic concentration of implanted argon have been analyzed.

3.9.1.1 Composition and Structure

The recorded RBS spectra of virgin and 130 keV Ar⁺ implanted CR-39 specimen at fluence of 1×10¹⁶ Ar⁺ cm⁻² is shown in Fig. 3.1.

![Fig. 3.1 RBS spectra of (a) virgin and (b) implanted CR-39 specimen at 130 keV to a fluence of 1×10¹⁶ Ar⁺ cm⁻²](image)

It has been noticed clearly from Fig. 3.1 ‘b’, that argon ion implantation has completely modified the RBS spectra of virgin CR-39 (Fig. 3.1 ‘a’). For the quantitative analysis of the RBS spectra of both virgin and argon implanted CR-39, Rutherford
Backscattering Manipulation Program (RUMP) software [1] has been used. Using this software, the complete analysis has been carried out. The RUMP fitted spectra of the virgin and implanted CR-39 specimens has been presented in the Fig. 3.2.

Using RUMP analysis, the edge present at energy value ~510 keV in the spectra of Fig. 3.2 (‘a’ & ‘b’) has been identified as of carbon. And oxygen has been identified at an energy value of ~730 keV. Analysis also demonstrates that the peak present at energy value of ~1300 keV in the implanted specimen (Fig. 3.2 ‘b’) belong to argon. Analysis clearly revealed that there are structural modifications in the polymeric matrix as an effect of argon ion implantation.

The composition of carbon and oxygen has been analyzed using RUMP simulations. Analysis yielded an increase in the concentration of carbon (C) from 32 at.% to 51 at.% in implanted specimen in comparison to virgin specimen and the oxygen (O) concentration has also been found to be increase from 19 at.% to 25 at.. Analysis also revealed the presence of argon and it is about 0.7 at.% in the implanted layer. This indicates that the argon ion implantation has produced significant changes in the surface composition in the implanted layers of the polymeric matrix. This is because of the reason that ion beam interaction generally results in the chain-scissioning, crosslinking, evaporation of volatile components near the surface region of the polymeric specimens [2-7]. It is also clear from the Fig. 3.2 ‘b’ that there is variation in the carbon spectra of the implanted CR-39 surface between 0.38 MeV to 0.51 MeV as compared to the unimplanted one (Fig. 3.2 ‘a’). This increase in the C concentration indicates towards the carbon
enriched surface layer in the implanted polymeric matrix which results in the formation of carbonaceous network [2-3,5,8-10]. Hence, it can be inferred that carbonization occurs near the surface as a result of ion implantation. Analysis also reveals that the structure of the polymeric specimen has been modified.

Therefore, one can conclude that argon ion implantation produces significant changes in the surface composition of the implanted polymeric specimen. An increase in the C composition after ion implantation results in the formation of a carbonaceous network containing carbon-enriched clusters within the ion penetration range in near surface regions. The effect of carbonization is of considerable interest because of significant change of the structure and composition of argon ion implanted CR-39 specimens. It has also been noticed from the earlier studies [10-13] that ion implantation results in dehydrogenation in the implanted surface of the specimen although hydrogen cannot be measurable by RBS technique. This decrease in the composition of hydrogen results in the relative increase in the composition of carbon [10,14-17]. Thus, the increase in the concentration of carbon results in carbonaceous layer in the implanted layer.

3.9.1.2 Backscattered Energies

Kinematic factor is used to establish a relationship between incident ($E_0$) and backscattered energies ($E_1$) given by the relation [18-21]:

$$E_1 = KE_0$$

Using RUMP fitted RBS spectra (Fig. 3.2) the values of backscattered energies for carbon, oxygen and argon have been determined. These experimentally determined backscattered energies along with the corresponding values calculated directly from the equation (3.1) presented in Table 3.1a.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass number</th>
<th>Kinematic factor ‘K’</th>
<th>Incident energy $E_0$ (MeV)</th>
<th>Backscattered $E_1$ (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>Carbon</td>
<td>12</td>
<td>0.253</td>
<td>2</td>
<td>0.510</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16</td>
<td>0.362</td>
<td>2</td>
<td>0.730</td>
</tr>
<tr>
<td>Argon</td>
<td>40</td>
<td>0.680</td>
<td>2</td>
<td>1.300</td>
</tr>
</tbody>
</table>

It is clear from the Table 3.1a that the experimental and calculated backscattered energies are in well agreement with each other.
3.9.1.3 Elemental Identification in the Target

Backscattered energies give the quantitative confirmation of the different masses of individual elements present in the target material. If the incident and backscattered energies are known for a scattering angle, then the mass of target components can be determined [18-21] using equation:

\[
K = \left[ \frac{1 - \left( \frac{M_1}{M_2} \right)^2 \sin^2 \theta}{1 + \left( \frac{M_1}{M_2} \right)} \right]^{1/2} \left[ \frac{1 - \left( \frac{M_1}{M_2} \right)^2 \sin^2 \theta}{1 + \left( \frac{M_1}{M_2} \right)} \right] \]
\]

where \( M_1 \) is the mass of the incident particle, \( M_2 \) is the mass of the stationary target, and \( \theta \) is the scattering angle. Using this relation, we have identified the individual elements carbon, oxygen and argon present in the specimen.

3.9.1.4 Calculation of Differential Cross Section

Rutherford differential cross section is a measure of the probability with which a projectile is elastically scattered from target atom [18-20] and is based on the Coulomb interaction potential. It is calculated by the formula:

\[
\frac{d\sigma}{d\Omega} = \left( \frac{Z_1Z_2e^2}{4E} \right)^2 \frac{4}{\sin^4 \theta} \left[ 1 - \left( \frac{M_1}{M_2} \right)^2 \sin^2 \theta \right]^{1/2} + \cos \theta \]
\]

where \( E \) is the energy of the projectile, \( Z_1 \) and \( Z_2 \) are the atomic numbers of the projectile and the target atom respectively. Using this formula we have calculated differential cross sections for carbon, oxygen and argon elements and found a good agreement in calculated and theoretical values [18-20] as given in Table 3.1b.

<table>
<thead>
<tr>
<th>Table 3.1b</th>
<th>Theoretical and calculated cross sections for different elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Mass number</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>12</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16</td>
</tr>
<tr>
<td>Argon</td>
<td>40</td>
</tr>
</tbody>
</table>
3.9.1.5 Calculation of Implant Fluence

Using RBS data, the implantation fluence in the CR-39 specimen after Ar\(^+\) implantation has been confirmed and verified [18-19] using formula

\[
(Nt)_{Ar} = \frac{A_{Ar}}{H_{CR-39}} \frac{\sigma_{CR-39}(E_0)}{\sigma_{Ar}(E_0)} \frac{\varepsilon}{[\varepsilon_0]_{CR-39}}
\]

where

\((Nt)_{Ar}\) = total no. of implanted atoms per unit area  
\(A_{Ar}\) = area of the implanted signal  
\(\sigma_{CR-39}(E_0)\) = scattering cross-section of target at incident energy  
\(\sigma_{Ar}(E_0)\) = scattering cross-section of implanted ions at incident energy  
\(H_{CR-39}\) = height of target signal  
\(\varepsilon\) = Channel width  
\([\varepsilon_0]_{CR-39}\) = stopping cross-section factor (surface energy approximation) of the target

Using the calculated values of different parameters, the retained implantation fluence comes out to be 0.93x10\(^{16}\) Ar\(^+\) cm\(^{-2}\) which is in well agreement with the real implanted ion fluence of 1x10\(^{16}\) Ar\(^+\) cm\(^{-2}\).

3.9.1.6 Calculation of Atomic Concentration

The atomic concentration of implanted argon \(N_{Ar}\) in the CR-39 specimen is calculated using formula [18-19]

\[
\frac{N_{Ar}}{N_{CR-39}} = \frac{H_{Ar}}{H_{CR-39}} \frac{\sigma_{CR-39}(E_0)}{\sigma_{Ar}(E_0)} \left[\frac{\varepsilon_0}{[\varepsilon_0]_{Ar}}\right]_{CR-39} \left[\frac{\varepsilon_0}{[\varepsilon_0]_{CR-39}}\right]_{Ar}
\]

where

\(H_{Ar}\) = height of implanted signal  
\([\varepsilon_0]_{Ar}\) = stopping cross-section factor of implanted ions in target  
\([\varepsilon_0]_{CR-39}\) = stopping cross-section factor (surface energy approximation) of target

The concentration of implanted argon has been calculated using height measurements and its value comes out to be 0.62 at.% which is in well agreement with the value 0.7 at.% calculated using RUMP fitted RBS spectra.

3.9.1.7 Calculation of Projected Range

The value of projected range of the implanted argon in CR-39 specimen comes out to be 198 nm using RUMP fitted RBS spectra which is in good agreement with the value 187 nm as per Stopping and Range of Ions in Matter (SRIM) simulations [22].
3.9.2 X-ray Photoelectron Spectroscopy

In the present work XPS characterization were carried out to examine the chemical states of various elements in the implanted specimens. Fig. 3.3 depicts the XPS spectra for the C (1s), O (1s) and Ar (2p) levels of 130 keV argon implanted CR-39 specimen with a fluence of \(1 \times 10^{16}\) \(\text{Ar}^+\) \(\text{cm}^{-2}\). All the spectra were recorded at the surface only.

![XPS spectra](image)

Fig. 3.3  XPS spectra of implanted CR-39 specimen at 130 keV with \(1 \times 10^{16}\) \(\text{Ar}^+\) \(\text{cm}^{-2}\) for (a) C(1s), (b) O(1s) and (c) Ar(2p)

It can be clearly seen from the Fig 3.3 that all the three spectra for the C(1s), O(1s) and Ar(2p) levels in the implanted surface are asymmetric [23]. Therefore, it is evident that more than one bonding states may be present under the peaks appearing in these spectra (Fig. 3.3). It is known that in the virgin CR-39; C-O, C=O, C-H and C=C (aliphatic) bonding exist corresponding to its monomer structure as shown in Fig. 2.1.

In the O(1s) spectra (Fig. 3.3 ‘b’), there is one peak present at 530.82 eV which indicates the presence of oxygen in the implanted surface mainly in the form of carbon containing C=O bonds [24]. The other oxygen bonds of the unimplanted surface would
have been scissioned due to the effect of argon ion implantation. The spectra of Ar(2p) (Fig. 3.3 ‘c’) is comparatively weaker but shows clearly a peak present at 243.86 eV indicating that the implanted argon may be sitting in isolated positions within the matrix or in small aggregates [25-27].

The asymmetric nature spectra of the C(1s) level (Fig. 3.3 ‘a’) shows the peak centered at 283.86 eV. This energy lies very close to the graphitic and amorphous carbon (C-C) states besides the aliphatic carbon (C=C) [23-24, 26]. This suggests the formation of the mixture of these three states during argon ion implantation in CR-39 matrix. The other bonding states would have been scissioned due to the emission of the hydrogen and oxygen gaseous molecules from the surface of CR-39 during implantation. Therefore, the 283.86 eV peak position in the C(1s) spectra (Fig. 3.3 ‘a’) indicates the formation of amorphous carbon containing graphatic structures in the near surface regions of CR-39 as an effect of argon ion implantation.

3.9.3 Atomic Force Microscopy

Surface morphology of the pre- and post-implanted specimens was examined using atomic force microscopy. The root mean square roughness (Rrms) and average roughness (Rav) values for virgin and ion implanted samples were calculated. Fig. 3.4 (a-d) shows the two-dimensional 10μm×10μm AFM images of virgin and 130 keV Ar+ implanted CR-39 samples for fluences ranging from 5x10^{14} ions cm\(^{-2}\) to 1x10^{16} ions cm\(^{-2}\). The AFM images were analyzed using Nova-Px software provided with the instrument. These images were investigated in terms of root mean square (Rrms) and average (Rav) roughness values. It has been observed that the surface topography of the virgin CR-39 specimen (Fig. 3.4 ‘a’) was uniform and smooth compared to argon ion implanted (Fig. 3.4 ‘b’, ‘c’, & ‘d’) specimens.

For virgin CR-39 samples (Fig. 3.4 ‘a’), the root mean square roughness (Rrms) and average roughness values (Rav) was found to be 8.34 nm and 5.57 nm respectively. These roughness values have been found to be increased after Ar+ implantation. For the lowest fluence of 5x10^{14} Ar+ cm\(^{-2}\) (Fig. 3.4 ‘b’), the calculated values are 14.08 nm and 7.27 nm for Rrms and Rav respectively. With further increase in ion fluence (Fig. 3.4 ‘c’), the Rrms and Rav values increase to 17.08 nm and 10.53 nm respectively. At highest fluence of 1x10^{16} Ar+ cm\(^{-2}\) (Fig. 3.4 ‘d’), there is a maximum increase in the root mean square and average roughness values upto 19.12 nm and 12.56 nm respectively. Table 3.2 presents the Rrms and Rav roughness values for virgin and argon ion implanted specimens.
Fig. 3.4 Two-dimensional AFM images of (a) virgin and implanted CR-39 specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$ and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

Table 3.2 Variation of root mean square roughness and average roughness values with ion fluence

<table>
<thead>
<tr>
<th>Ion Fluence (Ar$^+$ cm$^{-2}$)</th>
<th>Root mean square roughness $R_{rms}$ (nm)</th>
<th>Average roughness $R_{av}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin CR-39</td>
<td>8.34</td>
<td>5.57</td>
</tr>
<tr>
<td>$5 \times 10^{14}$</td>
<td>14.08</td>
<td>7.27</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>17.08</td>
<td>10.53</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>19.12</td>
<td>12.56</td>
</tr>
</tbody>
</table>

It is clear from the Table 3.2 that the roughness values increase with increasing ion fluence. The observed rms roughness and average roughness values of samples are plotted as a function of ion fluence and are shown in Fig. 3.5. The changes observed in the topographical images and roughness values may be due to the interaction of argon ion beam with the CR-39 specimens which results in the formation of cross-linked and carbon-rich clusters in the implanted layer of the matrix [2, 28-29]. Such cross-linked surface has been considered as a factor of degradation in the uniformity in the polymeric
chains which results in changes in the free volume fraction in the modified surface layer [12,30-32]. Thus, it can be clearly reveal from the AFM images that surface morphology of the specimens has been affected by argon ion implantation which leads to a consistent increase in the degree of modification in the polymeric specimens and hence led to increase in surface roughness values [30,33].

### 3.9.4 UV-Visible Spectroscopy

UV-Visible Spectroscopy has been performed to analyze the effect of argon ion implantation on CR-39 specimens. From the UV-Visible spectra of pre- and post-implanted specimens, structural analysis and color examination have been performed.

#### 3.9.4.1 Structural Analysis

The UV-Visible absorption spectra in the wavelength range 190-900 nm for virgin (curve ‘a’) and argon implanted (curve ‘b’, ‘c’, & ‘d’) CR-39 samples to fluences $5 \times 10^{14}$, $1 \times 10^{15}$, and $1 \times 10^{16}$ ions cm$^{-2}$ is shown in Fig. 3.6. These spectra have been analyzed to explain the existence of the peaks; their shifts and broadening as a result of ion implantation.
The UV-visible spectrum of virgin CR-39 sample (curve ‘a’, Fig.3.6) has two peaks at 226 and 248 nm. These peaks in the absorption spectra are due to electronic transitions taking place between highest occupied molecular orbital to lowest unoccupied molecular orbital. Furthermore, these transitions are associated with n-π* and π-π* orbital which is likely to be associated with double bond between carbon and oxygen with lone pair of electrons present on oxygen [34-38]. Furthermore, these two existing bands in the virgin spectra have been merged after implantation.

The effect of argon ion implantation on CR-39 polymer results in shifting and broadening of peaks as shown in Fig.3.6. This may be due to the fact that as a result of implantation, various processes such as ionization, excitation, formation of free radicals, recombination and scissioning of bonds, cross-linking and different oxidation processes take place which results in the formation of new double and triple bonds, aromatic species etc. [39-43]. The observed red shift after implantation also corresponds to the increase in conjugation with increasing ion fluence resulting in a decreased HOMO-LUMO gap forcing the position of n-π* and π-π* towards lower energy [35, 42-43]. Moreover, the changes observed in the structure of virgin specimen after implantation can be attributed to the production of defects such as anions, cations, radicals, organic species etc. [35].
3.9.4.2 Color Examination

It has been observed that there are sharp changes in the surface color of CR-39 specimen after argon ion implantation. The virgin CR-39 sample was transparent and colorless. The transparent CR-39 sample changes to light brown for a dose of $5 \times 10^{14}$ $\text{Ar}^+ \text{cm}^{-2}$. At the highest dose of $1 \times 10^{16}$ $\text{Ar}^+ \text{cm}^{-2}$, the color changes to dark brown. This color transformation is closely related to the structural modifications in the implanted polymeric matrix [8,34]. The change in the color of the specimens after ion implantation is due to the fact that ion implantation causes structural modifications in the polymeric matrix. This in turn leads to the degradation of polymeric chains, cross-linking, creation of free radicals, molecular rearrangement which results in the formation of conjugated carbon-carbon double bonds and hence results in the carbonization of the surface layer with increasing ion fluence [34].

These changes in the color are correlated with the increase in optical absorption and intensity with increase in ion fluence as discussed above. This coloration phenomenon is also consisted with the red shift of the absorption edge (Fig 3.6). The change in the color may be due to the formation of carbonaceous layer in the implanted specimens as confirmed by RBS studies.

3.9.5 Dielectric Spectroscopy

Dielectric measurements [44-53] have been used to analyze the dielectric behaviour of the Ar$^+$ implanted CR-39 specimens. Using these measurements, dielectric constant, dielectric loss, dissipation factor, spreading factor, average relaxation time and molecular relaxation time have been calculated.

3.9.5.1 Dielectric constant and Dielectric loss

Figs. 3.7 and 3.8 show the variation of the dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) respectively as a function of frequency for virgin and argon ion implanted CR-39 samples at 130 keV to fluences $5 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ ions cm$^{-2}$. The spectra were recorded for the pre- and post-implanted CR-39 specimens in the frequency range of 100 Hz to 90 MHz. Fig. 3.7 shows the variation in the value of dielectric constant with increasing frequency. For virgin CR-39 (curve ‘a’, Fig 3.7), there is a increase in the value of dielectric constant from 4.76 (at 100 Hz) to 16.2 (at 84.6 MHz). For ion fluence $5 \times 10^{14}$ $\text{Ar}^+ \text{cm}^{-2}$ (curve ‘b’, Fig 3.7), the dielectric constant increases from 4.67 (at 100 Hz) to a maximum value of 16.1 (at 84.7 MHz). With further increase in fluence to $1 \times 10^{15}$ $\text{Ar}^+ \text{cm}^{-2}$.
Fig. 3.7  Plot of dielectric constant vs. frequency for (a) virgin and implanted CR-39 specimens at 130 keV to (b) 5×10^{14}, (c) 1×10^{15} and (d) 1×10^{16} Ar^+ cm^-2 (curve ‘c’, Fig 3.7). ε’ increases from 4.51 (at 100 Hz) to a maximum value of 15.8 (at 84.8 MHz). For the highest implantation dose of 1×10^{16} Ar^+ cm^-2 (curve ‘d’, Fig 3.7) ε’ increases from 4.2 (at 100 Hz) to a maximum value of 15.5 (at 84.8 MHz).

It is clear from the Fig. 3.7 (curves ‘a’, ‘b’, ‘c’, &‘d’) that the value of dielectric constant shows a variation with increase in frequency i.e. it firstly increases upto a frequency of ~85 MHz and afterwards it starts decreasing for all the specimens. This
observed increase in the value of dielectric constant in the polymeric matrix can be explained in terms of dipole orientation polarization mechanism. This mechanism explains the polarization as well as orientation of dipoles as a function of frequency [44-47]. This may be due to the fact that as the frequency increases, the field tries to orient the dipoles along its direction. As in this frequency region, the dominating mechanism is dipole orientation polarization. Hence, there will be preferential orientation of dipoles in the direction of applied field [53] and results in the increase in the values of the dielectric constant.

It is also clear from the Fig. 3.7 that after frequency of ~85 MHz, the value of dielectric constant starts decreasing. This decline in the value may be attributed to the change in the direction of polarization of the dipoles with the applied field. As after this frequency, the dipole orientation polarization cannot attain its equilibrium value as dipoles start reversing their direction of orientation. This decreases the probability of polarization of dipole and hence results in the change of the dipole orientation polarization mechanism to the atomic polarization [54] with further increase in frequency. This difference in the values of dielectric constant measured at low and high frequencies is called the strength of the relaxation in polymers [53, 55-59].

Fig. 3.8 (curves ‘a’, ‘b’, ‘c’ &‘d’) presents the plots of dielectric loss ($\varepsilon''$) versus frequency for virgin and implanted CR-39 specimens. It is clear from the Fig. 3.8 that the value of $\varepsilon''$ increases upto ~83 MHz frequency and then starts decreasing with further increase in frequency. This behaviour may be due to the reason that there occurs a random orientation of dipoles upto frequency range of ~83 MHz. However, with further increase in frequency, the dipoles in the polymeric chain are coupled to the adjacent dipoles of the same chain. So there occurs a preferential orientation of the dipoles in response to the applied field [60]. This results in the decrease in the value of dielectric loss after ~83 MHz frequency.

3.9.5.2 Dissipation factor

The dissipation factor ($\tan \delta$) behaviour of virgin and 130 keV argon implanted CR-39 specimens has also been studied. Fig. 3.9 (curves ‘a’, ‘b’, ‘c’, &‘d’) presents the plot showing the variation of dissipation factor with frequency for pre- and post-implanted CR-39 specimens to fluence $5\times10^{14}$, $1\times10^{15}$ and $1\times10^{16}$ Ar$^+$ cm$^{-2}$. It is well known that in high frequency alternating fields there is always a phase difference between polarization and field, which gives the dissipation factor [55,58].
It is clear from the Fig. 3.9 that dissipation factor shows an increasing trend with ion fluence. Also the position of tan δ peak remains almost unaffected after implantation. As this peak corresponds to the vibrations of the main chain hence it is interesting to observe that even after implantation the main sources of this peak remain almost unaffected [56,59]. Moreover, dissipation factor is proportional to the electrical energy lost as heat in the polarization process in the presence of applied field [60]. Therefore it also increases with increasing ion fluence.
Hence, it has been observed that the value of dielectric constant (Fig. 3.7) decreases whereas dielectric loss (Fig. 3.8) and dissipation factor (Fig. 3.9) increases with increasing ion fluence. This may be due to the fact that implantation generally induces disorder in the structure of polymeric specimens and leads to cross-linking, formation of free radicals, chain-scissioning etc. [2,34,52,61] as observed through UV-Visible, AFM and RBS results. This result in the formation of $\pi$-electron clouds with the applied field.
aligned in the direction of the molecular chains. This change in the direction of polarization causes the decline in dielectric constant values after implantation [34,59].

### 3.9.5.3 a.c. conductivity

The a. c. conductivity at various frequencies for virgin and implanted CR-39 specimens has been calculated using the following formula [45, 62-63]

$$\sigma_{a.c.} = 2\pi f \varepsilon_0 \varepsilon''$$  \hspace{1cm} (3.6)

where $f$ is the frequency in Hz, $\varepsilon_0$ is the permittivity of free space and $\varepsilon''$ is the dielectric loss. Fig. 3.10 shows the plot of a. c. conductivity for virgin and 130 keV argon ion implanted CR-39 samples to fluences $5\times10^{14}$, $1\times10^{15}$ and $1\times10^{16}$ ions cm$^{-2}$ at various frequencies in the range of 10 MHz to 80 MHz.

![Fig. 3.10 Plot of a.c. conductivity with ion fluence at various frequencies for virgin and implanted CR-39 specimens at 130 keV](image)

The a. c. conductivity (Fig. 3.10) shows an increasing trend with frequency and ion fluence. This enhancement in the conductivity after implantation may be attributed to the formation of carbon-rich clusters with conjugated bonds in the polymeric matrix [37,52,64]. Moreover, the formation of $\pi$-bonded carbon enriched domains created in the implanted layers of CR-39 may be the main reason behind the modifications in the dielectric properties (dielectric constant, dielectric loss and a. c. conductivity). These
alterations in the dielectric properties of the specimens reveal that implantation supports the formation of carbon enriched domains in the polymeric matrix as confirmed by the RBS and XPS results.

3.9.5.4 Cole-Cole Plot

The dielectric relaxation occurring in virgin and argon implanted polymeric specimens has been studied in detail through Cole-Cole analysis in the 100 Hz to 90 MHz frequency range. The plot of real part ($\varepsilon'$) of the complex permittivity in the x-axis and imaginary part ($\varepsilon''$) of that in the y-axis is known as the Cole-Cole plot. The Cole-Cole plots are useful to confirm the distribution of relaxation time. Fig. 3.11 (curves ‘a’, ‘b’, ‘c’, &‘d’) shows the Cole-Cole plots for virgin and 130 keV Ar$^+$ implanted CR-39 specimens to fluences $5\times10^{14}$, $1\times10^{15}$ and $1\times10^{16}$ ions cm$^{-2}$. Cole-Cole plots are used to determine the spreading factor ($\alpha$), average relaxation time ($\tau_0$) and molecular relaxation time ($\tau$).

![Cole-Cole plots](image)

Fig. 3.11 Cole-Cole plot of (a) virgin and argon ion implanted CR-39 specimens at 130 keV to fluences (b) $5\times10^{14}$, (c) $1\times10^{15}$ and (d) $1\times10^{16}$ ions cm$^{-2}$

It is clear from the Fig. 3.11 (curves ‘a’, ‘b’, ‘c’, &‘d’) that Cole-Cole plots are imperfect semicircular in nature. With increasing ion fluence, distortions in the shape of
the Cole-Cole plots are increasing. This deviation in the shape of the Cole-Cole plots is due to the polydispersive nature of the amorphous CR-39 for which value of spreading factor is greater than 0 [53,65-67]. This polydispersive nature in polymers further increases owing to disorder due to ion implantation [67]. As the Cole-Cole plots are related to the relaxation phenomena [57,60,68] taking place in matrix, therefore, the changes observed in the nature of these curve after implantation also indicate towards the disorderness in the matrix and hence results in the formation of conjugated π-bonded clusters [37].

### 3.9.5.5 Spreading Factor ($\alpha$)

The value of spreading factor ($\alpha$) has been deduced from the expression for the maximum value of imaginary part of complex permittivity [63,65]:

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_{\infty}) \tan[(1-\alpha)\pi/4]}{2}$$  

(3.7)

where ($\varepsilon_s$) is the low frequency value of dielectric constant, ($\varepsilon_{\infty}$) is the high frequency value of dielectric constant.

The plot of variation of spreading factor of pre- and post-implanted CR-39 specimens with ion fluence is shown in Fig. 3.12. The calculated value of $\alpha$ is listed in Table 3.3.

![Fig. 3.12 Plot of spreading factor (\alpha) with ion fluence for virgin and argon ion implanted CR-39 specimens at 130 keV](image-url)
Table 3.3  Variation of spreading factor ($\alpha$), average relaxation time ($\tau_0$) and molecular relaxation time ($\tau$) at various ion fluences

<table>
<thead>
<tr>
<th>Ion fluence (Ar$^+$ cm$^{-2}$)</th>
<th>Spreading factor ($\alpha$)</th>
<th>Average relaxation time $\tau_0$ (s)</th>
<th>Molecular relaxation time $\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin CR-39</td>
<td>1.30</td>
<td>1.12 x 10$^{-9}$</td>
<td>2.02 x 10$^{-9}$</td>
</tr>
<tr>
<td>5 x 10$^{14}$</td>
<td>1.31</td>
<td>0.33 x 10$^{-9}$</td>
<td>0.60 x 10$^{-9}$</td>
</tr>
<tr>
<td>1 x 10$^{15}$</td>
<td>1.33</td>
<td>0.13 x 10$^{-9}$</td>
<td>0.24 x 10$^{-9}$</td>
</tr>
<tr>
<td>1 x 10$^{16}$</td>
<td>1.34</td>
<td>0.05 x 10$^{-9}$</td>
<td>0.11 x 10$^{-9}$</td>
</tr>
</tbody>
</table>

It is clear from the table that the value of spreading factor is greater than 0 which indicates that there is a broad distribution of relaxation times in the specimens and hence exhibit polydispersive nature [63,69]. This polydispersive nature in polymers further increases owing to disorder due to ion implantation. Moreover, this increase in the value of $\alpha$ with increasing ion fluence (listed in Table 3.3) may be attributed to the increase in disordering [70] in CR-39 matrix. Further, it is apparent from Fig. 3.11 that relaxation process differs from the debye process. Since, it is well known that polymers hardly follow monodispersive Debye theory of relaxation (for which $\alpha$=0) and exhibit much broader dispersion owing to distribution of relaxation time [53,57].

3.9.5.6 Average relaxation time ($\tau_0$)

The average relaxation time $\tau_0$ for virgin and implanted CR-39 specimens was calculated using the relation [63,71]:

$$\left[ \frac{(\epsilon_p - \epsilon')^2 + (\epsilon')^2}{(\epsilon_p - \epsilon_m)^2 + (\epsilon')^2} \right]^{1/2} = (\omega \tau_0)^{1-\alpha} \quad (3.8)$$

where $\epsilon_p$ is the low frequency values of $\epsilon'$ and $\epsilon_m$ is the high frequency values of $\epsilon'$ and $\alpha$ is the spreading factor of relaxation time.

Fig. 3.13 presents the plot of average relaxation time for virgin and implanted CR-39 specimens at various doses. The calculated values of $\tau_0$ is listed in Table 3.3. The decrease in average relaxation time with increasing ion fluence has been observed clearly from Fig. 3.13. This may be due to the implantation induced structural modification in the CR-39 matrix and the formation of carbon enriched domains in the implanted layers.

3.9.5.7 Molecular relaxation time ($\tau$)

Further by utilizing the values of $\tau_0$, the molecular relaxation time ($\tau$) for virgin and implanted CR-39 specimens is calculated using the formula [63,72]:
\[ \tau = \left[ \frac{2\varepsilon_i + \varepsilon_e}{3\varepsilon_i} \right] \tau_0 \]  

(3.9)

The plot of molecular relaxation time for virgin and implanted CR-39 specimens at various doses is shown in Fig. 3.14. The calculated values of \( \tau \) is listed in Table 3.3.

Fig. 3.13 Variation of average relaxation time \( (\tau_0) \) with ion fluences for virgin and argon ion implanted CR-39 specimens at 130 keV

Fig. 3.14 Variation of molecular relaxation time \( (\tau) \) with ion fluences for virgin and argon ion implanted CR-39 specimens at 130 keV

91
Fig. 3.14 depicts clearly the decrease in molecular relaxation time with increasing ion fluence. This is similar to the earlier trend of average relaxation time (Fig. 3.13). This may be due to the carbonization of the CR-39 matrix due to argon ion implantation as already seen from the RBS and XPS analysis. Therefore, Figs. 3.13 and 3.14 alongwith Table 3.3 clearly indicate that the values of average and molecular relaxation times decrease with increasing ion fluence. This can be attributed to the formation of carbonaceous network containing carbon enriched structures in the implanted layers as analyzed using by RBS and XPS studies. Moreover, the decrease in the values of relaxation time may also be attributed to the improvement in the conductivity [58,73] of CR-39 specimens as a result of implantation.

3.9.6 Dielectric Constant and Dielectric Loss using Optical Absorption and Reflection Studies

The dielectric constant and dielectric loss have also been calculated using UV-Visible Spectroscopy. The data of optical absorption and reflection has been used for these calculations for virgin and argon ion implanted CR-39 specimens in the frequency range of .42 - .75 PHz corresponding to the visible region wavelength (400-700 nm). In this frequency range, the response of the specimens to the applied field is mainly due to electronic polarization [44-45]. This type of polarization occurs due to the deformation or translation of the originally symmetrical distribution of the electron clouds of atoms or molecules on the application of electric field. This is essentially the displacement of the outer electronic clouds with respect to the internal atomic cores by external fields. It is largely responsible for a number of optical properties of the materials. [46-47].

The complex refractive index \( n^* \), which consists of the refractive index ‘\( n \)’ and the extinction coefficient ‘\( k \)’, can be expressed [34,44, 48] as

\[
n^* = n - ik
\]  

(3.10)

Further, refractive index and extinction coefficient is related with complex dielectric permittivity:

\[
n^* = n - ik = \sqrt{\varepsilon^*} = \sqrt{\varepsilon' - ik^2}
\]  

(3.11)

where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary part of the complex permittivity and are known as dielectric constant and dielectric loss respectively. On solving, one get

\[
\varepsilon' = n^2 - k^2
\]  

(3.12)
\[ \varepsilon^* = 2nk \]  

(3.13)

The real part (\( \varepsilon' \)) is closely related to the refractive index and imaginary part (\( \varepsilon^* \)) to the extinction coefficient which reduces the losses of photon energy when optical wave propagates through the media [34,48]. In order to study the dielectric constant and dielectric loss in the visible region, the values of refractive index and extinction coefficient have been calculated. The extinction coefficient (\( k \)) for virgin and implanted CR-39 specimens is calculated using [48]

\[ k = \frac{\alpha \lambda}{4\pi} \]  

(3.14)

where \( \alpha \) is the absorption coefficient (calculated using the absorbance data in Fig.3.6) and \( \lambda \) is the wavelength. The variation of extinction coefficient for virgin (curve ‘a’) and argon ion implanted CR-39 specimens (curves ‘b’, ‘c’, & ‘d’) as a function of wavelength in the range of 400-700 nm is shown in Fig. 3.15.

![Variation in extinction coefficient with wavelength](image)

**Fig. 3.15** Variation in extinction coefficient with wavelength of (a) virgin and implanted CR-39 specimens at 130 keV to (b) \( 5 \times 10^{14} \), (c) \( 1 \times 10^{15} \) and (d) \( 1 \times 10^{16} \) \( \text{Ar}^+ \text{cm}^{-2} \)

The value of extinction coefficient remains almost constant for virgin sample (curve ‘a’, Fig. 3.15) whereas it shows a decreasing trend (curve ‘b’, ‘c’ and ‘d’, Fig. 3.15) with increase in wavelength for all the implanted specimens. Moreover, the value of
extinction coefficient increases with increase in ion fluence.

Fig. 3.16 shows the reflectivity (%R) spectra in the visible region for pre- and post-implanted CR-39 specimens. It is clear from the Fig. 3.16 (curve ‘a’, ‘b’, ‘c’ & ‘d’) that the reflectivity of the specimens decreases with increasing ion fluence.

![Reflectivity spectra](image)

**Fig. 3.16** Reflectivity spectra recorded in the visible region of (a) virgin and implanted CR-39 specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

Using the values of extinction coefficient and reflectance, the refractive index ($n$) of virgin and implanted specimens has been calculated using [34,48-51]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

where R is the reflectance.

The variations of refractive index for virgin and implanted CR-39 specimens with increasing ion fluence in the visible region are shown in Fig. 3.17. It is clear from the Fig. 3.17 that refractive index shows a decreasing trend with increasing ion fluence.

The changes observed in the variation of refractive index are associated with the various processes taking place in the polymeric matrix after ion implantation. It is well known that ion beam interaction results in the chain-scission, formation of free radicals, cross-linking which in turn lead to the formation of unsaturated delocalized $\pi$-electron
clouds. This corresponds to the change in the direction of polarization of the dipoles in response to applied field and hence refractive index decreases with ion fluence [34].

![Refractive index vs Wavelength](image)

**Fig. 3.17** Variation in refractive index with wavelength (a) virgin and implanted CR-39 specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$ and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

Figs. 3.18 and 3.19 present the plots of dielectric constant and dielectric loss respectively as a function of wavelength in the visible region. It is observed from these figures that the value of $\varepsilon'$ (Fig. 3.18) decreases whereas value of $\varepsilon''$ (Fig. 3.19) increases with increasing ion fluence. These changes in the value of dielectric constant are attributed to the formation of $\pi$-electrons. The orientation of these $\pi$-bonded electrons in the direction of applied field results in electronic polarization. Moreover, the net polarization of these $\pi$-electrons tends to align with the molecular chains and hence results in the decline in the value of $\varepsilon'$ with increasing fluence. However, the dielectric loss (curves ‘a, ‘b’, ‘c’ & ‘d’, Fig. 3.19) increases with increasing ion fluence. This increase in the dielectric loss values is associated with the build up of electronic polarization between the dipoles in the direction of applied field [34, 46].

These variations in the dielectric constant and dielectric loss may be attributed to the electronic polarization taking place in the polymeric specimens. Moreover, ion beam interaction of polymers induces disruption of chemical bonds with their subsequent cross-linking and conjugation leading to the formation of carbon rich structures and hence
causes variations in the properties of the specimens. As a result, π-bonded carbon cluster formation takes place [2,52].

Fig. 3.18 Variation in dielectric constant with wavelength (a) virgin and implanted CR-39 specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$ & (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

Fig. 3.19 Variation in dielectric loss with wavelength of (a) virgin and implanted CR-39 specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$
3.9.7 Electrical Properties

Current-Voltage (I-V) characteristics for virgin and 130 keV argon ion implanted CR-39 specimens with different fluences are shown in Fig. 3.20. These I-V characteristics were recorded in the applied voltage range of 10-50 V. For virgin CR-39 specimen (curve ‘a’, Fig. 3.20), there is slight increase in current with applied voltage. After Ar⁺ implantation, the value of current increases (curves ‘b’, ‘c’ & ‘d’, Fig. 3.20) with increase in the ion fluence. However, at fluences of $5 \times 10^{14}$ Ar⁺ cm⁻² (curve ‘b’) and $1 \times 10^{15}$ Ar⁺ cm⁻² (curve ‘c’), the corresponding increase in current with applied voltage is less noticeable. Whereas there is a slight increase in the value of current with applied voltage for the highest fluence of $1 \times 10^{16}$ Ar⁺ cm⁻² (curve ‘d’). This increase in current is found to be maximum for the highest implantation dose (curve ‘d’) in comparison to virgin (curve ‘a’) CR-39 specimen.

![I-V Characteristics for virgin and implanted CR-39 specimens](image)

**Fig. 3.20** I-V Characteristics for (a) virgin and implanted CR-39 specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar⁺ cm⁻²

It is evident from the Fig. 3.20 (curves ‘a’, ‘b’, ‘c’ & ‘d’) that the increase in current is not proportional to the corresponding increase in voltage for all the specimens. Hence the possibility of Ohmic conduction mechanism is ruled out from the observed behaviour of I-V characteristics. Moreover, it can also be seen clearly from Fig. 3.20 (curves ‘b’, ‘c’ & ‘d’) that the current increases continuously with increasing argon ion...
fluence. This can be explained on the basis of formation of conjugated bonds as a result of ion implantation, which promotes the delocalization of charge carriers and hence leads to the formation of carbonaceous structure in the implanted specimens [37,74]. The formation of π-bonded carbonaceous clusters in the implanted layers induces electronic hopping process between individual conducting islands embedded in polymeric matrix [52,75]. Thus, they facilitate the flow of current and contribute towards the modification in the conductivity of implanted polymers. The possible conduction mechanism operating in the argon implanted CR-39 specimens can be studied using different conduction mechanisms.

To reveal the charge transport mechanism in virgin and implanted CR-39 specimens, I-V data is plotted in the form $\ln (I)$ vs. $V^{1/2}$ (Fig. 3.1).

![Graph](image)

**Fig. 3.1** Plot of $\ln (I)$ vs. $V^{1/2}$ for (a) virgin and implanted CR-39 specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

Various conduction mechanisms like Poole Frankel effect, Schottky emission, Space Charge Limited Conduction and Hopping [76-80] have been used to analyze the Current-Voltage (I-V) characteristic measurements for the pre- and post-implanted polymeric matrix. Detailed study of the conduction mechanisms operating in the polymeric matrix is carried out using fundamental thermionic emission equation [76,81] given by:
\[ I = AT^2 \exp \left( \frac{\beta_{\exp} V^{1/2}}{kTd^{1/2}} \right) \]  

(3.16)

where \( I \) is the current, \( A \) is the Richardson constant \((1.2 \times 10^6 \text{ Am}^{-2})\), \( V \) is the applied voltage, \( d \) is the sample thickness, \( T \) is the absolute temperature, \( k \) is the Boltzmann constant, and \( \beta \) is a constant characteristic of the conduction process.

The experimental value of \( \beta \) i.e. \( \beta_{\exp} \) for virgin and implanted specimens has been calculated using the relation [82]:

\[
\ln I = \left( \frac{\beta V^{1/2}}{K T d^{1/2}} \right)
\]

(3.17)

On solving above equation, one gets

\[ \beta_{\exp} = sK T d^{1/2} \]  

(3.18)

where \( s \) is the slope \( \left( s = \Delta \ln I / \Delta V^{1/2} \right) \) of the graph plotted between \( \ln I \) and \( V^{1/2} \).

The theoretical values of \( \beta \) for Schottky emission as well as for Poole-Frenkel emission are given by [79-80,82]:

**Schottky emission** (\( \beta_{RS} \)):

\[
\beta_{RS} = \left( \frac{e^3}{4 \pi \varepsilon \varepsilon_0} \right)^{1/2}
\]

(3.19)

**Poole-Frenkel emission** (\( \beta_{PF} \)):

\[
\beta_{PF} = \left( \frac{e^3}{\pi \varepsilon \varepsilon_0} \right)^{1/2}
\]

(3.20)

where \( \varepsilon \) is the dielectric constant and \( \varepsilon_0 \) is the permittivity of the free space.

The \( \beta_{\exp} \) values for virgin and argon ion implanted CR-39 specimens have been compared with the theoretically calculated values \( \beta_{RS} \) and \( \beta_{PF} \) for Poole-Frenkel and Schottky Emission conduction parameter respectively and are listed in Table 3.4.

The experimental value (\( \beta_{\exp} \)) has been found to be in good agreement with the theoretical value of \( \beta_{PF} \) for virgin CR-39 specimens. This leads to the conclusion that Poole–Frenkel mechanism is the dominating mechanism in case of the virgin CR-39 specimen. However, after implantation, the values of \( \beta_{\exp} \) was close to the theoretical value of \( \beta_{RS} \) leading to the conclusion that Schottky emission is the dominant charge transport mechanism operating in the argon implanted CR-39 specimens.
Table 3.4  A comparison between the theoretical and experimental $\beta$ coefficients of virgin and implanted CR-39 specimens

<table>
<thead>
<tr>
<th>Ion Fluence (Ar$^+$cm$^{-2}$)</th>
<th>Theoretical values of conduction parameter</th>
<th>Experimental values of conduction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Schottky emission ($\beta_{ss}$) (eV-m$^{1/2}$ V$^{-1/2}$)</td>
<td>Poole Frenkel emission ($\beta_{PF}$) (eV-m$^{1/2}$ V$^{-1/2}$)</td>
</tr>
<tr>
<td>Virgin</td>
<td>1.74 x 10^{-5}</td>
<td>3.48 x 10^{-5}</td>
</tr>
<tr>
<td>5 x 10^{14}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 x 10^{15}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 x 10^{16}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The transition in the conduction mechanism from Poole- Frenkel (for virgin CR-39) to Schottky emission (for implanted CR-39 specimens) may be due to the improvement in the conductivity of these specimens as a result of implantation [79-80]. This may be due to abrupt increase in the concentration of charge carriers with increase in ion fluence which results in the enhancement in the conductivity of the polymeric specimens.

The observed increase in the conductivity of the CR-39 specimens also results from the Hopping mechanism. It is the predominant mechanism of conduction for charges between localized states usually generated by thermal excitations. In this conduction mechanism the charge carriers execute discrete jumps from one site to another [45,56,83]. This results in the hopping of the charge carriers across the defect sites of the polymeric matrix and hence results in the increase in conductivity in the implanted layer of specimens.

However, for space charge linear conduction mechanism (SCLC) to occur, the slope of the I-V characteristic curves should be greater than or equal to 2, but in the present case the value of slope comes out to be less than 2 therefore, this conduction mechanism is ruled out [77,84].

Hence, the increase in the conductivity of the CR-39 specimens may be due to the formation of $\pi$- bonded carbon clusters in the implanted layers as a result of argon ion implantation [34,52,58]. The formation of such clusters may have been contributed significantly towards the enhancement in the conductivity of implanted matrix. Thus, ion implantation results in the electrically conductive surface [85-86]. In the present studies,
the outcomes of RBS and XPS analysis give a clear indication of the carbonization in the implanted layers of CR-39 specimens. This increase in the carbon composition after argon ion implantation as revealed by RBS results contributes towards the enhancement in the conductivity of the CR-39 specimens. Also, the dielectric and UV-Visible measurements are consistent with the results obtained by I-V characteristics.

Thus, it can be concluded that there are significant modifications in the surface properties of the CR-39 samples after argon ion implantation. The ion beam interaction with the polymeric matrix is responsible for the formation of carbonaceous network structure. RBS and XPS measurements show that the structure and elemental composition of the virgin sample has been modified completely. It also confirms the increase in carbon compositions in the implanted region of CR-39 matrix which indicate towards the formation of carbonization in implanted layers of specimens. The study of dielectric parameters results in the modifications in the values of dielectric constant and dielectric loss and these variations can be attributed to the formation of extended network of conjugated bonds. Also, the Cole-Cole analysis of virgin and implanted CR-39 specimens indicates a deviation from Debye relaxation phenomena. Moreover, the shapes of the Cole-Cole plots confirmed the structural disordering in implanted CR-39 specimens. From I–V characteristic measurements, it has been observed that the Schottky emission is the dominant charge transport mechanism operating in implanted specimens. Hence the results of different characterization techniques agree well with each other.
3.10 Effects of Argon Ion Implantation on Polycarbonate

The polycarbonate (PC) specimens were implanted with 130 keV Ar\(^+\) ions with various fluences of \(1\times10^{14}\), \(1\times10^{15}\) and \(1\times10^{16}\) Ar\(^+\) cm\(^{-2}\). The effects of argon ion implantation on the structural, optical, dielectric and electrical properties of PC specimens have been discussed in the following sections.

3.10.1 Rutherford Backscattering Spectroscopy

The composition and structure of the virgin and argon ion implanted polycarbonate specimens have been analyzed using RBS measurements. RBS spectra have been used to identify the various elements present in the implanted layer and their differential cross-sections have been calculated using kinematic factors. Also, the projected range, retained dose and atomic concentration of implanted argon have been calculated.

3.10.1.1 Composition and Structure

Fig. 3.22 ‘a’ and Fig. 3.22 ‘b’ presents the recorded RBS spectra of virgin and 130 keV Ar\(^+\) ion implanted polycarbonate specimen at fluence of \(1\times10^{16}\) Ar\(^+\) cm\(^{-2}\).

![RBS spectra](image)

**Fig. 3.22** RBS spectra of (a) virgin and (b) implanted polycarbonate specimen at 130 keV to \(1\times10^{16}\) Ar\(^+\) cm\(^{-2}\)

It is clear from the Fig. 3.22 ‘b’ that the surface of the Ar\(^+\) implanted PC specimen has been modified completely. The RBS spectra of both pre- and post-implanted PC have been analyzed using Rutherford Backscattering Manipulation Program (RUMP) software [1]. Fig. 3.23 presents the RUMP fitted spectra of the pre- and post-implanted specimens. Analysis in the Fig. 3.23 revealed that the edge present at energy value \(~520\) keV in the spectra of Fig. 3.23 (‘a’ & ‘b’) has been identified as of carbon and corresponding to \(~700\) keV energy value, oxygen has been identified. In comparison to virgin PC, it has
been noticed that there occurs a peak in Fig. 3.23 ‘b’ corresponding to energy values ~1300 keV which indicates the presence of argon in the implanted layer of PC matrix.

The composition of the identified elements C, O and Ar has been determined using RUMP simulations which yielded an increase in the concentration of carbon and decrease in the concentration of oxygen after implantation. It has been found that the carbon concentration increases near the surface from to 48 at.% (for virgin) to 74 at.% (at fluence $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$) and oxygen concentration decreases from 9 at.% (for virgin) to 4 at.% (at fluence $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$) respectively. Analysis also revealed the presence of argon and it is about 0.4 at.% in the implanted layer of the specimen. Hence, it has been concluded that argon ion implantation has produced significant changes in the surface composition in the implanted layer of the polymeric matrix. This is due to the reason that ion beam interaction results in various processes such as ionization and excitation in the polymeric matrix which leads to the creation of dangling bonds, free radicals, chain-scission, cross-linking etc. These processes lead to the formation of cross-linked and carbon-rich clusters in the surface area of polymeric matrix during the implantation process [10,31].

It is also clearly evident from the Fig. 3.23 ‘b’ that the carbon spectra shows variation (first decreases and then increases again) between 0.39 MeV to 0.55 MeV. This variation in the spectra is due to the various process viz. chain-scissioning, evaporation of volatile components, cross-linking etc. taking place near the surface region as a result of ion implantation. Moreover, the increase in carbon concentration results in the formation of carbonization near the modified surface regions [3-4,7]. Therefore, one can conclude that after ion implantation, carbonization increases and as a result carbon enriched
structure is formed near the surface regions. The effect of carbonization is of considerable interest because of significant change of the structure and composition of argon ion implanted PC specimens. It has also been discerned from the earlier studies [10,87-89] that ion implantation results in dehydrogenation in the implanted surface of the specimen though it is not measurable by RBS technique. The decrease in the composition of hydrogen results in the relative increase in the composition of carbon and oxygen redistribution. [17,85,90].

3.10.1.2 Backscattered Energies

Kinematic factor is a measure of backscattered energies of the scattered particles. It establishes relationship between incident ($E_0$) and backscattered ($E_1$) energies [18-21] using equation (3.1).

Using RUMP fitted RBS spectra (Fig. 3.23) the values of backscattered energies for carbon, oxygen and argon have been determined. These experimentally determined backscattered energies along with the corresponding values calculated directly from the equation (3.1) presented in Table 3.5.

<table>
<thead>
<tr>
<th>Table 3.5</th>
<th>Backscattered energies ($E_1$) for different elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Mass number</td>
</tr>
<tr>
<td>Carbon</td>
<td>12</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16</td>
</tr>
<tr>
<td>Argon</td>
<td>40</td>
</tr>
</tbody>
</table>

The experimental and calculated backscattered energy values are found to be in good agreement with each other.

3.10.1.3 Elemental Identification in the Target

Backscattered energies give the quantitative confirmation of the different masses of individual elements present in the target material. Using the relation given by equation (3.2), we have identified the individual elements i.e. carbon, oxygen and argon present in the specimen.

3.10.1.4 Calculation of Differential Cross Section

Rutherford differential cross section is a measure of the probability with which a projectile is elastically scattered from target atom [18-20] and is based on the Coulomb
interaction potential. Using the formula as given by equation (3.3), we have calculated the values of differential cross sections for carbon, oxygen and argon elements and the values are listed in Table 3.1b. It has been found that the calculated values are in good agreement with the theoretical values [18-20].

### 3.10.1.5 Calculation of implanted fluence

Using RBS data, the dose in the implanted PC specimens has been confirmed and verified using formula [18-19] as given by equation (3.4). Using the calculated values of different parameters, the retained implantation fluence comes out to be 0.96 x10^16 Ar^+ cm^{-2} which is in well agreement with the real implanted ion fluence of 1x10^{16} Ar^+ cm^{-2}.

### 3.10.1.6 Calculation of atomic concentration

The atomic concentration of implanted argon (N_{Ar}) in the PC specimen is calculated using formula [18-19] as given by equation (3.5).

The concentration of implanted argon has been calculated using height measurements and its value comes out to be 0.32 at.% which is in well agreement with the value 0.4 at.% calculated using RUMP fitted RBS spectra.

### 3.10.1.7 Calculation of Projected Range

The value of projected range of the implanted Ar^+ in the PC specimen comes out to be 205 nm using RUMP fitted RBS spectra which is in good agreement with the value 192 nm as per Stopping and Range of Ions in Matter (SRIM) simulations [22].

### 3.10.2 X-Ray Photoelectron Spectroscopy

In the present work the chemical states of the various elements in the implanted layers were carried out using XPS characterization of the implanted surfaces. Fig. 3.24 shows the XPS spectra for the C (1s), O (1s) and Ar (2p) levels of the 130 keV argon ion implanted PC specimen with a fluence of 1x10^{16} Ar^+ cm^{-2}. All the spectra were recorded at the surface only.

All the three spectra in Fig. 3.24 for the C (1s), O (1s) and Ar (2p) levels of argon ion implanted PC are seen to be asymmetric clearly [23]. This indicates that more than one bonding state may be present in these spectra. It is known that in the virgin PC specimen C-O, C=O, C-H and C=C (Benzene ring) bonding exist corresponding to its monomer structure as shown in Fig. 2.2.

In the O(1s) spectra (Fig. 3.24 ‘b’) the peak at 532.32 eV indicates the presence of C-O bonds only [24]. The other oxygen bonds like C=O present in the unimplanted
surface would have been degraded due to the effect of argon ion implantation. The spectra of Ar (2p) (Fig. 3.24 ‘c’) although weak but indicates two bonding states of argon present at 243.92 eV and 241.82 eV indicating that the implanted argon may be sitting in isolated positions within the matrix or in small aggregates [25-27].

![XPS spectra of implanted PC specimen at 130 keV with 1x10^{16} \text{Ar}^+ \text{ cm}^{-2} for (a) C(1s), (b) O(1s) and (c) Ar(2p)]

The asymmetric nature spectra of the C(1s) spectra (Fig. 3.24 ‘a’) shows the peak centered at 284.7 eV line. This line energy lies very close to the C=C (aromatic), graphitic and amorphous carbon (C-C) states [23-24,26]. Therefore, it can be inferred from this asymmetric peak at 284.7 eV that the mixture of above three states would have been formed during argon ion implantation in PC matrix. The other bonding states would have been scissioned due to the emission of the hydrogen and oxygen gaseous molecules from the surface of PC during implantation. Therefore, the 284.7 eV peak position in the C(1s) spectra (Fig. 3.24 ‘a’) suggests the formation of amorphous carbon containing graphatic structures in the near surface regions of PC as an effect of argon ion implantation.
3.10.3 Atomic Force Microscopy

Surface morphology of the unimplanted and argon implanted PC specimens was examined using atomic force microscopy. Fig. 3.25 (a-d) shows the two-dimensional AFM images (recorded at 10μm×10μm size) of virgin and 130 keV argon ion implanted PC specimens for fluences ranging from $1\times10^{14}$ ions cm$^{-2}$ to $1\times10^{16}$ ions cm$^{-2}$.

![AFM images](image)

**Fig. 3.25** Two-dimensional AFM images of (a) virgin and and implanted PC specimens at 130 keV to (b) $1\times10^{14}$, (c) $1\times10^{15}$, and (d) $1\times10^{16}$ Ar$^+$ cm$^{-2}$

For virgin PC sample (Fig. 3.25 ‘a’) surface appears to be smooth and uniform. However, after argon ion implantation, the PC specimens (Fig. 3.25 ‘b’, ‘c’ & ‘d’) show a remarkable change in the surface topography. The changes observed in the surface morphology of the PC specimens are further correlated with the calculated root mean square ($R_{\text{rms}}$) and average roughness ($R_{\text{av}}$) values. Nova Px software was used to calculate the root mean square roughness ($R_{\text{rms}}$) and average roughness ($R_{\text{av}}$). For virgin PC specimen, the root mean square roughness ($R_{\text{rms}}$) and average roughness ($R_{\text{av}}$) values as calculated are 10.70 nm and 8.18 nm respectively. After argon ion implantation, these values ($R_{\text{rms}}$ and $R_{\text{av}}$) have been found to increase. For the lowest fluence of $1\times10^{14}$ Ar$^+$ cm$^{-2}$ (Fig. 3.25 ‘b’) the calculated values of $R_{\text{rms}}$ and $R_{\text{av}}$ are 13.24 nm and 8.78 nm.
respectively. With further increase in ion fluence (Fig. 3.25 ‘c’), the \( R_{\text{rms}} \) and \( R_{\text{av}} \) values increase to 16.44 nm and 9.82 nm respectively. Moreover, at the highest fluence of \( 1 \times 10^{16} \) \( \text{Ar}^+ \text{cm}^{-2} \) (Fig. 3.25 ‘d’), there is a maximum increase in the root mean square and average roughness values upto 25.90 nm and 17.20 nm respectively. Table 3.6 shows the root mean square and average roughness values for virgin and argon ion implanted PC specimens at various fluences. The observed \( R_{\text{rms}} \) and \( R_{\text{av}} \) roughness values are plotted as a function of ion fluence in Fig. 3.26.

**Table 3.6 Variation of root mean square roughness and average roughness values with ion fluence**

<table>
<thead>
<tr>
<th>Ion Fluence (( \text{Ar}^+ \text{cm}^{-2} ))</th>
<th>Root mean square roughness ( R_{\text{rms}} ) (nm)</th>
<th>Average roughness ( R_{\text{av}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PC</td>
<td>10.70</td>
<td>8.18</td>
</tr>
<tr>
<td>( 1 \times 10^{14} )</td>
<td>13.24</td>
<td>8.78</td>
</tr>
<tr>
<td>( 1 \times 10^{15} )</td>
<td>16.44</td>
<td>9.82</td>
</tr>
<tr>
<td>( 1 \times 10^{16} )</td>
<td>25.90</td>
<td>17.20</td>
</tr>
</tbody>
</table>

**Fig. 3.26 Plot of \( R_{\text{rms}} \) and \( R_{\text{av}} \) roughness values of virgin and implanted PC specimens at 130 keV to \( 1 \times 10^{14} \), \( 1 \times 10^{15} \), and \( 1 \times 10^{16} \) \( \text{Ar}^+ \text{cm}^{-2} \)**

This increase in the \( R_{\text{rms}} \) and \( R_{\text{av}} \) values indicate towards the degradation in the uniformity [28-29] on the surface of PC specimens as a result of argon ion implantation. The changes observed in the surface morphology and roughness values of PC specimens
may be due to ion beam interaction and its energy loss in the PC matrix during implantation. Also, ion implantation results in structural and compositional changes, so the increase in the roughness values may be attributed to the formation of cross-linked and carbon-rich clusters in the surface area of PC during the implantation process. [31,91]. Moreover, this increase in the surface roughness value is related to progressive degradation of the polymeric chain due to cross-linking leading to changes in the free volume fraction in the modified surface layer [30,32,92-93]. AFM images clearly indicate that there is a consistent increase in the degree of modification led to a systematic increase in surface roughness.

3.10.4 UV- Visible Spectroscopy

UV- Visible Spectroscopy has been performed to analyze the effect of argon ion implantation on PC specimens. From the UV-Visible spectra of pre- and post-implanted specimens, structural analysis and color examination have been performed.

3.10.4.1 Structural Analysis

Fig. 3.27 (curves a-d) presents the UV-visible absorption spectra of virgin and implanted polycarbonate specimens at fluences of $1 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$.

![UV-Visible absorption spectra](image)

Fig. 3.27 UV-Visible absorption spectra (a) virgin and implanted PC specimens at 130 keV to (b) $1 \times 10^{14}$, (c) $1 \times 10^{15}$ and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$
Absorption peaks in UV-region are due to electronic transitions between occupied and unoccupied molecular orbitals and the spectrum in this region is particularly sensitive to conjugated bonds [37-38, 94-96]. Curve ‘a’ in Fig. 3.27, the absorption spectrum of virgin PC shows the presence of two peaks at 240 nm and 274 nm. These peaks are due to the electronic transition of n- π* and π-π* orbital which is likely to be associated with the carbonyl and phenyl groups in polycarbonate [37-38].

Further, it is also clear from the Fig. 3.27 that after Ar⁺ implantation, the two bands in the virgin specimen merged to one band with increased intensity in the implanted specimens. The fundamental absorption edge of virgin PC (curve ‘a’) shifts towards higher wavelength and simultaneously edge flattens with increasing ion fluence. Also the optical density increases with increase in ion fluence for the polymeric samples. This is due to the reason that ion beam interaction results in various processes such as ionization and excitation in the polymeric matrix which leads to the creation of dangling bonds, free radicals, chain-scission, loss of volatile fragments, cross-linking etc. [61,97-98,100]. These alterations in the PC specimens as a result of implantation leads to the formation of double or triple bonds or aromatic species which is responsible for red shift in the peaks [99]. Moreover, this shift in the peaks may be due to the increase in the number of conjugated bonds with increasing ion fluence results in a decreased HOMO-LUMO gap forcing the position of n-π* and π-π* transitions towards lower energy [38,43,89]. Furthermore, this broadening of the peaks and simultaneously flattening of the absorption edge with increasing implantation dose may be attributed to the production of defects such as anions, cations, radicals, organic species or centers etc.[37-38]. Such defects may result in the formation of new energy levels leading to the broadening of peaks [100]. Thus, it can be inferred that the argon ion implantation induces the modifications of the absorption bands.

3.10.4.2 Color Examination

The visual examination of specimens indicates that the color of the polycarbonate specimens is changed after argon ion implantation. The virgin PC sample was transparent and colorless. The color of the PC specimen changes from transparent (virgin PC) to light brown for a dose of 1x10¹⁴ Ar⁺ cm⁻² and at the highest dose of 1x10¹⁶ Ar⁺ cm⁻² to dark brown. The color transformation is related closely to the structural change as a result of ion implantation [8,34]. The observed change in the color of the PC specimen is due to the reason that ion implantation causes structural modifications in the polymeric matrix. Ion
beam treatment of polymers leads to the degradation of polymeric chains, cross-linking, creation of free radicals, molecular rearrangement which results in the formation of conjugated carbon-carbon double bonds and hence results in the carbonization of the surface layer of the polymeric specimen with increasing ion fluence [2,15,34,61,94-96].

Also, the changes in the color of the specimen from transparent (virgin) to dark brown (at highest fluence of $1 \times 10^{16}$ $\text{Ar}^+$ $\text{cm}^{-2}$) is correlated with the increase in the absorbance. These color changes are accompanying by the gradual increase in absorbance and intensity in the specimens with increase in ion fluence as discussed above. Also, the color change is associated with the formation of carbonaceous layer in the implanted specimens as indicated by RBS and XPS studies.

### 3.10.5 Dielectric Spectroscopy

Dielectric measurements [44-47,96-100] have been used to analyze the dielectric response of the $\text{Ar}^+$ implanted PC specimens. Using these measurements, dielectric constant, dielectric loss, dissipation factor, spreading factor, average relaxation time and molecular relaxation time have been calculated.

#### 3.10.5.1 Dielectric constant and Dielectric loss

The variation of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) as a function of frequency has been presented in Figs. 3.28 and 3.29 respectively for virgin and argon ion implanted polycarbonate samples. The dielectric properties of pre- and post-implanted PC specimens have been studied in the frequency range of 100 Hz to 90 MHz. The value of dielectric constant (curves ‘a’, ‘b’, ‘c’, &‘d’, Fig. 3.28) shows variation with frequency for all the PC specimens. In virgin PC (curve ‘a’, Fig 3.28) the value of dielectric constant increases from a value of 2.48 (at 100 Hz) to a maximum value of 13.4 (at 84.4 MHz). After implantation with $1 \times 10^{14}$ $\text{Ar}^+$ $\text{cm}^{-2}$ (curve ‘b’, Fig 3.28) the dielectric constant increases from 2.39 (at 100 Hz) to a maximum value of 13.2 (at 84.5 MHz). For a dose of $1 \times 10^{15}$ $\text{Ar}^+$ $\text{cm}^{-2}$ (curve ‘c’, Fig 3.28), $\varepsilon'$ increases from 2.24 (at frequency of 100 Hz) to a maximum value of 13.1 (at frequency of 84.6 MHz), and with the highest implantation dose of $1 \times 10^{16}$ $\text{Ar}^+$ $\text{cm}^{-2}$ (curve ‘d’, Fig 3.28) $\varepsilon'$ increases from 2.12 (at frequency of 100 Hz) to a maximum value of 13 (at 84.7 MHz).

The value of dielectric constant (curves ‘a’, ‘b’, ‘c’, &‘d’, Fig. 3.28) shows a variation from low frequency region to high frequency region for all the PC specimens. It is clear from the Fig. 3.28 that the value of $\varepsilon'$ increases up to the frequency of ~85 MHz.
Fig. 3.28 Plot of dielectric constant vs. frequency for (a) virgin and implanted PC specimens at 130 keV to (b) $1 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ $\text{Ar}^+ \text{ cm}^{-2}$.

This observed behaviour can be explained in terms of dipole orientation polarization mechanism. This polarization mechanism provides a reasonable explanation for the polarization as well as orientation of dipoles as a function of frequency [46-47]. However, in the absence of external electric field, the specimen will not exhibit any polarization as the distribution of individual dipoles is random [101-102] with all directions having equal probability. As the frequency increases, the field tries to orient the dipoles along its direction. Hence, there will be preferential orientation in the direction
Fig. 3.29 Variation in dielectric loss vs. frequency for (a) virgin and implanted PC specimens at 130 keV to (b) 1×10^{14}, (c) 1×10^{15}, and (d) 1×10^{16} Ar^+ cm^{-2} of applied field [53]. This results in increase of the values of the dielectric constant with increase in frequency.

However, after frequency of ~85 MHz, the value of dielectric constant falls. This change in the behaviour of $\varepsilon'$ can be explained in terms that the dipole orientation polarization (which is predominant upto the frequency of ~85 MHz) changes to atomic polarization [54] with further increase in frequency. As after 85 MHz frequency, the
dipole orientation polarization cannot attain its equilibrium value as dipoles start reversing their direction of orientation. This decreases the probability of polarization of dipole and hence atomic polarization results in the changes observed in the values of dielectric constant \[54,102\]. The difference in the values of dielectric constant measured at low and high frequencies is called the strength of the relaxation in polymers [45, 54,56].

Fig. 3.29 (Curves ‘a’, ‘b’, ‘c’ &‘d’) depicts the variation in the dielectric loss (\(\varepsilon''\)) as a function of frequency. The increase in \(\varepsilon''\) is observed upto frequency range ~83 MHz which may be due to the independent polarization of dipoles with applied field [102]. However, with further increase in frequency, the dipoles in a chain are coupled to the neighbouring dipoles of the same chain. So the motion of any dipole affects the motion of neighbours and in turn influences its response to the applied field [57]. This results in the decrease in the value of dielectric loss after frequency range ~83 MHz.

3.10.5.2 Dissipation factor

It is well known that in high frequency alternating fields there is always a phase difference between polarization and field, which give rise to dissipation factor [45,58]. The plot of dissipation factor (tan \(\delta\)) as a function of frequency is shown in Fig. 3.30 (curves ‘a’, ‘b’, ‘c’, &‘d’). It is clear from the figure that dissipation factor of polycarbonate specimens shows an increasing trend with increasing ion fluence as well as with frequency. It is also observed from the Fig. 3.30 that the position of tan \(\delta\) peak remains almost the same for virgin and implanted PC samples. Since this peak corresponds to the vibrations of the main chain hence it can be interpreted that even after implantation the main sources of this loss peak remain almost unaffected [56,59]. Moreover, dissipation factor is proportional to the electrical energy lost as heat in the polarization process in the presence of applied field [60] therefore it also increases with increasing ion fluence.

Hence, it is discerned that dielectric constant (Fig. 3.28) decreases whereas dielectric loss (Fig. 3.29) and dissipation factor (Fig. 3.30) increases with increasing ion fluence. These variations in the dielectric properties may be due to the fact that implantation generally induces destruction processes like scissioning of polymeric chains, creation of dangling bonds, formation of free radicals, etc. in the structure of polymeric specimens [2,61,103] and leads to degradation of the polymeric chains as observed through RBS, XPS, and UV-Visible spectroscopic analysis. Further, these modifications in the implanted PC lead to the formation of \(\pi\)-electron clouds with the applied field.
aligned in the direction of the molecular chains. This change in the direction of polarization causes the variations in the dielectric properties after implantation [34,104].

Fig. 3.30 Variation in dielectric loss tangent with frequency for (a) virgin and implanted PC specimens to (b) $1 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$.

3.10.5.3 a.c. conductivity

The a. c. conductivity at various frequencies for virgin and implanted PC specimens has been calculated using the formula given by equation (3.6). Fig. 3.31 shows the variation in a. c. conductivity of virgin and argon ion implanted polycarbonate samples in the frequencies range of 10 MHz to 80 MHz.
It is clear from the Fig. 3.31 that the value of a. c. conductivity increases with increasing frequency and ion fluence. This enhancement in the conductivity may be attributed to the structural changes occurring in the polymeric matrix and formation of carbon enriched domains [74,105] in the implanted layers of PC. These modifications in the dielectric properties of the specimens reveal that implantation results in the formation of carbonaceous clusters in the polymeric matrix as revealed by the RBS and XPS results.

3.10.5.4 Cole-Cole Plot

Cole-Cole plots are a succesful tool to analyze the dielectric data of the materials. The dielectric relaxation occurring in virgin and argon implanted polymeric specimens has been studied in detail through Cole-Cole plot in the 100 Hz to 90 MHz frequency range. The plot of real part ($\varepsilon'$) of the complex permittivity on the x-axis and imaginary part ($\varepsilon''$) of that on the y-axis is known as the Cole-Cole plot. The Cole-Cole plots are useful to study the distribution of relaxation time. Fig. 3.32 (curves ‘a’, ‘b’, ‘c’, &‘d’) shows the Cole-Cole plots for virgin and 130 keV Ar$^+$ implanted polycarbonate specimens to fluences $1\times10^{14}$, $1\times10^{15}$ and $1\times10^{16}$ ions cm$^{-2}$. Cole-Cole plots are used to determine the spreading factor ($\alpha$), average relaxation time ($\tau_0$) and molecular relaxation time ($\tau$).
Fig. 3.32  Cole-Cole plot of (a) virgin and implanted PC specimens at 130 keV to (b) $1 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

Fig. 3.32 (curves ‘a’, ‘b’, ‘c’, &‘d’) shows that Cole-Cole plots are imperfect semicircular in nature. The distortions in the shape of these plots are increasing with increasing ion fluence. This deviation in the shape of the Cole-Cole plots is due to the polydisperse nature of the amorphous polycarbonate for which value of spreading factor is not equal to 0 [53-54,67,106-107]. This polydisperse nature in polymers further increases owing to disorder due to ion implantation [67]. As the Cole-Cole plots are related to the relaxation phenomena [57,60,68] taking place in matrix, therefore, the changes observed in the nature of the curve after implantation also indicate towards the disorderness in the matrix and hence results in the formation of conjugated $\pi$-bonded clusters [37].

3.10.5.5  Spreading Factor ($\alpha$)

The value of spreading factor ($\alpha$) has been deduced from the expression for the maximum value of imaginary part of complex permittivity as given by the equation (3.7).
The plot of variation of spreading factor of pre- and post-implanted PC specimens with ion fluence is shown in Fig. 3.33. The calculated value of $\alpha$ is listed in Table 3.7. It has been found that the value of spreading factor increases with increasing ion fluence. Since its value is greater than 0 so it points towards the broad distribution of relaxation time [69,108] in the specimens and hence exhibit polydispersive nature. This increase in the value of $\alpha$ with increasing ion fluence (listed in Table 3.7) may be attributed to the increase in disordering in PC matrix [70]. It has also been discerned that polymers follow non-Debye theory of relaxation (for which $\alpha=0$) and hence exhibit much broader dispersion owing to distribution of relaxation time [53,57,106].

![Graph showing variation of spreading factor with ion fluence](image)

**Fig. 3.33** Variation of spreading factor ($\alpha$) with ion fluences for virgin and argon ion implanted polycarbonate specimen at 130 keV

**Table 3.7** Variation of spreading factor ($\alpha$), average relaxation time ($\tau_0$) and molecular relaxation time ($\tau$) at various ion fluences

<table>
<thead>
<tr>
<th>Ion fluence (Ar$^+$ cm$^{-2}$)</th>
<th>Spreading factor ($\alpha$)</th>
<th>Average relaxation time $\tau_0$ (s)</th>
<th>Molecular relaxation time $\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PC</td>
<td>0.66</td>
<td>$2.20 \times 10^{-9}$</td>
<td>$1.60 \times 10^{-9}$</td>
</tr>
<tr>
<td>$1 \times 10^{14}$</td>
<td>0.70</td>
<td>$0.36 \times 10^{-9}$</td>
<td>$0.27 \times 10^{-9}$</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>0.72</td>
<td>$0.24 \times 10^{-9}$</td>
<td>$0.17 \times 10^{-9}$</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>0.73</td>
<td>$0.15 \times 10^{-9}$</td>
<td>$0.11 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
3.10.5.6 Average relaxation time ($\tau_0$)

The average relaxation time $\tau_0$ for virgin and implanted PC specimens was calculated using the relation given by equation (3.8). Fig. 3.34 presents the plot of average relaxation time for virgin and implanted PC specimens at various doses. The measured values of $\tau_0$ is listed in Table 3.7.

![Graph of Average Relaxation Time vs Ion Fluence](image)

**Fig. 3.34** Variation of average relaxation time ($\tau_0$) with ion fluences for virgin and argon ion implanted polycarbonate specimen at 130 keV

From the Fig. 3.34, it is clearly observed that average relaxation time decreases with increasing ion fluence. This may be due to the implantation induced structural changes in the PC matrix and the formation of carbon enriched domains in the implanted layers.

3.10.5.7 Molecular relaxation time ($\tau$)

The molecular relaxation time ($\tau$) for virgin and implanted PC specimens is calculated using the formula as given by equation (3.9). Fig. 3.35 presents the plot of molecular relaxation time for virgin and implanted PC specimens at various doses. The measured values of ($\tau$) is listed in Table 3.7. Fig. 3.35 depicts clearly the decrease in molecular relaxation time with increasing ion fluence. This is similar to the earlier trend of average relaxation time (3.34). This may be due to the carbonization of the PC matrix due to argon ion implantation as already seen from the RBS and XPS analysis.
Therefore, it is clearly revealed from the Figs. 3.34 and 3.35 alongwith Table 3.7 that the values of average and molecular relaxation times decrease with increasing ion fluence. This can be attributed to the argon ion implantation induced structural damaged in the implanted layers and the formation of carbonaceous network in the modified surface layers as revealed by RBS and XPS analysis. Moreover, the decrease in the values of relaxation time may also be attributed to the improvement in the conductivity \([58,73]\) of PC specimens as a result of implantation.

3.10.6 Dielectric Constant and Dielectric Loss using Optical Absorption and Reflection Studies

In the present work we have also calculated the dielectric constant and dielectric loss using UV-Visible spectroscopy. The data of optical absorption and reflection has been used for these calculations for virgin and argon ion implanted PC specimens in the frequency range of \(0.42 - 0.75\) PHz corresponding to the visible region wavelength (400-700 nm). In this frequency range, the response of the specimens to the applied field is mainly due to electronic polarization \([44-45]\). This type of polarization occurs due to the deformation or translation of the originally symmetrical distribution of the electron clouds.
of atoms or molecules on the application of electric field. This is essentially the displacement of the outer electronic clouds with respect to the internal atomic cores by external fields. It is largely responsible for a number of optical properties of the materials [46-47,54].

In the present context the dielectric constant and dielectric loss are defined by equations (3.12) and (3.13) respectively. For studying the dielectric constant and dielectric loss in the visible region, the values of extinction coefficient and refractive index have been calculated using equations (3.14) and (3.15) respectively.

Fig. 3.36 shows the variation of extinction coefficient for virgin (curve ‘a’) and argon ion implanted PC specimens (curves ‘b’, ‘c’, & ‘d’) as a function of wavelength in the range of 400-700 nm.

Fig. 3.36 Variation in extinction coefficient with wavelength of (a) virgin and implanted PC specimens to (b) $1 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

It can be inferred from the Fig. 3.36 that the extinction coefficient remains constant for virgin PC whereas it shows a decreasing trend with wavelength for the implanted specimens. Moreover, extinction coefficient increases with increase in ion fluence.

Fig. 3.37 shows the reflectivity (%R) spectra in the visible region for virgin and argon implanted PC specimens. It is clear from the Fig. 3.37 that reflectivity of the PC specimens decreases with ion fluence. This may be due to the disordering created in the implanted specimens as a result of ion implantation [2].
The variations of refractive index for virgin and argon ion implanted polycarbonate specimens with increasing ion fluence as a function of wavelength are shown in Fig. 3.38. It is clear from the figure that refractive index decreases with increasing ion fluence.

Fig. 3.37 Reflectivity spectra recorded in the visible region of (a) virgin and implanted PC specimens to (b) $1 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

Fig. 3.38 Variation in refractive index with wavelength of (a) virgin and implanted PC specimens at 130 keV to (b) $1 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$
These changes observed in the refractive index of PC specimens may be due to ion beam interaction and its energy loss in the polymeric matrix during implantation. It is well known that ion beam interaction results in the formation of unsaturated delocalized π-electron clouds by either fusion of aromatic rings or increase in conjugation length of aliphatic bonds by bond breaking and reconstruction of the polymeric chains [96]. This corresponds to the change in the direction of polarization of the dipoles in response to applied field and hence refractive index decreases with increasing ion fluence [34].

The values of dielectric constant and dielectric loss have been calculated using the refractive index and extinction coefficient as discussed above. The variations of dielectric constant and dielectric loss with wavelength in the visible region are shown in Fig. 3.39 and 3.40 respectively. 

![Graph showing variation in dielectric constant with wavelength](image)

**Fig. 3.39** Variation in dielectric constant with wavelength of (a) virgin and implanted PC specimens at 130 keV to (b) $1 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

It can be inferred from the Fig. 3.39 (curves ‘a’, ‘b’, ‘c’ & ‘d’) that the value of dielectric constant decreases with increasing ion fluence. It is well known that dielectric constant depends on the polarization of π-electrons. This decline in the value of $\varepsilon'$ with ion fluence indicates that the net polarization of π-electrons tends to align with the molecular chains that are oriented in the direction of field. On the other hand in Fig. 3.40 (curves ‘a’, ‘b’, ‘c’ & ‘d’), $\varepsilon''$ has been found to increases with ion fluence.
This increase in the dielectric loss values is associated with the build up of electronic polarization between the dipoles in the direction of applied field [34,46].

### 3.3.7 Electrical Properties

Fig. 3.41 shows the Current-Voltage (I-V) characteristics for virgin as well as for 130 keV argon implanted PC specimens to fluences $1 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$. The I-V characteristics were recorded in the applied voltage range of 10-50 V. For virgin PC specimen (curve ‘a’, Fig. 3.41) the increase in current with applied voltage is less noticeable. After Ar$^+$ implantation, the value of current increases (curves ‘b’, ‘c’ & ‘d’, Fig. 3.41) slightly with applied voltage for the fluences $1 \times 10^{14}$ to $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$. The increase in current is found to be maximum for the highest implantation dose of $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$ (curve ‘d’, Fig. 3.41) in comparison to virgin (curve ‘a’, Fig. 3.41) PC specimen.

Fig. 3.41 shows that the increase in current is not proportional to the corresponding increase in voltage for all the specimens. So these observations indicate that there is the possibility of Ohmic conduction mechanism is ruled out. It can also be discerned from Fig. 3.41 (curves ‘b’, ‘c’ & ‘d’) that the current increases continuously with increasing argon ion fluence. This may be due to the reason that ion beam interaction generally leads to chain-scissioning, cross-linking in the polymeric matrix resulting in the creation of
conjugated double and triple bonds. These conjugated carbon bonds promotes the delocalization of charge carriers and hence leads to the formation of carbonaceous structure in the implanted specimens [37,81,109]. As a result of implantation, the formation of \( \pi \)-bonded carbonaceous clusters in the implanted layers induces electronic hopping process between individual conducting islands embedded in polymeric matrix [37,110]. Thus, they assist the flow of current and results in the modification in the conductivity of implanted polymers. The possible conduction mechanism taking place in the argon implanted PC specimens can be studied using different conduction mechanisms.

To analyze the charge transport mechanism in virgin and implanted PC specimens, I-V data is plotted in the form \( \ln (I) \) vs. \( V^{1/2} \) in Fig. 3.42. Different conduction mechanisms like Poole Frankel effect, Schottky emission, Space Charge Limited Conduction and Hopping [76-80] have been used to describe the I-V characteristic measurements in the polymeric matrix. The study of these conduction mechanisms operating in the polymeric matrix is carried out using fundamental thermionic emission equation (3.16).
Fig. 3.42 Plot of ln(I) vs. V^{1/2} for (a) virgin and implanted PC specimens at 130 keV to (b) 1\times10^{14}, (c) 1\times10^{15}, and (d) 1\times10^{16} \text{ Ar}^+\text{cm}^{-2}

The experimental value of $\beta$ i.e. $\beta_{\text{exp}}$ for virgin and implanted specimens has been calculated using the equations (3.17) and (3.18) and are given in Table 3.8.

The theoretical values of $\beta$ for \textbf{Schottky emission} as well as for \textbf{Poole-Frenkel emission} are calculated by equations (3.19) and (3.20) and are listed in Table 3.8.

**Table 3.8** A comparison between the theoretical and experimental $\beta$ coefficients of virgin and implanted PC specimens

<table>
<thead>
<tr>
<th>Ion Fluence (Ar^+cm^{-2})</th>
<th>Theoretical values of conduction parameter</th>
<th>Experimental values of conduction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky emission ($\beta_{RS}$) (eV-m^{1/2} V^{-1/2})</td>
<td>Poole Frenkel emission ($\beta_{PF}$) (eV-m^{1/2} V^{-1/2})</td>
<td>($\beta_{exp}$) (eV-m^{1/2} V^{-1/2})</td>
</tr>
<tr>
<td>Virgin</td>
<td>2.39 \times 10^{-5}</td>
<td>4.79 \times 10^{-5}</td>
</tr>
<tr>
<td>1 \times 10^{14}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 \times 10^{15}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 \times 10^{16}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is clear from the table that, the experimental value ($\beta_{exp}$) for virgin PC specimen is very close to the theoretically calculated value of $\beta_{PF}$. This indicates that the probable
mechanism of charge transport in virgin sample is Poole–Frenkel. However, after implantation, it has been found that the values of $\beta_{exp}$ was close to the theoretical value of $\beta_{RS}$, leading to the conclusion that Schottky emission is the dominant charge transport mechanism operating in the argon implanted PC specimens. This transition in the conduction mechanism from Poole-Frenkel (for virgin PC) to Schottky emission (for implanted PC specimens) may be due to the improvement in the conductivity of these specimens as a result of implantation [79-80]. This can be attributed to the conduction through the charge carriers released as a result of argon ion implantation which results in the enhancement in the conductivity of the polymeric specimens.

This increase in conductivity of the specimens also results from the Hopping mechanism. Hopping is the predominant mechanism of conduction for charges between localized states usually generated by thermal excitations. This conduction mechanism requires the charge carriers to execute discrete jumps from one site to another [83]. The observed increase in the conductivity of the PC specimens also results from the hopping of charge carriers across the defect sites of the material.

However, in the present case, the value of the I-V characteristic slope is not in accordance with the slope of space charge linear conduction mechanism (SCLC) for which slope should be greater than or equal to 2. Therefore, this conduction mechanism is ruled out [58,82].

Hence, it can be concluded that ion implantation results in the increase in the surface conductivity in the PC specimens. Also, the transition in the conduction mechanism from Poole-Frenkel (for virgin PC) to Schottky emission (for implanted PC specimens) indicates towards the enhancement in the conductivity of the PC specimens after argon ion implantation. This may be due to the formation of charge carriers resulting from $\pi$- bonded carbon clusters in the implanted layers of the polymeric matrix [34,58]. Therefore, formation of such clusters may have been contributed significantly towards the enhancement in the conductivity of implanted matrix. Also, RBS spectroscopic measurements confirm the formation of carbonisation in the implanted layers of the specimens. Hence, the increase in the number of carbon atoms is responsible for the formation of carbonaceous network containing $\pi$-electron clouds in the implanted PC matrix. Also, the variations observed in the topographical images as well as structure have been confirmed by AFM and UV-Visible spectroscopy. The changes observed on the
surface of specimens as an effect of Ar$^+$ implantation may be attributed towards the degradation process taking place in the polymeric chains which results in the formation of cross-linking and carbon-rich structures in the polymeric chains. Also, the Cole-Cole analysis of virgin and implanted PC specimens indicates towards the polydispersive nature. Moreover, the shapes of the Cole-Cole curves confirmed the structural disordering in implanted PC specimens. I-V characteristic measurements showed that Schottky emission is the dominant charge transport mechanism operating in implanted specimens. Hence the results of different characterization techniques agree well with each other.
3.4 Effects of Argon Ion Implantation on Polypropylene (PP)

The polypropylene samples were implanted with 130 keV Ar\textsuperscript{+} ions with different fluences ranging from 5×10\textsuperscript{14}, 1×10\textsuperscript{15} and 1×10\textsuperscript{16} ions cm\textsuperscript{-2}. The effect of argon ion implantation on structural, dielectric, electrical and optical properties of pre- and post-implanted PP specimens is investigated and the results are discussed in the following sections.

3.4.1 Rutherford Backscattering Spectroscopy

RBS measurements have been used to analyze the composition and structure of the Ar\textsuperscript{+} implanted surface layers of PP. From the RBS spectra of pre- and post-implanted PP specimens, the various elements present in the implanted layer and their differential cross-sections have been calculated using the kinematic factors. Also, the projected range, retained dose and atomic concentration of implanted argon have been analyzed.

3.4.1.1 Composition and Structure

From the recorded RBS spectra of virgin Fig. 3.43 ‘a’ and 130 keV Ar\textsuperscript{+} ion implanted Fig. 3.43‘b’ polypropylene specimen at fluence of 1×10\textsuperscript{16} Ar\textsuperscript{+} cm\textsuperscript{-2}, it has been noticed clearly that argon ion implantation has completely modified the RBS spectra of virgin PP.

Fig. 3.43 RBS spectra of (a) virgin and (b) implanted polypropylene specimen at 130 keV to 1x10\textsuperscript{16}Ar\textsuperscript{+} cm\textsuperscript{-2}

For the quantitative analysis of the RBS spectra of both virgin and argon implanted PP, Rutherford Backscattering Manipulation Program (RUMP) software [1] has been used. The RUMP fitted spectra of the virgin and implanted PP specimens is presented in Fig. 3.44. Using RUMP analysis, the edge present at energy value ~510 keV in the spectra
Fig. 3.44 RUMP fitted RBS spectra of (a) virgin and (b) argon ion implanted polypropylene at fluence $1 \times 10^{16}$ Ar$^+ \text{ cm}^{-2}$

of Fig. 3.44 (‘a’ & ‘b’) has been identified as of carbon. The peaks present at energy value $\sim 680$ keV and $\sim 1320$ keV belong to oxygen and argon respectively. Although oxygen was not present in the virgin PP originally but the presence of oxygen in the implanted PP may be because of the diffused oxygen on the surface of this specimen which was thoroughly cleaned unfortunately using acetone. However, it was not observed in the nitrogen implanted PP specimen which was not cleaned in the way as in earlier case.

The composition of carbon has been analyzed by RUMP simulations. Simulation yielded an increase in the concentration of C in implanted specimen in comparison to virgin specimen. It has been found that for the fluence of $1 \times 10^{16}$ Ar$^+ \text{ cm}^{-2}$, the carbon concentration increases near the surface from to 33 at.% to 46 at.% This indicates that the argon ion implantation has produced significant changes in the surface composition in the implanted layer of the polymeric matrix. Analysis also revealed the presence of argon and it is about 0.15 at.% in the implanted layer of the specimen.

It is also clear from the Fig. 3.44 (‘b’) that there is variation (first decreases and then increases again) in the carbon spectra of the implanted PP surface between 0.38 MeV to 0.51 MeV as compared to the unimplanted one (Fig. ‘a’, 3.44). The decreasing of the spectra points towards the formation of carbonaceous network accompanied by scissioning of polymeric chains, cross-linking, liberation of volatile components near the surface region as a result of ion implantation. This points toward the carbon enriched layer in the implanted polymeric matrix [3,11].

Hence, it can be inferred that carbonization occurs near the surface as a result of ion implantation and a carbonaceous network has formed in the implanted layers. The
effect of carbonization is of considerable interest because of significant change of the structure and composition of argon ion implanted PP specimens. It has also been noticed from the earlier studies [12-13,75,89] that dehydrogenation also takes place in the implanted surface of the specimen though it is not measurable by RBS technique. This decrease in the composition of hydrogen results in the relative increase in the composition of carbon. [16,17,111]. Thus, the increase in the concentration of carbon results in carbonaceous layer in the implanted layer.

3.4.1.2 Backscattered Energies

It is well known that kinematic factor is a measure of backscattered energies of the scattered particles during RBS studies and establishes relationship between incident ($E_0$) and backscattered ($E_1$) energies given by equation (3.1).

Using RUMP fitted RBS spectra the values of backscattered energies for carbon, oxygen and argon has been determined. Table 3.9 presents these experimentally determined backscattered energies along with corresponding values calculated directly using equation (3.1).

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass number</th>
<th>Kinematic factor ‘K’</th>
<th>Incident energy $E_0$ (MeV)</th>
<th>Backscattered $E_1$ (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>12</td>
<td>0.253</td>
<td>2</td>
<td>0.510</td>
</tr>
<tr>
<td>Argon</td>
<td>40</td>
<td>0.680</td>
<td>2</td>
<td>1.320</td>
</tr>
</tbody>
</table>

It has been observed that the experimental and calculated backscattered energies values are in well agreement.

3.4.1.3 Elemental Identification in the Target

In RBS studies, energies of backscattered particles give the quantitative information of the different masses of individual elements present in the target material. Using the relation given by equation (3.2), we have identified the individual elements i.e. carbon and argon present in the specimen.

3.4.1.4 Calculation of Differential Cross Section

The differential cross section is a measure of the probability with which a projectile is elastically scattered from target atom [18-20] and is based on the Coulomb interaction potential. Again using equation (3.3), we have calculated the values of
differential cross sections for carbon and argon elements and the values are listed in Table 3.1b. The calculated values have been found to be in good agreement with the theoretical values.

3.4.1.5 Calculation of Implanted Fluence

From the data obtained from the RBS spectra (Fig. 3.44) the implantation dose in the implanted PP specimens has been confirmed and verified using formula [18-19] as given by equation (3.4). Using the calculated values of different parameters, the retained implantation fluence comes out to be $0.99 \times 10^{16}$ Ar$^+$ cm$^{-2}$ which is in well agreement with the real implanted ion fluence of $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$.

3.4.1.6 Calculation of Atomic Concentration

The atomic concentration of implanted argon ($N_{Ar}$) in the PP specimen is calculated using formula [18-19] as given by equation (3.5). The atomic concentration of implanted argon has been calculated using height measurements and its value comes out to be 0.12 at.% which is in well agreement with the value 0.15 at.% calculated using RUMP fitted RBS spectra.

3.4.1.7 Calculation of Projected Range

The value of projected range of the Ar$^+$ implanted PP specimen comes out to be 214 nm using RUMP fitted RBS spectra which is in very good agreement with the value 212 nm as per Stopping and Range of Ions in Matter (SRIM) simulations [22].

3.4.2 Atomic Force Microscopy

AFM study was performed to characterize the surface topography and roughness values of the virgin and argon ion implanted polypropylene specimens to different fluences. The two-dimensional AFM images (recorded at 2μm × 2μm size) of virgin and 130 keV Ar$^+$ ion implanted PP samples to fluences $5 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ ions cm$^{-2}$ is shown in Fig. 3.45 (a-d).

The surface topographical image for virgin PP Fig 3.45 ‘a’ appears to be uniform and smooth. The root mean square roughness (R$_{rms}$) and average roughness (R$_{av}$) has been calculated using Nova Px software. The calculated root mean square roughness (R$_{rms}$) and average roughness (R$_{av}$) values for virgin PP sample are 4.90 nm and 3.36 nm respectively. However, after argon ion implantation, the surface morphology of the specimens has been observed to be change and there is enhancement in the R$_{rms}$ and R$_{av}$ roughness values. After implantation with $5 \times 10^{14}$ Ar$^+$ cm$^{-2}$ (‘b’, Fig 3.45), the calculated
values of $R_{\text{rms}}$ and $R_{\text{av}}$ are 8.54 nm and 6.76 nm respectively. For a dose of $1 \times 10^{15}$ Ar$^+$ cm$^{-2}$ (Fig 3.45‘c’), the $R_{\text{rms}}$ and $R_{\text{av}}$ values increase to 11.43 nm and 9.53 nm respectively and with the highest implantation dose of $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$ Fig 3.45 ‘d’, these values increases to 19.12 nm and 11.39 nm. The $R_{\text{rms}}$ and $R_{\text{av}}$ values of virgin and implanted PP specimens are listed in Table 3.10.

Table 3.10  Variation of root mean square roughness and average roughness values with ion fluence

<table>
<thead>
<tr>
<th>Ion Fluence (Ar$^+$ cm$^{-2}$)</th>
<th>Root mean square roughness $R_{\text{rms}}$ (nm)</th>
<th>Average roughness $R_{\text{av}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PP</td>
<td>4.90</td>
<td>3.36</td>
</tr>
<tr>
<td>$5 \times 10^{14}$</td>
<td>8.54</td>
<td>6.76</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>11.43</td>
<td>9.53</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>19.12</td>
<td>11.39</td>
</tr>
</tbody>
</table>

Fig. 3.46 presents the plot of rms and average roughness values of as a function of ion fluence. The enhancement in the $R_{\text{rms}}$ and $R_{\text{av}}$ roughness values can be attributed to degradation process taking place in the polymeric chains [28-29] due to implantation.
Moreover, it has been noticed that the uniformity in the specimens with increasing ion fluence is lost. The changes observed on the surface of polymeric specimens as an effect of Ar$^+$ ion implantation may be due to the formation of cross-linking and carbon-rich structures in the polymeric chains. This leads to the degradation in the uniformity in the polymeric chains which results in the changes in the free volume fraction in the modified layer. This in turn leads to the changes in the structure of the implanted surface [30,112-114]. Thus, AFM images reflect the modification on the surface of the polymeric specimens by ion implantation.

### 3.4.3 UV-Visible Spectroscopy

UV-Visible Spectroscopy has been performed to analyze the effect of argon ion implantation on PP specimens. From the UV-Visible spectra of pre- and post-implanted specimens structural analysis and color examination have been carried out.

#### 3.4.3.1 Structural Analysis

UV-Visible absorption spectroscopy is a suitable technique for analyzing the structural changes in the polymeric specimens induced by ion implantation. Fig. 3.47 (curves a-d) presents the UV-Visible absorption spectra of virgin and argon implanted (fluences of $5\times10^{14}$, $1\times10^{15}$, and $1\times10^{16}$ ions cm$^{-2}$) PP specimens. In case of virgin spectra
(curve ‘a’), two absorption peaks at observed at 240 nm and 273 nm. Such characteristic absorption peaks are due to electronic transitions between HOMO to LUMO and are associated with σ-σ* transitions [37-38,115-117]. These transitions are due to the presence of alkane group in the polypropylene specimen.

It is observed from the Fig. 3.47 that optical absorption increases with increasing fluence and absorption edge shifts from UV towards visible region and flattens out. Furthermore, with increasing ion fluence, the two existing bands in the virgin specimen have merged to one band with continuous increase in intensity and hence results in the broadening of the peaks. This increase in intensity also corresponds to the changes observed in the color of PP specimens.

Also, the bathochromic shift and flattening of the edge due to implantation indicates towards the formation of delocalized conjugated bonds in the implanted polymeric matrix [37,100]. This increase in optical absorption and red shift of the absorption edge is due to the fact that as a result of implantation, the original bonds in the PP matrix got ruptured and leads to chain scission, cross linking, free radicals, and new bond formation etc. [34,61,115,117]. It suggests the significant change in the structure of the implanted layers due to the formation of carbonaceous structure causing an increase in conjugation which also agrees well with the result of RBS studies.

![Figure 3.47](image_url)  
**Fig. 3.47** UV-Visible absorption spectra (a) virgin and implanted PP specimens at 130 keV to (b) 5×10^{14}, (c) 1×10^{15}, and (d) 1×10^{16} Ar⁺ cm⁻²
3.4.3.2 Color Examination

On visual examination the color of implanted PP specimens has been found to be changed. It changes from transparent (in virgin) to light brown and to grayish black with increasing implantation fluence. The color transformation is related closely to the structural change after ion implantation [2,8,115].

The change in color of the specimen after ion implantation may be because of the reason that ion beam treatment of polymers results in the rupturing of chemical bonds, formation of free radicals etc. and hence leads to the creation of conjugated $\pi$-electron clouds, cross linking and hence results in carbonization of the surface layer [34,116-117].

3.4.4 Dielectric Spectroscopy

The dielectric response related to dielectric constant, dielectric loss, dissipation factor, spreading factor, average relaxation time and molecular relaxation time in the Ar$^+$ implanted PP specimens have been analyzed using Dielectric measurements [44-47].

3.4.4.1 Dielectric constant and Dielectric loss

Figs. 3.48 and 3.49 presents the variation of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) respectively as a function of frequency for virgin and argon ion implanted polypropylene samples in the frequency range of 100 Hz to 90 MHz. It is clear from the Fig. 3.48 that the value of dielectric constant varies with frequency for all the PP specimens. In virgin PP (curve ‘a’, Fig 3.48) the value of dielectric constant increases from a value of 1.94 (at 100 Hz) to a maximum value of 7.68 (at 87.8 MHz). After implantation with 5x10$^{14}$ Ar$^+$ cm$^{-2}$ (curve ‘b’, Fig 3.48), the dielectric constant increases from 1.47 (at 100 Hz) to a maximum value of 7.64 (at 87.9 MHz). For a dose of 1x10$^{15}$ Ar$^+$ cm$^{-2}$ (curve ‘c’, Fig 3.48), $\varepsilon'$ increases from 1.23 (at 100 Hz) to a maximum value of 7.62 (at 88 MHz), and with the highest implantation dose of 1x10$^{16}$ Ar$^+$ cm$^{-2}$(curve ‘d’, Fig 3.48) $\varepsilon'$ increases from 1.13 (at 100 Hz) to a maximum value of 7.6 (at 88.1 MHz).

The value of dielectric constant (Fig. 3.48) shows a variation from low frequency region to high frequency region for all the PP specimens. It is observed form the Fig. 3.48 that the value of $\varepsilon'$ increases upto the frequency of ~88 MHz. This observed behaviour can be explained in terms of dipole orientation polarization mechanism which provides a reasonable explanation for the polarization as well as orientation of dipoles as a function of frequency [47,118-119]. As with increasing frequency, the field tries to orient the dipoles along its direction. Hence, there will be preferential orientation in the direction of
Fig. 3.48  Plot of dielectric constant vs. frequency for (a) virgin and implanted PP specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$ applied field [53] which results in increase in the values of the dielectric constant with increase in frequency. However, after frequency of $\sim 88$ MHz, the value of dielectric constant falls. This change in the behaviour of $\varepsilon'$ can be attributed to the change of the dipole orientation polarization to atomic polarization [54] with increasing frequency. The difference in the values of dielectric constant measured at low and high frequencies is called the strength of the relaxation in polymers [53,55-56].
Fig. 3.49 (curves ‘a’, ‘b’, ‘c’ &‘d’) depicts the variation in the dielectric loss ($\varepsilon''$) as a function of frequency. The increase in $\varepsilon''$ is observed up to frequency range ~84 MHz which may be due to the independent polarization of dipoles with applied field [102]. With further increase in frequency, the dipoles in a chain are coupled to the neighboring dipoles of the same chain. So the motion of any dipole affects the motion of the adjacent dipoles of the main chain and in turn influences its response to the applied field [57]. This results in the decrease in the value of dielectric loss after frequency range ~84 MHz.

![Graph](image-url)

Fig. 3.49 Variation in dielectric loss vs. frequency for (a) virgin and implanted PP specimens at 130 keV to (b) $5\times10^{14}$, (c) $1\times10^{15}$ and (d) $1\times10^{16}$ Ar+ cm$^{-2}$
3.4.4.2 Dissipation factor

Dissipation factor generally arises in high frequency alternating fields when there occurs a phase difference between polarization and field [58]. Fig. 3.50 (curves ‘a’, ‘b’, ‘c’, &‘d’) presents the plot of dissipation factor (\( \tan \delta \)) as a function of frequency. It is clear from the Fig. 3.50 that dissipation factor of polypropylene specimen shows an increasing trend with ion fluence as well as with frequency.

Fig. 3.50 Variation in dielectric loss tangent with frequency for (a) virgin and implanted PP specimens at 130 keV to (b) \( 5 \times 10^{14} \), (c) \( 1 \times 10^{15} \) and (d) \( 1 \times 10^{16} \) Ar\(^+\)cm\(^{-2}\)
It is also noticed that the peak position of tan δ remains almost the same for virgin and implanted PP samples. This peak is due to the vibrations of the main chain hence even after implantation the main sources of this loss peak remain almost unaffected [56,59].

It is clear from the figures (3.48, 3.49 & 3.50) that dielectric constant ($\varepsilon'$) decreases whereas dielectric loss ($\varepsilon''$) and dissipation factor (tan δ) increases with increasing ion fluence. This may be due to the fact that implantation results the disordering [34,86,120] in the structure of polymeric specimens as observed through RBS, AFM and UV-Visible spectroscopy results.

3.4.4.3 a. c. conductivity

The a. c. conductivity at various frequencies for virgin and implanted PP specimens has been calculated using equation (3.6). The variation in a. c. conductivity of virgin and implanted PP samples to fluences $5 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ ions cm$^{-2}$ is shown in Fig. 3.51. The a. c. conductivity has been calculated in the frequencies range of 30 MHz to 80 MHz.

![Graph showing the variation of a. c. conductivity with ion fluences at various frequencies for virgin and implanted PP specimens at 130 keV](image)

Fig. 3.51 Plot of a. c. conductivity with ion fluences at various frequencies for virgin and implanted PP specimens at 130 keV

Fig. 3.51 shows that the a.c. conductivity increases with increasing frequency and ion fluence. This enhancement in the conductivity after implantation may be attributed to the formation of carbon-rich clusters with conjugated bonds in the polymeric matrix [37,121]. Thus the variations in the dielectric properties may be due to the formation of carbonaceous network containing carbon clusters in the implanted layers of the specimens.
3.4.4.4 Cole-Cole Plot

Fig. 3.52 (curves ‘a’, ‘b’, ‘c’, &‘d’) shows the Cole-Cole plots for virgin and 130 keV Ar\(^+\) implanted polypropylene specimens in the 100 Hz - 90 MHz frequency range. The spreading factor (\(\alpha\)), average relaxation time (\(\tau_0\)) and molecular relaxation time (\(\tau\)) has been determined using Cole-Cole plots.

It is clear from the Fig. 3.52 (curves ‘a’, ‘b’, ‘c’, &‘d’) that curves of the Cole-Cole plots are imperfect semicircular in nature. Further, the height of the curves in the Cole-Cole plots increases with increasing ion fluence. This deviation in the shape and increase in height of the curves of the Cole-Cole plots is due to the polydispersive nature of the amorphous PP [53,65-67]. Also the polydispersive nature of these specimens further increases owing to disorder as a result of ion implantation [67,122-123]. This in turn results in the much larger dispersion owing to distribution of relaxation time. As the Cole-Cole plots are related to the relaxation phenomena [57,60,68] taking place in matrix,
therefore, the changes observed in the nature of the curve after implantation also indicate towards the disorderness in the matrix and hence results in the formation of conjugated π-bonded clusters [37].

3.4.4.5 Spreading Factor ($\alpha$)

The value of spreading factor ($\alpha$) has been calculated from the expression for the maximum value of imaginary part of complex permittivity as given by the equation (3.7). Fig. 3.53 presents the plot of variation of spreading factor for PP specimens as a function of ion fluence. The calculated value of $\alpha$ is listed in Table 3.11.

**Table 3.11  Variation of spreading factor ($\alpha$), average relaxation time ($\tau_0$) and molecular relaxation time ($\tau$) at various ion fluences**

<table>
<thead>
<tr>
<th>Ion fluence (Ar$^+$ cm$^{-2}$)</th>
<th>Spreading factor ($\alpha$)</th>
<th>Average relaxation time ($\tau_0$) (s)</th>
<th>Molecular relaxation time ($\tau$) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PP</td>
<td>1.43</td>
<td>$1.27 \times 10^{-9}$</td>
<td>$2.52 \times 10^{-9}$</td>
</tr>
<tr>
<td>$5 \times 10^{14}$</td>
<td>1.44</td>
<td>$0.77 \times 10^{-9}$</td>
<td>$1.84 \times 10^{-9}$</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>1.46</td>
<td>$0.49 \times 10^{-9}$</td>
<td>$1.34 \times 10^{-9}$</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>1.49</td>
<td>$0.33 \times 10^{-9}$</td>
<td>$0.97 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

**Fig. 3.53** Variation of spreading factor ($\alpha$) for with ion fluences for virgin and argon ion implanted polypropylene specimen at 130 keV
It has been observed that the value of spreading factor increases with increase in ion fluence. This indicates that there is a broad distribution of relaxation times \([53,122]\) in the specimens and hence exhibit polydisperse nature. Moreover, this increase in the value of \(\alpha\) with increasing ion fluence (listed in Table 3.11) may be attributed to the increase in disordering \([70]\) and hence to the height of the curves of the Cole-Cole plots after implantation.

### 3.4.4.6 Average relaxation time (\(\tau_0\))

The average relaxation time \(\tau_0\) for virgin and implanted PP specimens was calculated using the relation given by equation (3.8). The plot of average relaxation time for virgin and implanted PP specimens at various doses is shown in Fig. 3.54. The measured values of \(\tau_0\) is listed in Table 3.11. It is clear from the Fig. 3.54 that average relaxation time decreases with ion fluence. This may be due to the implantation induced structural disordering in the PP matrix.

![Graph showing variation of average relaxation time with ion fluence](image)

**Fig. 3.54** Variation of average relaxation time (\(\tau_0\)) with ion fluences for virgin and argon ion implanted polycarbonate specimen at 130 keV

### 3.4.4.7 Molecular relaxation time (\(\tau\))

Further by utilising the values of \(\tau_0\), the molecular relaxation time (\(\tau\)) for pre- and post-implanted PP specimens is calculated using the formula as given by equation (3.9).
The plot of molecular relaxation time for virgin and implanted PP specimens at various doses is presented in Fig. 3.55. The measured values of ($\tau$) are listed in Table 3.11. It is clear from the Fig. 3.55 that molecular relaxation time decreases with increasing ion fluence. This is similar to the earlier trend of average relaxation time (3.54). This may be due to the carbonization of the PP matrix due to argon ion implantation as already seen from the RBS studies.

![Molecular Relaxation Time vs Ion fluence](image_url)

**Fig. 3.55 Variation of molecular relaxation time ($\tau$) with ion fluences for virgin and argon ion implanted polypropylene specimen at 130 keV**

It is clear from Table 3.11 that both the average and molecular relaxation times decrease with argon ion fluence. This may be due to the fact that with increase in implantation dose, structural disordering and carbonization of the PP matrix increase thereby decreasing the relaxation time. This decrease in the values of relaxation time may also be attributed to the improvement in the conductivity [58,73] of PP specimens as a result of implantation.

### 3.4.5 Dielectric Constant and Dielectric Loss using Optical Absorption and Reflection Studies

The dielectric constant and dielectric loss have also been calculated using UV-Visible Spectroscopy. The data for optical absorption and reflection has been used for these calculations for virgin and argon ion implanted PP specimens in the frequency range of .42 - .75 PHz corresponding to the visible region wavelength (400-700 nm). In this frequency range, the response of the specimens to the applied field is mainly due to
electronic polarization [44-45]. It is responsible for a number of optical properties of the materials [46-47,101]. In the present context the dielectric constant and dielectric loss are defined by equations (3.12) and (3.13) respectively. For studying the dielectric constant and dielectric loss in the visible region, the values of extinction coefficient and refractive index have been calculated using equations (3.14) and (3.15) respectively.

![Extinction coefficient vs Wavelength](image1)

Fig. 3.56 Variation in extinction coefficient with wavelength of (a) virgin and implanted PP specimens to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ $\text{Ar}^+ \text{cm}^{-2}$

![Reflectivity spectra](image2)

Fig. 3.57 Reflectivity spectra recorded in the visible region of (a) virgin and implanted PP specimens to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ $\text{Ar}^+ \text{cm}^{-2}$
The variation of extinction coefficient for virgin and argon ion implanted PP specimens as a function of wavelength in the range of 400-700 nm is shown in Fig. 3.56. It is clear from the Fig. 3.56 that the extinction coefficient remains constant for virgin PP whereas it shows a decreasing trend for all the implanted specimens with wavelength. Further, it increases with increase in ion fluence.

Fig. 3.57 shows the reflectivity (%R) spectra in the visible region for virgin and argon implanted PP specimens. It is clear from the Fig. 3.57 that reflectivity decreases with increasing ion fluence. This may be due to the disordering created in the implanted specimens as a result of ion implantation.

The variations of refractive index as a function of wavelength for virgin and 130 keV argon ion implanted PP specimens with fluence $5 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ ions cm$^{-2}$ is shown in Fig. 3.58.

![Diagram of refractive index variation](image)

**Fig. 3.58** Variation in refractive index with wavelength of (a) virgin and implanted PP specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

It is clear from the Fig. 3.58 that after implantation, noticeable change has been observed in the values of refractive index. The value of refractive index decreases with increasing ion fluence. This signifies that when an ion beam interacts with polymeric surface then it results in the energy losses, scissioning of the polymeric chain, releases small volatile species and cross-links the unsaturated adjacent radicals. As a result, carbon enriched conjugated multiple bonds are formed [34,37,52]
Using the calculated values of refractive index and extinction coefficient, the values of dielectric constant and dielectric loss has been calculated. Fig. 3.51 and 3.52 show the plots of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) respectively with wavelength in the visible region.

![Graph showing dielectric constant and loss with wavelength]  

**Fig. 3.59** Variation in dielectric constant with wavelength of (a) virgin and implanted PP specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$

![Graph showing dielectric loss with wavelength]  

**Fig. 3.60** Variation in dielectric loss with wavelength of (a) virgin and implanted PP specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$ and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$
The value of $\varepsilon'$ (Fig. 3.59) shows a decreasing trend with increasing ion fluence for all the specimens. However, it is clear from the Fig. 3.60 that the value of $\varepsilon''$ increases after ion implantation. These modifications in the behaviour of the dielectric properties after ion implantation are due to the fact that when an ion beam interacts with polymeric surface, a large number density of cross-link is introduced and numerous double and triple bonds and free radicals are formed which promotes the delocalization of charge carriers. Moreover, in response to an applied field, these charge carriers tend to polarize in the direction of molecular chain. This net polarization is associated with the build up of electronic polarization between the dipoles in the direction of applied field [34,47]. This change in the direction of polarization results in the changes in the dielectric properties.

### 3.4.6 Electrical Properties

Fig. 3.61 shows the Current-Voltage (I-V) characteristics for pre- and post-implanted polypropylene specimens to fluences ranging from $5 \times 10^{14}$ to $1 \times 10^{16} \text{ Ar}^+ \text{ cm}^{-2}$. The I-V characteristics were recorded in the applied voltage range of 10-50 V. Curve ‘a’ in Fig. 3.61 for virgin PP specimen shows that the variation in the value of current with applied voltage is almost constant. However, for the fluences $5 \times 10^{14} \text{ Ar}^+ \text{ cm}^{-2}$ to $1 \times 10^{16} \text{ Ar}^+ \text{ cm}^{-2}$ (curves ‘b’, ‘c’ and ‘d’, Fig. 3.61), there is a slight increase in the value of current with applied voltage. It has also been observed from the curve ‘d’, Fig. 3.61 that

![I-V Characteristics](image)

**Fig. 3.61** I-V Characteristics for (a) virgin and implanted PP specimens at 130 keV to (b) $5 \times 10^{14}$, (c) $1 \times 10^{15}$, and (d) $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$
the increase in current is maximum for the highest implantation dose of $1 \times 10^{16}$ Ar$^+$ cm$^{-2}$ in comparison to virgin PP specimen.

Fig. 3.61 (curves ‘a’, ‘b’, ‘c’ &‘d’) reveals that the increase in current is not proportional to the corresponding increase in the applied voltage for all the specimens. Thus, it can be inferred that there is no possibility of Ohmic conduction mechanism in these specimens. Moreover, it can also be seen clearly from Fig. 3.61 (curves ‘b’, ‘c’ &‘d’) that the current increases continuously with increasing argon ion fluence. This can be explained on the basis that ion implantation results in rupturing of chemical bonds, formation of free radicals and conjugated system which is associated with the carbonaceous clusters. Therefore, formation of this carbonaceous network in the implanted layer results in significant enhancement in the conductivity [85] as a result of implantation. These carbonaceous clusters induce electronic hopping process among different conducting sites embedded in polymeric matrix [83,116]. This enhances the motion of the charge carriers which contribute towards the modification in the conductivity of implanted polymers. The possible conduction mechanism operating in the argon implanted PP specimens can be studied using different conduction mechanisms.

To reveal the charge transport mechanism in virgin and implanted PP specimens, the I-V data is plotted in the form ln ($I$) vs. $V^{1/2}$ in Fig. 3.62.

![Fig. 3.62 Plot of ln (I) vs. V^{1/2} for (a) virgin and implanted PP specimens at 130 keV to (b) 5×10^{14}, (c) 1×10^{15}, and (d) 1×10^{16} Ar^+ cm^{-2}](image-url)
Similar to the earlier cases of CR-39 and PC polymers different conduction mechanisms have been used to describe the I-V characteristic measurements in the polymeric matrix. The experimental value of $\beta$ i.e. $\beta_{\text{exp}}$ for virgin and implanted specimens has been calculated using the equations (3.17) and (3.18) and are given in Table 3.12. The theoretical values of $\beta$ for Schottky emission as well as for Poole-Frenkel emission are calculated by equations (3.19) and (3.20) and are listed in Table 3.12.

### Table 3.12  A comparison between the theoretical and experimental $\beta$ coefficients of virgin and implanted PP specimens

<table>
<thead>
<tr>
<th>Ion Fluence $(\text{Ar}^+ \text{cm}^{-2})$</th>
<th>Theoretical values of conduction parameter</th>
<th>Experimental values of conduction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Schottky emission $(\beta_{RS})$ (eV-m$^{1/2}$ V$^{-1/2}$)</td>
<td>Poole Frenkel emission $(\beta_{PF})$ (eV-m$^{1/2}$ V$^{-1/2}$)</td>
</tr>
<tr>
<td>Virgin</td>
<td>$2.68 \times 10^{-5}$</td>
<td>$5.36 \times 10^{-5}$</td>
</tr>
<tr>
<td>$5 \times 10^{14}$</td>
<td>$4.94 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>$2.61 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>$2.38 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.24 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

It has been noticed from the table that, the experimental value $(\beta_{\text{exp}})$ for virgin PP has been found to be in good agreement with the theoretical value of $\beta_{PF}$. This leads to the conclusion that Poole–Frenkel mechanism is the dominating mechanism in case of the virgin PP specimen. However, after implantation, the values of $\beta_{\text{exp}}$ found to be close to the theoretical value of $\beta_{RS}$. This transition of the conduction mechanism may be due to the improvement in the conductivity [37,76,79-80] after implantation. This may be due to abrupt increase in the concentration of charge carriers with increase in ion fluence which results in the enhancement in the conductivity of the polymeric specimens. Moreover, the increased conductivity of the PP specimens may be due to the formation of $\pi$- bonded carbon clusters in the implanted layers as a result of implantation [34,52,58].

For the space charge linear conduction mechanism (SCLC) to occur, the slope of the I-V characteristic curves should be greater than or equal to 2, but in the present case the value of slope comes out to be less than 2 therefore, this conduction mechanism is
ruled out [78,82] in the similar manner as in case of CR-39 and PC specimens in the present study.

Thus, it can be concluded that argon ion beam treatment of PP results in modifications in the surface properties of the specimens. There is an increase in the carbon concentration near the surface as studied by RBS spectra indicates that implantation has produced significant changes in the surface composition in the implanted layer of the polymeric matrix. AFM studies shows that surface morphology of the specimens has been changed as a result of implantation. The increase in the rms and average roughness values indicates towards the degradation in the uniformity in the polymeric chains which results in the changes in the free volume fraction in the modified layer. This in turn leads to the changes in the composition of the elements in modified surface layers [30,91,112]. Also, the Cole-Cole analysis of PP specimens indicates that specimens obey non-Debye relaxation phenomena and the shapes of these curves confirmed the structural disordering in implanted PP specimens. From I–V characteristic measurements, it has been observed that the Schottky emission is the dominant charge transport mechanism operating in all the specimens. All these results indicate towards the structural modification of the polymer as a result of ion implantation.
3.5 Effects of Nitrogen Ion Implantation on CR-39

The effect of nitrogen ion implantation on the structure, optical, dielectric and electrical properties of CR-39 specimens is investigated and the results are discussed in the following sections. The specimens were implanted with 100 keV nitrogen ion to various fluences $1 \times 10^{15}$, $1 \times 10^{16}$, $2 \times 10^{16}$ ions cm$^{-2}$. Similar studies as in case of argon ion implanted CR-39 have been carried out in this case also.

3.5.1 Rutherford Backscattering Spectroscopy

Rutherford Backscattering Spectroscopy is used to analyze the composition and structure of the modified surface layers of nitrogen ion implanted CR-39 specimen. From the RBS spectra of pre- and post-implanted CR-39 specimens, the various elements present in the implanted layer have been identified and their differential cross-sections have been calculated using the kinematic factors. Also, the projected range, retained dose and atomic concentration of implanted argon have been analyzed.

3.5.1.1 Composition and Structure

Fig. 3.63 represents the recorded RBS spectra of virgin (‘a’, Fig. 3.63) and 100 keV N$^+$ implanted (‘b’, Fig. 3.63) CR-39 specimen at fluence of $2 \times 10^{16}$ N$^+$ cm$^{-2}$.

![RBS spectra](image)

Fig. 3.63 RBS spectra of (a) virgin and (b) implanted CR-39 specimen at 100 keV to $2 \times 10^{16}$ N$^+$ cm$^{-2}$

Fig. 3.63 (‘b’) clearly reveals that the structure of the virgin specimen Fig. 3.63 (‘a’) has been modified completely. Rutherford Backscattering Manipulation Program (RUMP) software [1] has been used for the quantitative analysis of the RBS spectra of pre- and post-implanted specimens. Fig. 3.64 shows the RUMP fitted spectra of the virgin and implanted CR-39 specimens.

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From the analysis of Fig. 3.64 (‘a’ & ‘b’) it has been revealed that the edge present at energy value ~515 keV in the spectra belongs to carbon and corresponding to energy value of ~705 keV in the spectra of Fig. 3.64 (‘a’ & ‘b’), oxygen has been identified. In addition, we observed that there is a hump corresponding to energy value ~620 keV in the implanted specimen (Fig. ‘b’, 3.64). Fitting of observed spectrum with RUMP software clearly demonstrates the presence of nitrogen in the post implanted matrix corresponding to this energy value. Thus, it can be inferred from the RUMP simulation that there are variations in the concentration of carbon and oxygen in implanted specimen in comparison to virgin specimen.

Also, it has been found that for the implanted specimen at fluence $2 \times 10^{16}$ N$^+$ cm$^{-2}$, the carbon concentration increases from to 32 at.% to 43 at.% and oxygen concentration from 19 at.% to 26 at.% respectively near the surface. This increase in the concentration of C point towards the carbonization of the implanted layers as a result of ion implantation. It is also clear from the Fig. 3.64 (‘b’) that there is variation in the carbon spectra of the implanted CR-39 surface between 0.43 MeV to 0.53 MeV as compared to the virgin (Fig. ‘a’, 3.64). This variation in the C spectra indicates towards the change in the composition of carbon. Hence, nitrogen ion implantation results in the carbonization and oxygen redistribution in the modified layers of the CR-39 specimens.

The effect of carbonization is of considerable interest because of significant change of the structure and composition of argon ion implanted CR-39 specimens. It has also been noticed from the earlier studies [10-13] that ion implantation results in dehydrogenation in the implanted surface of the specimen although hydrogen cannot be measurable by RBS technique [13,93]. This decrease in the composition of hydrogen
results in the relative increase in the composition of carbon [10,14-17]. This indicates that nitrogen ion implantation produces significant changes in the surface composition of the implanted polymeric specimen.

### 3.5.1.2 Backscattered Energies

Backscattered energies of the scattered particles can be measured using kinematic factor using the relationship between incident ($E_0$) and backscattered ($E_1$) energies given by equation (3.1).

From the RUMP fitted RBS spectra, values of backscattered energies for carbon, oxygen and argon have been determined. These experimentally calculated backscattered energies are presented in Table 3.13a along with the corresponding values calculated directly from the equation (3.1).

**Table 3.13a Backscattered energies ($E_1$) for different elements**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass number</th>
<th>Kinematic factor ‘K’</th>
<th>Incident energy $E_0$ (MeV)</th>
<th>Backscattered $E_1$ (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>12</td>
<td>0.253</td>
<td>2</td>
<td>0.510</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16</td>
<td>0.362</td>
<td>2</td>
<td>0.705</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>14</td>
<td>0.311</td>
<td>2</td>
<td>0.620</td>
</tr>
</tbody>
</table>

It is clear from the table that the experimental and calculated backscattered energy values are in good agreement with each other.

### 3.5.1.3 Elemental Identification in the Target

Backscattered energies give the identification of the different masses of individual elements present in the target material. Using the relation given by equation (3.2), we have identified the individual elements i.e. carbon, oxygen and nitrogen present in the specimen.

### 3.5.1.4 Calculation of Differential Cross Section

Rutherford differential cross section is a measure of the probability with which a projectile is elastically scattered from target atom [18-20] and is based on the Coulomb interaction potential. Using the formula as given by equation (3.3), the values of differential cross sections for carbon, oxygen and nitrogen elements have been calculated and are listed in Table 3.13b. It has been found that the calculated values are in good agreement with the theoretical values [18-20].
Table 3.13b  Theoretical and calculated cross sections for different elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass number</th>
<th>Cross section (10^{-24} cm^2/steradian)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td>Carbon</td>
<td>12</td>
<td>0.037</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16</td>
<td>0.074</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>14</td>
<td>0.056</td>
</tr>
</tbody>
</table>

3.5.1.5 Calculation of Implanted Fluence

Using RBS data, the retained dose in the implanted CR-39 specimens has been confirmed and verified using formula [18-19] as given by equation (3.4). Using the calculated values of different parameters from Fig. 3.64, the retained implantation fluence comes out to be 1.93x10^{16} N^+ cm^{-2} which is in well agreement with the real implanted ion fluence of 2x10^{16} N^+ cm^{-2}.

3.5.1.6 Calculation of Atomic Concentration

The atomic concentration of implanted nitrogen (N_N) in the CR-39 specimen is calculated using formula [18-19] as given by equation (3.5). The concentration of implanted argon has been calculated using height measurements and its value comes out to be 1.33 at.% which is in well agreement with the value 1.4 at.% calculated using RUMP fitted RBS spectra.

3.5.1.7 Calculation of Projected Range

The value of projected range (R_p) of the implanted ions in the CR-39 specimen comes out to be 352 nm using RUMP fitted RBS spectra which is found to be in well agreement with the value 341 nm as per Stopping and Range of Ions in Matter (SRIM) simulations [22].

3.5.2 X-Ray Photoelectron Spectroscopy

Fig. 3.65 shows the XPS spectra for the C (1s), O (1s) and N (1s) levels of the 100 keV nitrogen ion implanted CR-39 specimen with a fluence of 2x10^{16} N^+ cm^{-2}. All the spectra were recorded at the surface only.

On examining all the three spectra in Fig. 3.65, its asymmetric nature [23] is clearly noticed. This indicates the presence of more than one bonding states of C (1s), O (1s) and N (1s). It has been identified from the monomer structure of virgin CR-39 specimen (Fig. 2.1) that C-O, C=O, C-H and C=C (aliphatic) bonding exist in it.
Fig. 3.65 XPS spectra of implanted CR-39 specimen at 100 keV with $2 \times 10^{16}$ N$^+$ cm$^{-2}$ for (a) C(1s), (b) O(1s) and (c) N(1s)

In the O(1s) spectra (Fig 3.65 ‘b’) the peak appearing at 531.74 eV suggests the presence of C=O bonds [8,24]. The other oxygen containing bonds present in the virgin surface would have been degraded during N$^+$ implantation. The spectra obtained for N(1s) (Fig. c, 3.65) state is weak and asymmetric also, showing mainly one peak appearing at 399.84 eV indicating the presence of most of the free state nitrogen [8,23].

In the spectra of C(1s) state (Fig. 3.65 ‘a’), one asymmetric peak is present which is centered at 284.58 eV line. This looks like the presence of interacting graphitic and amorphous carbon (C-C) states alongwith aliphatic carbon [23-24,26-27] formed during nitrogen ion implantation in CR-39 matrix. The other bonding states would have been scissioned due to the implantation induced evolution of the hydrogen and oxygen gaseous molecules from the surface of CR-39. Therefore, the present line at 284.58 eV position in the C(1s) spectra (Fig. 3.65 ‘a’) is clearly indicative of the formation of the graphitelike structures with the amorphous carbon in the near surface regions of CR-39.
3.5.3 Atomic Force Microscopy

Fig. 3.66 (‘a’, ‘b’, ‘c’, & ‘d’) shows the two dimensional topographical images (10μm × 10μm size) of virgin and 100 keV nitrogen ion implanted CR-39 specimens for the fluences ranging 1x10\(^{15}\), 1x10\(^{16}\) and 2x10\(^{16}\) ions cm\(^{-2}\). It is discerned from the Fig. 3.66 (‘a’) that the surface of the virgin sample is uniform and smooth compared to nitrogen ion implanted (‘b’, ‘c’, & ‘d’, Fig. 3.66) specimens.. The AFM images were analyzed using Nova-Px software provided with the instrument. The root mean square (R\(_{\text{rms}}\)) and average (R\(_{\text{av}}\)) roughness values have been calculated using this software.

The calculated root mean square roughness (R\(_{\text{rms}}\)) and average roughness (R\(_{\text{av}}\)) values for the virgin CR-39 sample 8.34 are nm and 5.57 nm respectively. After N\(^{+}\) implantation, the uniformity of the surface was lost and the surface shows a remarkable change. Moreover, the roughness values were observed to be increased progressively with increasing ion fluence. At a low fluence of 1x10\(^{15}\) N\(^{+}\) cm\(^{-2}\) (Fig. 3.66 ‘b’), the calculated values are 10.90 nm and 7.41 nm for R\(_{\text{rms}}\) and R\(_{\text{av}}\) respectively. With further increase in ion fluence Fig. 3.66 ‘c’, the R\(_{\text{rms}}\) and R\(_{\text{av}}\) values increase to 13.67 nm and 10.92 nm respectively.

![AFM images](image_url)

Fig. 3.66 Two-dimensional AFM images of (a) virgin and implanted CR-39 specimens at 100 keV to (b) 1x10\(^{15}\), (c) 1x10\(^{16}\), and (d) 2x10\(^{16}\) N\(^{+}\) cm\(^{-2}\)
Moreover, at the highest fluence of \(1\times10^{16} \text{ N}^+ \text{ cm}^{-2}\) (Fig. 3.66 ‘d’), there is a maximum increase in the root mean square and average roughness values up to 17.28 nm and 13.53 nm respectively. Table 3.14 presents the \(R_{\text{rms}}\) and \(R_{\text{av}}\) values for CR-39 specimens at different fluences. These observed rms roughness and average roughness values for all the samples are also plotted as a function of ion fluence in Fig. 3.67.

Table 3.14 Variation of root mean square roughness and average roughness values with ion fluence

<table>
<thead>
<tr>
<th>Ion Fluence (N^+ cm^2)</th>
<th>Root mean square roughness (R_{\text{rms}}) (nm)</th>
<th>Average roughness (R_{\text{av}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin CR-39</td>
<td>8.34</td>
<td>5.57</td>
</tr>
<tr>
<td>(1\times10^{15})</td>
<td>10.90</td>
<td>7.41</td>
</tr>
<tr>
<td>(1 \times 10^{16})</td>
<td>13.67</td>
<td>10.92</td>
</tr>
<tr>
<td>(2 \times 10^{16})</td>
<td>17.28</td>
<td>13.53</td>
</tr>
</tbody>
</table>

This increase in the roughness values with increasing ion fluence may be attributed to the interaction of nitrogen beam with CR-39 specimens which results in the formation of cross-linked and carbon-rich carbonaceous clusters [2, 28-29] in the surface layer. This in turn changes the free volume fraction in modified surface layers [11,30,33,123].
Thus the AFM images clearly indicates that surface morphology of the CR-39 specimens has been affected by nitrogen ion implantation leading to consistent increase in the degree of modification increase in surface roughness values [30,33].

3.5.4 UV-Visible Spectroscopy

3.5.4.1 Structural Analysis

The optical absorption studies have been performed using UV-visible spectrophotometer. The plot of UV-Visible absorption spectra for virgin and nitrogen implanted (fluences of $1\times10^{15}$, $1\times10^{16}$, and $2\times10^{16}$ ions cm$^{-2}$) CR-39 specimens are shown in Fig. 3.68 (curves a-d).

![UV-Visible absorption spectra](image)

Fig. 3.68 UV-Visible absorption spectra (a) virgin and implanted CR-39 specimens at 100 keV to (b) $1\times10^{15}$, (c) $1\times10^{16}$, and (d) $2\times10^{16}$ N$^+$ cm$^{-2}$

The UV-Visible absorption spectra of virgin CR-39 (‘a’, Fig. 3.68) have two peaks at 226 nm and 248 nm which are due to electronic transitions between occupied and unoccupied molecular orbitals. These transitions are attributed to the n- $\pi^*$ and $\pi-\pi^*$ orbital which is likely to be associated with double bond between carbon and oxygen with lone pair of electrons present on oxygen [37-38]. This type of transitions is characteristic of the compounds containing double or triple bonds. The two existing bands in the virgin spectra have been merged after implantation. The absorption spectra of the virgin specimen show a minimum absorption. However, after nitrogen ion implantation (curves
‘b’, ‘c’ &‘d’, Fig. 3.68), absorption increases with ion fluence. It is also clear from the Fig. 3.68 that the two existing bands in the virgin specimen have merged to one band with continuous increase in intensity. Fig. 3.68 (‘b’, ‘c’ &‘d’) shows that there is a shift in absorption edge from ultraviolet to the visible region and simultaneously edge flattens with increasing ion fluence. This results in bathochromic shift followed by the broadening of the peaks. These modifications may be due to the reason that ion implantation generally results in various effects such as ionization, production of free radicals, scissioning which induces cross-linking, bond and chain-scission that modifies the properties of the polymers. These changes are responsible for the enrichment of the carbon atoms in the polymeric chain as a consequence, optical density increases and absorption peaks shifts towards higher wavelength [7,52,115]. Thus, it has been observed that nitrogen ion implantation causes significant changes in the structure of the CR-39 specimens.

### 3.5.4.2 Color Examination

The visual examination of specimens indicates that the color of specimens is changed after N⁺ implantation. The virgin sample was transparent and colorless. After implantation, the change in the color of the samples has been observed. After implantation the color of the virgin CR-39 changed to light brown and then to dark brown with increasing ion fluence. The color transformation is related closely to the structural change after ion implantation [8,75].

It is well known that ion implantation causes structural modifications in the polymeric matrix. Since, ion implantation generally gives rise to the production of carbon enriched structures containing conjugated carbon bonds in the implanted surface layers of the specimens. Since, the extent of conjugation in the structure is used to characterize the color of the specimens. The increase in the number of carbon-carbon double and triple bonds after implantation [39,41,116] may be the possible cause behind sharp change in the color of N⁺ implanted specimens.

### 3.5.5 Dielectric Spectroscopy

In the present work dielectric behavior of the N⁺ implanted CR-39 specimens have been studied using dielectric measurements [44-47]. These measurements have been carried out to examine the effect of implantation on dielectric constant, dielectric loss, dissipation factor, spreading factor, average relaxation time and molecular relaxation time in the polymeric matrix.
3.5.5.1 Dielectric constant and Dielectric loss

The variations of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) for virgin and nitrogen ion implanted CR-39 specimens at 100 keV to fluences $1 \times 10^{15}$, $1 \times 10^{16}$ and $2 \times 10^{16}$ ions cm$^{-2}$ as a function of frequency are presented in Fig. 3.69 and 3.70 respectively. The spectra recorded for the pre- and post-implanted CR-39 specimens is in the frequency range of 100 Hz to 90 MHz.

Fig. 3.69 Plot of dielectric constant vs. frequency for (a) virgin and implanted CR-39 specimens at 100 keV to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $2 \times 10^{16}$ N$^+$ cm$^{-2}$
Fig. 3.69 clearly reveals the variation in the dielectric constant value as a function of frequency for all the CR-39 specimens. Curve ‘a’, (Fig 3.69) for virgin CR-39 shows a increase in the value of dielectric constant from 4.76 (at frequency of 100 Hz) to a maximum value of 16.2 (at 86.2 MHz). However, after nitrogen ion implantation, the CR-39 specimens (‘b’, ‘c’ and ‘d’, Fig. 3.69) show a slight variation in the value of dielectric constant as a function of frequency. For a fluence of $1 \times 10^{15}$ N$^+$ cm$^{-2}$ (curve ‘b’, Fig 3.69), the dielectric constant increases from 4.56 (at 100 Hz) to a maximum value of 15.7 (at 86.4 MHz). At a dose of $1 \times 10^{16}$ N$^+$ cm$^{-2}$ (curve ‘c’, Fig 3.69), $\varepsilon'$ increases from 4.35 (at 100 Hz) to a maximum value of 15.5 (at 86.5 MHz), and with the highest implantation dose of $2 \times 10^{16}$ N$^+$ cm$^{-2}$ (curve ‘d’, Fig 3.69) $\varepsilon'$ increases from 4.28 (at 100 Hz) to a maximum value of 15.3 (at 86.6 MHz).

The variation in the value of dielectric constant (Fig. 3.69) from low frequency region to high frequency region can be explained in terms of polarization mechanism. Since it is well known that, in the absence of external electric field, the specimen will not exhibit any polarization as the distribution of individual dipoles is random [102] with all directions having equal probability [53]. But as the frequency increases, the dipole tries to align in the direction of applied field. So, in the frequency region of 100 Hz - 87 MHz, the dominating mechanism is dipole orientation polarization which results in the increase in the value of dielectric constant.

However, after ~87 MHz frequency, the value of dielectric constant shows a decreasing trend for all the specimens (Fig. 3.69). At this frequency range, the polarization of dipoles is mainly due to atomic polarization. The decrease in the value of dielectric constant may be due to the reason that the dipole orientation polarization cannot attain its equilibrium value as dipoles starts reversing their direction of orientation with increasing frequency. This decreases the probability of polarization of dipole and hence the dipole orientation mechanism changes to atomic polarization [54,102,124]. This accounts for the decline in the values of dielectric constant. Hence, it can be concluded that there is a variation in the value of dielectric constant as a function of frequency and this difference in the values of dielectric constant measured at low and high frequencies is called the strength of the relaxation in polymers [53,55-56].

The plots of dielectric loss ($\varepsilon''$) versus frequency for virgin and implanted CR-39 specimens are shown in Fig. 3.70 (Curves ‘a’, ‘b’, ‘c’ & ‘d’). It is clear from the Fig. 3.72 that the value of $\varepsilon''$ increases upto ~84 MHz frequency and then starts decreasing with
Fig. 3.70 Variation in dielectric loss vs. frequency for (a) virgin and implanted CR-39 specimens at 100 keV to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $2 \times 10^{16} \text{N}^+ \text{cm}^{-2}$

Further increase in frequency. This behaviour may be due to the reason that there occurs a random orientation of dipoles up to frequency range of $\sim 84 \text{ MHz}$. However, with further increase in frequency, the dipoles in the polymeric chain are coupled to the adjacent dipoles of the same chain. So there occurs a preferential orientation of the dipoles in response to the applied field [57]. This results in the decrease in the value of dielectric loss after $\sim 84 \text{ MHz}$ frequency.
3.5.5.2 Dissipation factor

It is also well known that in high frequency alternating fields there is always a phase difference between polarization and field, which gives the dissipation factor [55,58,60]. Fig. 3.71 (curves ‘a’, ‘b’, ‘c’, &‘d’) shows the plot of dissipation factor (tan δ) as a function of frequency for the virgin and 100 keV N⁺ implanted CR-39 specimens to fluences 1×10¹⁵, 1×10¹⁶, and 2×10¹⁶ N⁺ cm⁻². It is clear from the Fig. 3.71 that the value of tan δ increases with increasing ion fluence.

Fig. 3.71 Variation in dissipation factor with frequency for (a) virgin and implanted CR-39 specimens to (b) 1×10¹⁵, (c) 1×10¹⁶, and (d) 2×10¹⁶ N⁺ cm⁻²
It is also observed from the figure that the position of tan δ peak remains almost the same for virgin and implanted CR-39 samples. Since this peak corresponds to the vibrations of the main chain so it is expected to remain unaffected even after implantation.

Hence, it can be concluded that nitrogen ion implantation results in the modifications in the dielectric properties viz. dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dissipation factor (tan $\delta$). These modifications can be attributed to degradation processes taking place inside the polymeric chain due to chain-scissioning, formation of free radicals etc. This results in the formation of carbon rich networks in the implanted layers of CR-39 matrix as confirmed by RBS, XPS, AFM and UV-Visible studies. These processes lead to the formation of $\pi$-electron clouds with the applied field aligned in the direction of the molecular chains and hence results in the decline in dielectric constant values after implantation [34].

3.5.5.3 a.c. conductivity

The a. c. conductivity in the range of 10 MHz to 80 MHz for pre- and post-implanted CR-39 specimens has been calculated using equation (3.6). Fig. 3.72 shows the variation in a. c. conductivity of virgin and nitrogen ion implanted CR-39 samples at 100 keV with fluences $1 \times 10^{15}$, $1 \times 10^{16}$ and $2 \times 10^{16}$ ions cm$^{-2}$ at various frequencies.

![Fig. 3.72](image-url)
The a. c. conductivity shows an increasing trend with increasing frequency. However, there is a very slight increase in the value of conductivity with increasing ion fluence. The increase in the value of conductivity indicates towards the formation of π-bonded carbon clusters in the ion implanted layers. [37,52,64]. Also RBS and XPS results indicate towards the formation of carbon enriched domains in the implanted layers of the polymeric matrix which may be responsible for this behavior of conductivity.

3.5.5.4 Cole-Cole Plot

The dielectric relaxation occurring in virgin and nitrogen implanted polymeric specimens has been studied in detail through Cole-Cole analysis in the frequency range of 100 Hz to 90 MHz. The plot of real part (ε') of the complex permittivity on x-axis and imaginary part (ε'') of that on y-axis is known as the Cole-Cole plot and is useful to confirm the distribution of relaxation time. Fig. 3.73 (curves ‘a’, ‘b’, ‘c’, &’d’) shows the Cole-Cole plots for virgin and 100 keV N⁺ implanted CR-39 specimens to fluences 1x10¹⁵, 1x10¹⁶ and 2x10¹⁶ ions cm⁻². Cole-Cole plots have been used to determine the spreading factor (α), average relaxation time (τ₀) and molecular relaxation time (τ).

Fig. 3.73 Cole-Cole plot of (a) virgin and implanted CR-39 specimens at 100 keV to (b) 1x10¹⁵, (c) 1x10¹⁶, and (d) 2x10¹⁶ N⁺ cm⁻²
It is clear from the Fig. 3.73 (curves ‘a’, ‘b’, ‘c’, &‘d’) that Cole-Cole plots are imperfect semicircular in nature. With increasing ion fluence, distortions in the shape and the height of the curves in the Cole-Cole plots are increasing. This deviation in the shape and increase in the height of the curves of Cole-Cole plots is due to the polydisperse nature of the amorphous CR-39 [53,65-67]. This polydisperse nature in polymers further increases owing to disorder due to ion implantation [67]. This results in much larger dispersion owing to disorder due to ion implantation [67]. This results in much larger dispersion owing to distribution of relaxation time. As the Cole-Cole plots are related to the relaxation phenomena [57,60,68] taking place in matrix, the variations observed in the nature of the curve in Cole-Cole plots after implantation indicate towards the disorderness in the matrix with the formation of conjugated π-bonded clusters [37].

3.5.5.5 Spreading Factor (α)

The value of spreading factor (α) has been deduced from the expression for the maximum value of imaginary part of complex permittivity as given by the equation (3.7). The variation of spreading factor for virgin and implanted CR-39 specimens as a function of ion fluence is shown in Fig. 3.74. The calculated value of α is listed in Table 3.15.

![Graph showing variation of spreading factor (α) with ion fluence for virgin and nitrogen ion implanted CR-39 specimen at 100 keV](image)

Fig. 3.74 Variation of spreading factor (α) with ion fluences for virgin and nitrogen ion implanted CR-39 specimen at 100 keV

It has been found that the value of spreading factor increases with increasing ion fluence and is greater than 0 which indicates that there is a broad distribution of relaxation times [53, 63, 69] in the specimens and hence it exhibits polydisperse nature. This
polydisperse nature in polymers further increases owing to disorder due to ion implantation. Moreover, this increase in the value of $\alpha$ with increasing ion fluence may be attributed to the increase in disordering [70] in CR-39 matrix.

3.5.5.6 Average relaxation time ($\tau_0$)

The average relaxation time $\tau_0$ for virgin and implanted CR-39 specimens was calculated was calculated using the relation given by equation (3.8). The plot of average relaxation time for virgin and implanted CR-39 specimens at various doses is shown in Fig. 3.75. The measured values of $\tau_0$ is listed in Table 3.15.

<table>
<thead>
<tr>
<th>Ion fluence (N$^+$ cm$^{-2}$)</th>
<th>Spreading factor ($\alpha$)</th>
<th>Average relaxation time $\tau_0$ (s)</th>
<th>Molecular relaxation time $\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin CR-39</td>
<td>1.30</td>
<td>1.12 x 10$^{-9}$</td>
<td>2.02 x 10$^{-9}$</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>1.33</td>
<td>0.22 x 10$^{-9}$</td>
<td>0.40 x 10$^{-9}$</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>1.34</td>
<td>0.07 x 10$^{-9}$</td>
<td>0.13 x 10$^{-9}$</td>
</tr>
<tr>
<td>$2 \times 10^{16}$</td>
<td>1.36</td>
<td>0.04 x 10$^{-9}$</td>
<td>0.09 x 10$^{-9}$</td>
</tr>
</tbody>
</table>

Fig. 3.75 Variation of average relaxation time ($\tau_0$) with ion fluences for virgin and nitrogen ion implanted CR-39 specimen at 100 keV

From the Fig. 3.75, it is clearly observed that average relaxation time decreases with increasing ion fluence which may be due to the structural modification in the polymeric matrix and the formation of carbon enriched domains in the implanted layers.
3.5.5.7 Molecular relaxation time ($\tau$)

The molecular relaxation time ($\tau$) for pre- and post-implanted specimens is calculated using the formula as given by equation (3.9). Fig. 3.76 presents the plot of molecular relaxation time for virgin and implanted specimens at various doses. The plot of molecular relaxation time for virgin and implanted CR-39 specimens at various doses is shown in Fig. 3.76. The measured values of ($\tau$) is listed in Table 3.15.

Fig. 3.76 depicts clearly the decrease in molecular relaxation time with increasing ion fluence. This is similar to the earlier trend of average relaxation time (3.75). This may be due to the carbonization of the CR-39 matrix due to nitrogen ion implantation as already seen from the RBS and XPS analysis.

![Graph showing variation of molecular relaxation time with ion fluence](image)

**Fig. 3.76 Variation of molecular relaxation time ($\tau$) with ion fluences for virgin and nitrogen ion implanted CR-39 specimen at 100 keV**

It is clear from Table 3.15 that both the relaxation times (i.e. average and molecular) decrease with increasing nitrogen ion fluence. This may be due to the fact that as a result of implantation structural disorderness in the matrix increases which in turn decreases the relaxation time. Further, this decrease in the values of relaxation time may also be attributed to the improvement in the conductivity [73] of CR-39 specimens as a result of implantation.
3.5.6 Dielectric Constant and Dielectric Loss using Optical Absorption and Reflection Studies

In the present work, the dielectric constant and dielectric loss have also been calculated using UV-Visible Spectroscopy. For these calculations the data of optical absorption and reflection has been used for virgin and nitrogen ion implanted CR-39 specimens in the frequency range of .42 - .75 PHz corresponding to the visible region wavelength (400-700 nm). In this frequency region, the response of the specimens to the applied field is mainly due to electronic polarization [44-45]. This type of polarization occurs mainly due to the displacement of the outer electronic clouds with respect to the internal atomic cores by external fields. It is responsible for a number of optical properties of the materials [46-47,54]. In the present perspective the dielectric constant and dielectric loss are defined by equations (3.12) and (3.13) respectively. To study dielectric constant and dielectric loss in the visible region, the values of extinction coefficient and refractive index have been calculated using equations (3.14) and (3.15) respectively.

Fig. 3.77 shows the variation of extinction coefficient for virgin (curve ‘a’) and nitrogen ion implanted CR-39 specimens (curves ‘b’, & ‘c’) as a function of wavelength in the range of 400-700 nm.

![Graph showing variation of extinction coefficient with wavelength for CR-39 specimens with different ion fluences.]

Fig. 3.77 Variation in extinction coefficient with wavelength of (a) virgin and implanted CR-39 specimens at 100 keV to (b) $1 \times 10^{16}$ and (c) $2 \times 10^{16}$ N$^+$ cm$^{-2}$

It can be inferred from the Fig. 3.77 that the extinction coefficient remains constant for virgin CR-39 whereas it shows a decreasing trend with wavelength. However, extinction coefficient increases with increase in ion fluence for the implanted specimens.
The reflectivity spectra in the visible region for virgin and nitrogen implanted CR-39 specimens are presented in Fig. 3.78. It has been observed that reflectivity decreases with increasing ion fluence which may be due to the disordering created in the implanted specimens as a result of ion implantation.

Fig. 3.78 Reflectivity spectra recorded in the visible region of (a) virgin and implanted CR-39 specimens at 100 keV to (b) $1 \times 10^{16}$ and (c) $2 \times 10^{16}$ N$^+$ cm$^{-2}$

Fig. 3.79 Variation in refractive index with wavelength of (a) virgin and implanted CR-39 specimens at 100 keV to (b) $1 \times 10^{16}$ and (c) $2 \times 10^{16}$ N$^+$ cm$^{-2}$
Fig. 3.79 shows the plot of refractive index for virgin and nitrogen ion implanted CR-39 specimens as a function of wavelength. It is clear from the figure that refractive index decreases with increasing ion fluence. This decrease in the value of refractive index may be due to the disordering in the implanted specimens. This disordering in the polymeric matrix lead to the formation of $\pi$-electron clouds with the polarization aligned in the direction of molecular chains [34]. This change in the direction of polarization lowers the value of refractive index.

The values of dielectric constant and dielectric loss have been calculated using the refractive index and extinction coefficient as discussed above. The variations of dielectric constant and dielectric loss with wavelength in the visible region are shown in Fig. 3.80 and 3.81 respectively. It can be inferred from the Fig. 3.80 that the value of $\varepsilon'$ decreases with increasing ion fluence. However, the dielectric loss (Fig. 3.81) increases with increasing ion fluence.

These changes observed in the values of dielectric properties may be due to ion beam interaction and its energy loss in the CR-39 matrix during implantation. As ion implantation of polymers generally leads to chain-scission, evolution of gaseous product and cross-linked conjugated multiple (double and triple) bonds. This in turn leads to the
Fig. 3.81 Variation in dielectric loss with wavelength of (a) virgin and implanted CR-39 specimens at 100 keV to (b) $1 \times 10^{16}$ and (c) $2 \times 10^{16} \text{N}^+ \text{cm}^{-2}$.

formation of conjugated bonds, which promotes the delocalization of charge carriers in the implanted specimens. These conjugated $\pi$-bonds tend to polarize the dipoles in the direction of applied field. This alignment of dipoles with the molecular chains corresponds to the decrease in the value of dielectric constant [34]. It can be concluded that nitrogen ion implantation induces changes in the dielectric properties.

### 3.5.7 Electrical Properties

Fig. 3.82 presents the Current–Voltage (I-V) characteristics in the applied voltage range of 10-50 V for pre- and post-implanted CR-39 specimens with various fluences $1 \times 10^{15}$, $1 \times 10^{16}$ and $2 \times 10^{16}$ ions $\text{cm}^{-2}$.

It is clear from the curve ‘a’, Fig. 3.82 (virgin CR-39) that there is an increase in the value of current with applied voltage. After $\text{N}^+$ implantation, there is an obvious increase in the value of current (curves ‘b’, ‘c’ & ‘d’) with increasing ion fluence. At a low fluence of $1 \times 10^{15} \text{N}^+ \text{cm}^{-2}$ (curve ‘b’), there is a corresponding increase in current with applied voltage. However, for fluences of $1 \times 10^{16}$ and $2 \times 10^{16} \text{N}^+ \text{cm}^{-2}$ (curves ‘c’ and ‘d’), the behaviour of the I-V characteristics is almost same and there is a slight increase in current with applied voltage.
It has also been found that the increase in current is not proportional to the corresponding increase in voltage for all the specimens. Hence the possibility of Ohmic conduction mechanism is ruled out. Moreover, it can also be seen clearly from Fig. 3.82 (curves ‘b’, ‘c’ & ‘d’) that the current increases continuously with increasing nitrogen ion fluence. This increase in the value of current for the implanted samples may be explained on the basis of formation of charge transfer complexes which facilitate the delocalization of these carriers. The formation of these complexes in the implanted layers induces electronic hopping process between individual conducting islands embedded in polymeric matrix [37,85,104,125]. Thus, they facilitate the flow of current and contribute towards the modification in the conductivity of implanted polymers. The possible conduction mechanism operating in the nitrogen implanted CR-39 specimens can be studied using different conduction mechanisms.

To reveal the charge transport mechanism in virgin and implanted CR-39 specimens, I–V data is plotted in the form \( \ln(I) \) vs. \( V^{1/2} \) (Fig. 3.83). Similar to the earlier cases in the present work, different conduction mechanisms have been used to describe the I-V characteristic measurements in the polymeric matrix. The experimental value of \( \beta \) i.e. \( \beta_{\text{exp}} \) for virgin and implanted specimens has been calculated using the equations (3.17) and (3.18) and are given in Table 3.16. The theoretical values of \( \beta \) for Schottky emission
as well as for Poole–Frenkel emission are calculated by equations (3.19) and (3.20) and are listed in Table 3.16.

![Plot of ln (I) vs. V$^{1/2}$ for (a) virgin and implanted CR-39 specimens at 100 keV to (b) 1×10$^{15}$, (c) 1×10$^{16}$, and (d) 2×10$^{16}$ N$^+$ cm$^{-2}$]

Table 3.16 A comparison between the theoretical and experimental $\beta$ coefficients of virgin and implanted CR-39 specimens

<table>
<thead>
<tr>
<th>Ion Fluence (N$^+$cm$^{-2}$)</th>
<th>Theoretical values of conduction parameter</th>
<th>Experimental values of conduction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Schottky emission ($\beta_{RS}$) (eV-m$^{1/2}$ V$^{-1/2}$)</td>
<td>Poole Frenkel emission ($\beta_{PF}$) (eV-m$^{1/2}$ V$^{-1/2}$)</td>
</tr>
<tr>
<td>Virgin</td>
<td>1.74 × 10$^{-5}$</td>
<td>3.48 × 10$^{-5}$</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2 \times 10^{16}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It has been noticed from the table that, the experimental value ($\beta_{exp}$) for virgin CR-39 has been found to be in good agreement with the theoretical value of $\beta_{PF}$. This leads to the conclusion that Poole–Frenkel mechanism is the dominating mechanism in case of the virgin CR-39 specimen. However, after implantation, the values of $\beta_{exp}$ found to be close to the theoretical value of $\beta_{RS}$ leading to the conclusion that Schottky emission
is the dominant charge transport mechanism operating in the nitrogen implanted CR-39 specimens. The transition from Poole- Frenkel (for virgin CR-39) to Schottky emission (for implanted CR-39 specimens) conduction mechanism may be due to the improvement in the conductivity of these specimens as a result of implantation [76,79-80]. This may also be due to increase in the concentration of charge carriers with increase in ion fluence which results in the enhancement in the conductivity of the polymeric specimens. Moreover, it has also been assumed that the conduction of charge carriers between localized states leads to the **Hopping** mechanism which results in the increase in the conductivity of the specimens.

For **space charge linear conduction mechanism** (SCLC) to occur, the slope of the I-V characteristic curves should be greater than or equal to 2, but in the present case the value of slope comes out to be less than 2 therefore, this conduction mechanism is ruled out [77-78,84].

Therefore, the obtained results show that nitrogen ion implantation results in the modifications in the surface properties of the CR-39 samples. RBS studies show that N⁺ implantation results in the carbonization and oxygen redistribution in the modified layers of the specimens. This increase in the concentration of carbon point towards the formation of carbonization layer in the implanted surface layer [3]. The changes in surface structure have been confirmed by XPS, AFM and UV-Visible spectroscopy. Also, the analysis of Cole-Cole plots results in the non-Debye relaxation phenomena and exhibit polydispersive nature of the pre- and post-implanted specimens. Moreover, the shapes of the Cole-Cole curves confirmed the structural disordering in implanted CR-39 specimens and decrease in the values of average and molecular relaxation times indicate towards the increase in the conductivity as a result of implantation. I–V characteristic shows that the value of current increase with increasing ion fluence and it has also been observed that Schottky emission is the dominant charge transport mechanism operating in implanted specimens. Hence the results of different characterization techniques agree well with each other.
3.6 Effects of Nitrogen Ion Implantation on Polycarbonate

The polycarbonate specimens were implanted by 100 keV nitrogen ion at various fluences of $1 \times 10^{15}$ N$^+$ cm$^{-2}$, $1 \times 10^{16}$ N$^+$ cm$^{-2}$ and $1 \times 10^{17}$ N$^+$ cm$^{-2}$. The effect of nitrogen ion implantation on the structure, optical, dielectric and electrical properties of PC specimens is investigated and the results are discussed in the following sections.

3.6.1 Rutherford Backscattering Spectroscopy

Rutherford Backscattering Spectroscopy has been used to investigate the composition and structure of the N$^+$ implanted modified surface layers of PC. From the RBS spectra of pre- and post-implanted PC specimens, the various elements present in the implanted layer and their differential cross-sections have been calculated using the kinematic factors. Also, the projected range, retained dose and atomic concentration of implanted argon have been analyzed.

3.6.1.1 Composition and Structure

The experimentally observed RBS spectra of virgin Fig. 3.84 ‘a’ and 100 keV N$^+$ implanted Fig. 3.84 ‘b’ polycarbonate specimen at fluence of $1 \times 10^{17}$ N$^+$ cm$^{-2}$ is shown in Fig. 3.84.

![RBS spectra of (a) virgin and (b) implanted polycarbonate specimen at 100 keV to $1 \times 10^{17}$ N$^+$ cm$^{-2}$](image)

Fig. 3.84 RBS spectra of (a) virgin and (b) implanted polycarbonate specimen at 100 keV to $1 \times 10^{17}$ N$^+$ cm$^{-2}$

Fig. 3.85 shows the Rutherford Backscattering Manipulation Program (RUMP) software [1] fitted spectra for the virgin Fig. 3.85 ‘a’ and nitrogen ion implanted Fig. 3.85 ‘b’ PC specimen. Quantitative analysis of the RBS data has been done using RUMP software. Fitting of the observed spectrum with RUMP software clearly demonstrates that the structure of the virgin PC has been modified after nitrogen ion implantation.
From the fitting of RBS spectra, the edge present at energy values of \( \sim 508 \text{ keV} \) in the spectra of Fig. 3.85 (‘a’ & ‘b’) has been identified as of carbon (C) and further oxygen (O) has been identified at \( \sim 700 \text{ keV} \) energy value. Also, simulation shows the presence of nitrogen in the near surface region of the implanted specimen corresponding to energy values of \( \sim 622 \text{ keV} \).

It is observed that the elemental composition has been modified as a result of nitrogen ion implantation. It has been found that the concentration of C increases from 48 at.% to 70 at.% and there is a depletion in the value of oxygen from 9 at.% to 7 at.% near the surface in the implanted specimen. This indicates that the nitrogen ion implantation has produced significant changes in the surface composition in the implanted layer of the polymeric matrix.

Moreover, it has also been observed that there is variation in the carbon spectra of the implanted PC (‘b’, Fig. 3.82) between 0.39 MeV to 0.53 MeV as compared to the unimplanted one (‘a’, Fig. 3.82). This variation in the C spectra indicates towards the change in the composition of carbon. This is may be due to the interaction of ion beam with the matrix which results in various processes viz. scissioning, crosslinking etc. \([3,93,111]\) and results in the carbon enriched surface layer in the implanted polymeric matrix \([3]\). Hence, it can be inferred that carbonization occurs near the surface as a result of ion implantation.

Though hydrogen cannot be detected by RBS measurements, but earlier studies \([11,75]\) it has been observed that ion implantation results in dehydrogenation in the implanted surface of the specimen. This in turn results in the relative increase in the

![Fig. 3.85 RUMP fitted RBS spectra of (a) virgin and (b) nitrogen ion implanted polycarbonate at fluence 1x10^{17} \text{ N}^+ \text{ cm}^{-2}]

---

\[ \text{Energy (MeV)} \]

Channel

Normalized Yield

Energy (MeV)

Normalized Yield

Channel

C

O

(b)

N

O

(a)
composition of carbon. [14,17,126]. Thus, the increase in the concentration of carbon results in the formation of carbonaceous layer in the implanted layer. Therefore, one can conclude that significant increase in the carbon concentration indicates towards the formation of carbon network in the implanted PC as a result of ion implantation. Thus, RBS studies revealed that there are pronounced changes in the near surface region of implanted specimen in the form of carbonaceous network.

3.6.1.2 Backscattered Energies

It is well known that kinematic factor is a measure of backscattered energies of the scattered particles during RBS studies and establishes relationship between incident (E₀) and backscattered (E₁) energies given by equation (3.1).

Using RUMP fitted RBS spectra the values of backscattered energies for carbon, oxygen and nitrogen has been determined. Table 3.17a presents these experimentally determined backscattered energies along with corresponding values calculated directly using equation (3.1).

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass number</th>
<th>Kinematic factor ‘K’</th>
<th>Incident energy E₀ (MeV)</th>
<th>Backscattered E₁ (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>12</td>
<td>0.252</td>
<td>2</td>
<td>0.508</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16</td>
<td>0.362</td>
<td>2</td>
<td>0.700</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>14</td>
<td>0.311</td>
<td>2</td>
<td>0.622</td>
</tr>
</tbody>
</table>

It has been observed that the experimental and calculated backscattered energy values are in well agreement with each other.

3.6.1.3 Elemental Identification in the Target

Backscattered energies give the quantitative information of the different masses of individual elements present in the target material. Using equation (3.2), the individual elements i.e. carbon, oxygen and nitrogen present in the specimen have been identified.

3.6.1.4 Calculation of Differential Cross Section

The differential scattering cross section is a measure of the probability with which a projectile is elastically scattered from target atom [18-20]. Using equation (3.3), we have calculated the differential cross sections for carbon, oxygen and nitrogen elements in the target and the values are listed in Table 3.13b. It has been found that the calculated values are in good agreement with the theoretical values [18-20].
3.6.1.5 Calculation of Implanted Fluence

Using RBS data, the dose in the implanted PC specimens has been confirmed and verified using formula [18-19] as given by equation (3.4). Using the calculated values of different parameters, the retained implantation fluence comes out to be \(0.97 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}\) which is in well agreement with the real implanted ion fluence of \(1 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}\).

3.6.1.6 Calculation of Atomic Concentration

The atomic concentration of implanted nitrogen \(N_N\) in the PC specimen is calculated using formula [18-19] as given by equation (3.5). The concentration of implanted nitrogen has been calculated using height measurements and its value comes out to be 0.09 at.% which is in well agreement with the value 0.11 at.% calculated using RUMP fitted RBS spectra.

3.6.1.7 Calculation of Projected Range

The value of projected range of the implanted nitrogen in PC specimen comes out to be 358 nm using RUMP fitted RBS spectra which is in good agreement with the value 344.9 nm as per Stopping and Range of Ions in Matter (SRIM) simulations.

3.6.2 X-Ray Photoelectron Spectroscopy

In the present work the structural studies were also tried to be carried out using XPS characterization of the surfaces of the implanted specimens. Fig. 3.86 shows the XPS spectra for the C (1s), O (1s) and N (1s) levels of the 100 keV nitrogen ion implanted PC specimen with a fluence of \(1 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}\). All spectra were recorded at the surface only.

It can be clearly seen from the Fig 3.86 that all the three spectra for the C (1s), O (1s) and N (1s) levels are asymmetric and therefore, more than one bonding state is evident [23]. It is known that in the virgin PC specimen C-O, C=O, C-H and C=C (Benzene ring) bonding exist corresponding to its monomer structure as shown in Fig. 2.2.

In the O(1s) spectra (Fig. 3.86 ‘b’) the single peak at 532.86 eV indicates the presence of C-O bonds [24]. The other C=O bonds present in the virgin surface would have been ruptured during implantation. The asymmetric nature spectra of N(1s) (Fig. 3.86 ‘c’) shows two bonding states at 399.64 eV and 399.1 eV indicating the presence of most of the free state nitrogen [23], however, the signal obtained for N(1s) state is weak.

In the C(1s) spectra (Fig. 3.86 ‘a’) the asymmetric peak is seen to be centered at 284.22 eV line. This seems to be the overlapping of the C=C (aromatic), graphitic and amorphous carbon (C-C) states [23-24,26-27] formed during nitrogen ion implantation.
The other bonding states would have been ruptured due to the implantation induced evolution of the hydrogen and oxygen from the surface of PC. Therefore, the present line at 284.22 eV position in the C(1s) spectra (Fig. 3.86 ‘a’) is clearly indicative of the presence of the formation of amorphous graphitelike structure at the near surface regions of polycarbonate.

### 3.6.3 Atomic Force Microscopy

Fig. 3.87 show two-dimensional topographical images of (a) virgin and after 100 keV N⁺ ion implantated polycarbonate specimens at various fluences. It is clear from the Fig. 3.87 ‘a’ that the surface of the virgin PC was smooth and uniform. Using Nova Px software, the root mean square roughness (R_{rms}) and average roughness (R_{av}) values of the specimens has been calculated. For virgin PC sample (Fig. 3.87 ‘a’), the calculated R_{rms} and R_{av} values are 10.70 nm and 8.18 nm respectively. After implantation, these values have been found to increase. The calculated values of R_{rms} and R_{av} are 14.02 nm and 10.34
Fig. 3.87 Plot of RMS roughness and average roughness values of virgin and implanted PC specimens at 100 keV to $1 \times 10^{15}$, $1 \times 10^{16}$, and $1 \times 10^{17}$ N$^+$ cm$^{-2}$

nm for the lowest fluence of $1 \times 10^{15}$ N$^+$ cm$^{-2}$ (Fig. 3.87 ‘b’). The $R_{rms}$ and $R_{av}$ values increase to 16.41 nm and 12.76 nm at fluence of $1 \times 10^{16}$ N$^+$ cm$^{-2}$ (Fig. 3.87 ‘c’) and at the highest fluence of $1 \times 10^{17}$ N$^+$ cm$^{-2}$ (Fig. 3.87 ‘d’), the $R_{rms}$ and $R_{av}$ values increase to 20.08 nm and 14.24 nm respectively. The maximum value for the root mean square and average roughness has been observed for the highest fluence. Table 3.18 presents the $R_{rms}$ and $R_{av}$ values for virgin and ion implanted specimens at various fluences. Fig. 3.88 shows the plot of root mean square and average roughness values as a function of ion fluence.

**Table 3.18** Variation of root mean square roughness and average roughness values with ion fluence

<table>
<thead>
<tr>
<th>Ion Fluence (N$^+$ cm$^{-2}$)</th>
<th>Root mean square roughness $R_{rms}$ (nm)</th>
<th>Average roughness $R_{av}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PC</td>
<td>10.70</td>
<td>8.18</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>14.02</td>
<td>10.34</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>16.41</td>
<td>12.76</td>
</tr>
<tr>
<td>$1 \times 10^{17}$</td>
<td>20.08</td>
<td>14.24</td>
</tr>
</tbody>
</table>
The continuous increase in the values of roughness parameter with increasing ion fluence may be attributed to the fact that ion beam interaction results in the structural and compositional changes which leads to a consistent increase in the degree of modification [85,90,111]. Moreover, this increase in the surface roughness values is related to progressive degradation of the polymeric chain due to cross-linking which leads to a change in the free volume fraction in the modified surface layer [30,32,126-128]. Hence, it can be clearly discerned from the AFM images that nitrogen ion implantation leads to a structural modifications in the implanted layers of the polymeric matrix.

### 3.6.4 UV-Visible Spectroscopy

UV-Visible Spectroscopy has been performed to examine the effect of nitrogen ion implantation on PC specimens. The structural analysis and color examination of the virgin and implanted specimens have been carried using UV-Visible spectra.

#### 3.6.4.1 Structural Analysis

Fig. 3.89 presents the UV-visible absorption spectra for the virgin and 100 keV nitrogen implanted PC specimens to fluences $1 \times 10^{15}$, $1 \times 10^{16}$ and $1 \times 10^{17}$ ions cm$^{-2}$. The absorption spectra of virgin PC show the presence of two peaks at 240 nm and 274 nm. These peaks in the absorption spectra are due to the electronic transitions between the highest occupied molecular orbital to the lowest unoccupied molecular orbital. These
Fig. 3.89 UV-Visible absorption spectra (a) virgin and implanted PC specimens at 100 keV to (b) 1×10^{15}, (c) 1×10^{16}, and (d) 1×10^{17} N^+ cm^{-2}.

peaks in the virgin PC can be due to the transitions from n-π* and π-π* orbital which is likely to be related with carbonyl and phenyl groups of the PC. Such type of transition is found in unsaturated centers of molecules i.e. the compound having double or triple bonds [38,129]. It has been noticed that after implantation, these bands (at 240 nm and 274 nm) merge to one band with continuous increase in the optical intensity alongwith the edge flattening. It is discerned from the Fig. 3.89 that the sharpness of the band edge of the virgin PC affected significantly after implantation due to the augmented disorder with increasing ion fluence. The bathochromic shift followed by broadening of the peaks has also been observed. These changes are due to the ion beam interaction of the polymer which produces excitation of atomic electrons and ionization leading to the rupturing of bonds, radical formation, chain scission etc. which results in the formation of conjugated system of carbon bonds [12,17,37-38,74]. This in turn results in the formation of carbonaceous networks in the implanted layer of the PC specimens. Thus, these results are in consistent with the results of XPS and RBS studies.

3.6.4.2 Color Examination

On visual examination, it has been observed that the color of specimens has been changed after implantation. It changes from transparent (in virgin) to light brown and to dark brown with increasing ion fluence. This color transformation may be attributed to the
fact that ion implantation produces structural changes in the specimens [2,8,115]. This is because of the reason that ion beam treatment of polymers results in the rupturing of chemical bonds, cross-linking, formation of free radicals etc. which results in the carbonization in the implanted surface layer of the specimen [34,10,75,116,128]. This increase in carbonization has also been observed through XPS and RBS studies.

3.6.5 Dielectric Spectroscopy

The dielectric behavior (dielectric constant, dielectric loss, dissipation factor, spreading factor, average relaxation time and molecular relaxation time) of the virgin and implanted PC specimens [44-47] has been analyzed using Dielectric measurements.

3.6.5.1 Dielectric constant and Dielectric loss

Fig. 3.90 and 3.91 presents the plot of the dielectric constant (ε′) and dielectric loss (ε″) respectively as a function of frequency for pre- and post- implanted PC samples in the frequency range of 100 Hz - 90 MHz. Fig. 3.90 clearly indicates a variation in the values of ε′ from low frequency region to high frequency region for all the PC specimens. It has been noticed from Fig. 3.90 that the value of dielectric constant increases with increase in frequency upto ~ 85 MHz and with further increase in frequency results in the decline in the dielectric constant value. For virgin PC (curve ‘a’, Fig 3.90) the value of dielectric constant increases from a value of 2.48 (at 100 Hz) to a maximum value of 13.4 (at 84.4 MHz). At a low fluence of 1x10^{15} N+ cm^{-2} (curve ‘b’, Fig 3.90), the value of ε′ increases from 2.27 (at 100 Hz) to a maximum value of 13.2 (at 84.5 MHz). For a dose of 1x10^{16} N+ cm^{-2} (curve ‘c’, Fig 3.90), ε′ increases from 2.16 (at 100 Hz) to a maximum value of 13.2 (at 84.6 MHz), and with the highest implantation dose of 1x10^{17} N+ cm^{-2} (curve ‘d’, Fig 3.90) ε′ increases from 2.13 (at 100 Hz) to a maximum value of 12.9 (at 85 MHz). This increase in the ε′ upto the frequency of ~85 MHz may be due to the dipole orientation polarization mechanism in this frequency range [44,47].

Further, it has been observed that the value of dielectric constant decreases after frequency ~85 MHz. This variation in the dielectric constant value may be associated with the change in the polarization mechanism from dipole orientation to atomic. Hence, with increasing frequency, atomic polarization results changes the response of dipoles with applied field [54,102] which results in the decrease in the value of dielectric constant.

The variation of dielectric loss (ε″) as a function of frequency for virgin and implanted specimens is shown in Fig. 3.91. It is clear from the Fig. 3.91 that the value of ε″ increases upto frequency range of ~82-83 MHz and then starts decreasing after this
Fig. 3.90 Plot of dielectric constant vs. frequency for (a) virgin and implanted PC specimens at 100 keV to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^{-2}$

frequency range. The increases in the value of dielectric loss may be due to the fact that the polarization of one dipole is independent of the neighbouring dipoles of the same chain with applied field [102]. Further with increase in frequency, these independent dipoles starts aligning with the direction of applied field and hence results in the decrease in the value of dielectric loss.
Fig. 3.91 Variation in dielectric loss vs. frequency for (a) virgin and implanted PC specimens at 100 keV to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^{-2}$

3.6.5.2 Dissipation factor

The variation in dissipation factor ($\tan \delta$) as a function of frequency for pre- and post-implanted PC specimens is shown in Fig. 3.92 in the frequency range of 100 HZ to 90 MHz. It is discerned from the Fig. 3.92 that the value of $\tan \delta$ increases with increasing ion fluence as well as with frequency. As dissipation factor is proportional to
the electrical energy lost as heat in the polarization process in the presence of applied field [60] therefore it also increases with increasing ion fluence. It is observed that the behaviour of tan δ shows the similar trend and almost same peak position for pre- and post-implanted PC specimens. This peak is due to the vibrations of the main chain hence after implantation the main sources of this loss peak remain almost unaffected [56,59].

Fig. 3.92 Variation in dissipation factor with frequency for (a) virgin and implanted PC specimens at 100 keV to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^2$.
Thus it can be concluded that nitrogen ion implantation results in the modifications in the values of dielectric constant (Fig. 3.90), dielectric loss (Fig. 3.91), and dissipation factor (Fig. 3.92). These modifications can be attributed to the degradation processes taking place inside the polymeric chain due to nitrogen ion implantation [2,61,103,116] as observed by XPS, RBS, AFM and UV-Visible studies.

3.6.5.3 a. c. conductivity

The a.c. conductivity for pre- and post-implanted specimens at various frequencies has been calculated using equation (3.6). The variation in a. c. conductivity of virgin and nitrogen ion implanted PC samples at various fluences in the range of 10 MHz to 80 MHz is shown in Fig. 3.93.

![Fig. 3.93 Plot of a. c. conductivity with ion fluences at various frequencies for virgin and implanted PC specimens at 100 keV](image)

Fig. 3.93 clearly show that the a. c. conductivity increases with increasing frequency and ion fluence. This enhancement in the conductivity of PC specimens may be attributed to the modifications in the structure of the polymeric matrix which results in the formation of new carbonaceous structure [34,58] in the implanted layers of the specimens. Moreover, the formation of π- bonded carbon enriched domains created in the implanted layers of PC may be the main reason behind the modifications in the dielectric constant, dielectric loss and a. c. conductivity. It can be concluded from these results that implantation support the formation of carbon enriched domains in the implanted layers of the polymeric matrix as revealed by XPS and RBS results.
3.6.5.4 Cole-Cole Plot

Cole-Cole plots are used to study the distribution of relaxation time taking place in the virgin and nitrogen implanted polymeric specimens. The plot of real part ($\varepsilon'$) of the complex permittivity on the x-axis and imaginary part ($\varepsilon''$) of that on the y-axis is known as the Cole-Cole plot. An analysis of real part ($\varepsilon'$) and imaginary part ($\varepsilon''$) of the complex permittivity has been elucidated using these plots. Fig. 3.94 (curves ‘a’, ‘b’, ‘c’, &‘d’) presents the Cole-Cole plots for virgin and 100 keV N$^+$ implanted PC specimens to fluences $1\times10^{15}$, $1\times10^{16}$ and $1\times10^{17}$ ions cm$^{-2}$ in the frequency range of 100 Hz - 90 MHz. The spreading factor ($\alpha$), average relaxation time ($\tau_0$) and molecular relaxation time ($\tau$) taking place in the polymeric specimens have been determined using these plots.

![Cole-Cole plot](image)

Fig. 3.94 Cole-Cole plot of (a) virgin and implanted PC specimens at 100 keV to (b) $1\times10^{15}$, (c) $1\times10^{16}$, and (d) $1\times10^{17}$ N$^+$ cm$^{-2}$

It is clear from the Fig. 3.94 (curves ‘a’, ‘b’, ‘c’, &‘d’) that Cole-Cole plots are imperfect semicircular in nature. Further, the distortions in the shape of the Cole-Cole plots increases with increasing ion fluence. This deviation in the shape of the curves of the Cole-Cole plots is due to the polydisperse nature of the amorphous PC. As the Cole-Cole plots are related to the relaxation phenomena [57,60,68] taking place in matrix,
therefore, the changes observed in the nature of the curve after implantation also indicate towards the disorderness in the matrix and hence results in the formation of conjugated π-bonded clusters [37].

3.6.5.5 Spreading Factor (\( \alpha \))

The value of spreading factor (\( \alpha \)) has been calculated from the expression for the maximum value of imaginary part of complex permittivity as given by the equation (3.7).

Fig. 3.95 presents the plot of spreading factor value for PC specimens as a function of ion fluence. The calculated value of \( \alpha \) is listed in Table 3.19. It is clear from the table that the value of spreading factor is not equal to 0 and increases with increase in ion fluence. This indicates that there is a broad distribution of relaxation times in the specimens and hence exhibit polydispersive nature [53,63,69]. Moreover, the increase in the value of \( \alpha \) points towards the increase in the disorderness [58,70] in the matrix.

![Graph showing the variation of spreading factor with ion fluence](image)

**Fig. 3.95** Variation of spreading factor (\( \alpha \)) with ion fluences for virgin and nitrogen ion implanted PC specimen at 100 keV

**Table 3.19** Variation of spreading factor (\( \alpha \)), average relaxation time (\( \tau_0 \)) and molecular relaxation time (\( \tau \)) at various ion fluences

<table>
<thead>
<tr>
<th>Ion fluence (N⁺ cm⁻²)</th>
<th>Spreading factor (( \alpha ))</th>
<th>Average relaxation time – ( \tau_0 ) (s)</th>
<th>Molecular relaxation time – ( \tau ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PC</td>
<td>0.66</td>
<td>2.20 ( \times 10^{-9} )</td>
<td>1.60 ( \times 10^{-9} )</td>
</tr>
<tr>
<td>1 ( \times 10^{15} )</td>
<td>0.68</td>
<td>0.55 ( \times 10^{-9} )</td>
<td>0.39 ( \times 10^{-9} )</td>
</tr>
<tr>
<td>1 ( \times 10^{16} )</td>
<td>0.71</td>
<td>0.52 ( \times 10^{-9} )</td>
<td>0.37 ( \times 10^{-9} )</td>
</tr>
<tr>
<td>1 ( \times 10^{17} )</td>
<td>0.77</td>
<td>0.47 ( \times 10^{-9} )</td>
<td>0.34 ( \times 10^{-9} )</td>
</tr>
</tbody>
</table>
3.6.5.6 Average relaxation time ($\tau_0$)

The average relaxation time $\tau_0$ for virgin and implanted PC specimens was calculated using the relation given by equation (3.8). The plot of average relaxation time for PC specimens at various doses is shown in Fig. 3.96. The measured values of $\tau_0$ is listed in Table 3.19.

![Graph](image)

Fig. 3.96 Variation of average relaxation time ($\tau_0$) with ion fluence for virgin and nitrogen ion implanted PC specimen at 100 keV

Fig. 3.96 shows that the average relaxation time decreases with increasing ion fluence. This may be due to the implantation induced structural changes in the PC matrix and the formation of carbon enriched domains in the implanted layers.

3.6.5.7 Molecular relaxation time ($\tau$)

The molecular relaxation time ($\tau$) for pre- and post- implanted PC specimens is calculated using the formula as given by equation (3.9). Fig. 3.97 show the plot of molecular relaxation time for virgin and implanted PC specimens at various doses. The measured values of ($\tau$) is listed in Table 3.19. Fig. 3.97 depicts clearly the decrease in molecular relaxation time with increasing ion fluence. This is similar to the earlier trend of average relaxation time (3.96). This may be due to the carbonization of the PC matrix due to nitrogen ion implantation as already seen from the RBS and XPS analysis.

It is clear from Figs. 3.96 and 3.97 alongwith Table 3.19 that the average and molecular relaxation times decreases with increasing argon ion fluence. This may be due to the fact that implantation causes structural modifications and disorderness in the
Fig. 3.97 Variation of molecular relaxation time (τ) with ion fluences for virgin and nitrogen ion implanted PC specimen at 100 keV

matrix thereby decreases relaxation time. Moreover, the decrease in the values of relaxation time may also be attributed to the improvement in the conductivity [58,73] of implanted specimens as studied through XPS and RBS analysis.

3.6.6 Dielectric Constant and Dielectric Loss using Optical Absorption and Reflection Studies

The dielectric constant and dielectric loss have also been calculated using UV-Visible Spectroscopy. The optical absorption and reflection data has been used for these calculations for pre- and post- implanted specimens in the frequency range of .42 - .75 PHz corresponding to the visible region wavelength (400-700 nm). The response of the specimens to the applied field is mainly due to electronic polarization in this frequency range and is responsible for a number of optical properties of the materials [44-47, 101]. In the present context the dielectric constant and dielectric loss are defined by equations (3.12) and (3.13) respectively. For studying the dielectric constant and dielectric loss in the visible region, the values of extinction coefficient and refractive index have been calculated using equations (3.14) and (3.15) respectively.

Fig. 3.98 shows the variation of extinction coefficient for virgin and nitrogen ion implanted PC specimens as a function of wavelength in the range of 400-700 nm. This spectrum indicates the dependence of change in value of extinction coefficient with increasing ion fluence. It can be inferred from the Fig. 3.98 that the extinction coefficient
Fig. 3.98 Variation in extinction coefficient with wavelength of (a) virgin and implanted PC specimens to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^{-2}$.

Fig. 3.99 Reflectivity spectra recorded in the visible region of (a) virgin and implanted PC specimens (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^{-2}$.

remains constant for virgin PC in the whole visible range whereas it shows a decreasing trend with wavelength for all the implanted specimens. However, the value of extinction coefficient increases with increase in ion fluence.

Fig. 3.99 shows the reflectance (%R) spectra in the visible region for pre- and post-implanted PC specimens. It is clear from the Fig. 3.99 that there are variations in the value
of %R with increasing ion fluence which may be due to the structural modifications in the implanted specimens.

Fig. 3.100 presents the plot of variations in the value of refractive index with increasing frequency as well as with increasing fluence. The modifications in the values of refractive index can be correlated with the energy loss of the incident ions inside the polymeric matrix which in turn increases the conjugation length of \( \pi \)-electron clouds in the implanted specimens [34,52].

The values of dielectric constant and dielectric loss have been calculated using the values of refractive index and extinction coefficient as discussed above. Fig. 3.101 and 3.102 presents the plots of dielectric constant and dielectric loss respectively with wavelength in the visible region. It is clear from the Fig. 3.101 that the value of dielectric constant decreases whereas value of dielectric loss (Fig. 3.102) shows an increasing trend with wavelength. These changes can be related to the structural rearrangement and generation of continuous extended network of conjugated bonds. The changes in the \( \epsilon' \) and \( \epsilon'' \) can be correlated to the electronic polarization of dipoles. This type of polarization occurs due to the deformation or translation of the originally symmetrical distribution of the electron clouds of atoms or molecules with applied field [46-47].
Fig. 3.101 Variation in dielectric constant with wavelength of (a) virgin and implanted PC specimens to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^{-2}$

\[
\varepsilon' = n^2 - k^2
\]

Fig. 3.102 Variation in dielectric loss with wavelength of (a) virgin and implanted PC specimens at 100 keV to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^{-2}$

\[
\varepsilon'' = 2nk
\]
3.6.7 Electrical Properties

The plot of Current-Voltage (I-V) characteristics recorded in the applied voltage range of 10-50 V for virgin and 100 keV N\textsuperscript{+} implanted PC specimens is shown in Fig. 3.103. It is clear from the curve ‘a’ (virgin PC) that the value of current increases with the applied voltage. There is a slight increase in the value of current with applied voltage for nitrogen implanted (curves ‘b’, ‘c’ & ‘d’) PC specimens. The value of current is found to be maximum for the highest implantation dose of 1x10\textsuperscript{17} N\textsuperscript{+} cm\textsuperscript{-2} (curve ‘d’).

![I-V Characteristics for 100 keV PC specimens](image)

Fig. 3.103  I-V Characteristics for (a) virgin and implanted PC specimens at 100 keV to (b) 1x10\textsuperscript{15}, (c) 1x10\textsuperscript{16}, and (d) 1x10\textsuperscript{17} N\textsuperscript{+} cm\textsuperscript{-2}

Fig. 3.103 (curves ‘a’, ‘b’, ‘c’ &‘d’) clearly reveals that the rate of increase of current is not proportional to the corresponding increase in voltage for all the PC specimens. Hence the possibility of Ohmic conduction mechanism is ruled out from the observed behaviour of I-V characteristics. Moreover, it can be discerned from Fig. 3.103 (curves ‘b’, ‘c’ & ‘d’) that the current increases continuously with increasing nitrogen ion fluence. This can be explained on the basis of formation of carbonaceous clusters due to the gradual escape of low mass, hydrogen rich degradation products from implanted material. The electronic hopping process (i.e. tunneling) easily takes place within these clusters as they generally acts as conducting islands within implanted polymeric matrix.
Thus, they facilitate the flow of current and contribute towards the modification in the conductivity of implanted polymers.

To reveal the charge transport mechanism in virgin and implanted PC specimens, I–V data is plotted in the form \( \ln (I) \) vs. \( V^{1/2} \) in the Fig. 3.104.

![Fig.3.104 Plot of \( \ln (I) \) vs. \( V^{1/2} \) for (a) virgin and implanted PC specimens at 100 keV to (b) \( 1 \times 10^{15} \), (c) \( 1 \times 10^{16} \), and (d) \( 1 \times 10^{17} \) N\(^+\)cm\(^{-2}\)]

Similar to the earlier cases of the present study, different conduction mechanisms have been used to describe the I-V characteristic measurements in the polymeric matrix. The experimental value of \( \beta \) i.e. \( \beta_{exp} \) for virgin and implanted specimens has been calculated using the equations (3.17) and (3.18) and are given in Table 3.20. The theoretical values of \( \beta \) for Schottky emission as well as for Poole-Frenkel emission are calculated by equations (3.19) and (3.20) and are listed in Table 3.20.

It is clear from the table that \( \beta_{exp} \) was in good agreement with the theoretical value of \( \beta_{pf} \) for virgin PC. However, it was noticed that after implantation the values of \( \beta_{exp} \) was close to the theoretical value of \( \beta_{ks} \) leading to the conclusion that Schottky emission is the dominant charge transport mechanism operating in implanted specimens. The transition in the type of conduction mechanism from Poole-Frenkel (for virgin PC) to Schottky emission (for implanted PC specimens) may be due to the improvement in the
Table 3.20  A comparison between the theoretical and experimental \( \beta \) coefficients of virgin and implanted PC specimens

<table>
<thead>
<tr>
<th>Ion Fluence (N(^+)cm(^{-2}))</th>
<th>Theoretical values of conduction parameter</th>
<th>Experimental values of conduction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Schottky emission (( \beta_{RS} )) (eV(\cdot)m(^{1/2}) V(^{-1/2}))</td>
<td>Poole Frenkel emission (( \beta_{PF} )) (eV(\cdot)m(^{1/2}) V(^{-1/2}))</td>
</tr>
<tr>
<td>Virgin</td>
<td>2.39 \times 10^{-5}</td>
<td>4.79 \times 10^{-5}</td>
</tr>
<tr>
<td>( 1 \times 10^{15} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 1 \times 10^{16} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 1 \times 10^{17} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

conductivity of these specimens as a result of implantation [58]. Moreover, it has also been assumed that the conduction of charge carriers between localized states leads to the Hopping mechanism which results in the increase the conductivity of the specimens [76,83].

For space charge linear conduction mechanism (SCLC) to occur, the slope of the I-V characteristic curves should be greater than or equal to 2, but in the present case the value of slope comes out to be less than 2 therefore, this conduction mechanism is ruled out [58,84].

Thus, it has been observed that nitrogen ion interaction with PC specimen results in the modifications in the surface properties of the samples. RBS studies show that the elemental composition of virgin PC has been modified as a result of N\(^+\) implantation. It has also been found that the carbon concentration increases and also oxygen redistribution takes place near the surface layer of the implanted specimen. Hence, the increase in the number of carbon atoms attributes towards the carbon enriched surface layer in the implanted polymeric matrix [3]. The structural modifications after implantation have been confirmed by XPS, AEM and UV-Visible studies. The variations in the dielectric properties (dielectric constant, dielectric loss, dissipation factor, a. c. conductivity) have also been studied. The conductivity of the PC specimens has been found to be increased which may be attributed to the formation of \( \pi \)-bonded carbon clusters in the implanted layers as a result of implantation [37,52]. Therefore, formation of such clusters may have been contributed significantly towards the enhancement in the conductivity of implanted
matrix. Moreover, the Cole-Cole analysis of pre- and post-implanted specimens indicates a deviation from the Debye relaxation phenomena. And, the shapes of the Cole-Cole curves confirmed the structural disordering in implanted PC specimens. From I–V characteristic measurements, it has been observed that the current increases with increasing ion fluence and Schottky emission is the dominant charge transport mechanism in implanted specimens.
3.7 Effects of Nitrogen Ion Implantation on Polypropylene

The polypropylene specimens were implanted by 100 keV N\(^+\) implantation with various fluences of 1x10\(^{15}\), 1x10\(^{16}\) and 1x10\(^{17}\) N\(^+\) cm\(^{-2}\). The effect of nitrogen ion implantation on the structural, optical, dielectric and electrical properties of PP specimens is investigated and the results are discussed in the following sections. Similar studies as in case of argon ion implanted PP has been carried out in this case also.

3.7.1 Rutherford Backscattering Spectroscopy

From the RBS spectra of pre- and post-implanted PP specimens, the various elements present in the implanted layer and their differential cross-sections have been calculated using the kinematic factors. Also, the projected range, retained dose and atomic concentration of implanted argon have been analyzed.

3.7.1.1 Composition and Structure

Fig. 3.105 shows the RBS spectra of pre- and post- implanted polypropylene specimen at fluence of 1x10\(^{17}\) N\(^+\) cm\(^{-2}\). It is clear from the Fig. 3.105 that nitrogen ion implantation produces significant changes in the PP specimen.

![RBS spectra](image)

Fig. 3.105 RBS spectra of (a) virgin and (b) implanted polypropylene specimen at 100 keV to 1x10\(^{17}\) N\(^+\) cm\(^{-2}\)

Fig. 3.106 shows the Rutherford Backscattering Manipulation Program (RUMP) software [1] fitted spectra for the virgin and nitrogen ion implanted PP specimen. RUMP software has been used for the quantitative analysis. The virgin (Fig. 3.106 ‘a’) and nitrogen implanted (Fig. 3.102 ‘b’) PP specimen indicate the presence of carbon element corresponding to energy values of ~507 keV. In addition, fitting of observed spectrum
Fig. 3.106 RUMP fitted RBS spectra of (a) virgin and (b) nitrogen ion implanted PP at 100 keV to a fluence $1 \times 10^{17}$ N$^+$ cm$^{-2}$

with RUMP software clearly demonstrates the presence of nitrogen in the post implanted matrix (Fig. 3.102 ‘b’). A peak corresponding to energy value ~602 keV indicates the presence of nitrogen in the implanted specimen (Fig. ‘b’, 3.106) which was not present in case of virgin specimen (Fig. ‘a’,3.106). Simulations yielded an increase in the concentration of carbon from 33 at.% to 42 at.% in implanted specimen in comparison to virgin specimen.

It has also been observed that there are variations in the carbon spectra between 0.4 MeV to 0.53 MeV. This may be due to the reason that ion beam treatment of polymers causes degradation of polymeric chains, cross-linking, creation of free radicals, molecular rearrangement which results in the formation of conjugated carbon-carbon double bonds and hence results in the carbonization of the surface layer with increasing ion fluence. This in turn induces structural disordering in the polymeric matrix [2-5,17,111,126].

Hence, one can demonstrate that ion implantation results in conjugation and hence carbonization near the modified surface. The effect of carbonization is of considerable interest because of significant change of the structure and composition of nitrogen ion implanted PP specimens. However, it has also been noticed from the earlier studies [11-12,75,89] that ion implantation results in dehydrogenation in the implanted surface of the specimen though it is not measurable by RBS technique. This decrease in the composition of hydrogen results in the relative increase in the composition of carbon and oxygen redistribution. [16-17,23].
3.7.1.2 Backscattered Energies

Backscattered energies of the scattered particles can be measured using kinematic factor using the relationship between incident ($E_0$) and backscattered ($E_1$) energies given by equation (3.1).

From the RUMP fitted RBS spectra, values of backscattered energies for carbon, oxygen and argon have been determined. These experimentally calculated backscattered energies are presented in Table 3.21 along with the corresponding values calculated directly from the equation (3.1).

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass number</th>
<th>Kinematic factor 'K'</th>
<th>Incident energy $E_0$ (MeV)</th>
<th>Backscattered $E_1$ (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>12</td>
<td>0.253</td>
<td>2</td>
<td>0.57</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>14</td>
<td>0.311</td>
<td>2</td>
<td>0.602</td>
</tr>
</tbody>
</table>

It is clear from the table that the experimental and calculated backscattered energy values are in good agreement with each other.

3.7.1.3 Elemental Identification in the Target

Backscattered energies give the quantitative information of the different masses of individual elements present in the target material. Using equation (3.2), the individual elements i.e. carbon and nitrogen present in the specimen have been identified.

3.7.1.4 Calculation of Differential Cross Section

The differential scattering cross section is a measure of the probability with which a projectile is elastically scattered from target atom [18-20]. Using equation (3.3), we have calculated the differential cross sections for carbon and nitrogen elements in the target and the values are listed in Table 3.13b. It has been found that the calculated values are in good agreement with the theoretical values [18-20].

3.7.1.5 Calculation of Implanted Fluence

The dose in the implanted PP specimens using RBS data has been confirmed and verified using formula [18-19] as given by equation (3.4). Using the calculated values of different parameters, the retained implantation fluence comes out to be $0.96 \times 10^{17}$ N$^+$ cm$^{-2}$ which is in well agreement with the real implanted ion fluence of $1 \times 10^{17}$ N$^+$ cm$^{-2}$. 

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3.7.1.6 Calculation of Atomic Concentration

The atomic concentration of implanted nitrogen \(N_x\) in the PP specimen is calculated [18-19] using equation (3.5). The concentration of implanted nitrogen has been calculated using height measurements and its value comes out to be 3.2 at.% which is in well agreement with the value 3.5 at.% calculated using RUMP fitted RBS spectra.

3.7.1.7 Calculation of Projected Range

The value of projected range of the implanted nitrogen ion in the PP specimen comes out to be 375 nm using RUMP fitted RBS spectra which is in good agreement with the value 367 nm as per Stopping and Range of Ions in Matter (SRIM) simulations [22].

3.7.2 Atomic Force Microscopy

Atomic Force Microscopy was performed to examine the surface morphology and roughness values of the virgin and ion implanted polymeric specimens. The two-dimensional AFM images recorded at 2μm × 2μm size for virgin and nitrogen implanted PP specimens to various fluences are shown in Fig. 3.107.

![AFM images](image)

Fig. 3.107 Two-dimensional AFM images of (a) virgin and implanted PP specimens at 100 keV to (b) 1\times10^{15}, (c) 1\times10^{16}, and (d) 1\times10^{17} N^+ cm^{-2}
It has been observed that the topographical images of the PP samples show a remarkable change after implantation. The cross-section of each AFM images were analyzed in terms of root mean square roughness ($R_{\text{rms}}$) and average roughness values ($R_{\text{av}}$) values. Nova Px software was used to calculate the root mean square roughness ($R_{\text{rms}}$) and average roughness ($R_{\text{av}}$) values. The calculated $R_{\text{rms}}$ and $R_{\text{av}}$ values for the virgin PP samples are 4.90 nm and 3.36 nm respectively. These values have been found to increase after ion implantation. For the lowest fluence of $1 \times 10^{15}$ N$^+$ cm$^{-2}$ (‘b’, Fig. 3.107), the calculated values of $R_{\text{rms}}$ and $R_{\text{av}}$ are 9.76 nm and 7.26 nm respectively.

Table 3.22 Variation of root mean square roughness and average roughness values with ion fluence

<table>
<thead>
<tr>
<th>Ion Fluence ($N^+ \text{ cm}^{-2}$)</th>
<th>Root mean square roughness $R_{\text{rms}}$ (nm)</th>
<th>Average roughness $R_{\text{av}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PP</td>
<td>4.90</td>
<td>3.36</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>9.76</td>
<td>7.26</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>13.78</td>
<td>10.82</td>
</tr>
<tr>
<td>$1 \times 10^{17}$</td>
<td>19.18</td>
<td>13.34</td>
</tr>
</tbody>
</table>

Fig. 3.108 Plot of $R_{\text{rms}}$ and $R_{\text{av}}$ roughness values of virgin and implanted PP specimens at 100 keV to $1 \times 10^{15}$, $1 \times 10^{16}$ and $1 \times 10^{17}$ N$^+$ cm$^{-2}$
Further, with increase in ion fluence (‘c’, Fig. 3.107), the $R_{\text{rms}}$ and $R_{av}$ values increase to 13.78 nm and 10.82 nm respectively. Moreover, at the highest fluence of $1 \times 10^{17}$ N<sup>+</sup> cm<sup>-2</sup> (‘d’, Fig. 3.107), there is a maximum increase in the root mean square and average roughness values upto 19.18 nm and 13.34 nm respectively. Table 3.22 presents the $R_{\text{rms}}$ and $R_{av}$ values for virgin and ion implanted specimens at various fluences. The observed rms roughness and average roughness values of samples are plotted as a function of ion fluence in Fig. 3.108.

It is clear from the Fig. 3.107 alongwith Table 3.22 that the $R_{\text{rms}}$ and $R_{av}$ values increase continuously with increasing ion fluence which is due to the reason that ion beam interaction results in the degradation in the uniformity on the surface of PP specimens. The increase in the roughness values may be attributed to the formation of cross-linked and carbon-rich clusters in the surface area of PP during the implantation process which is associated with the structural and compositional changes in the modified surface layers of the polymeric matrix [8,31]. Moreover, it is clearly revealed from the AFM images that there is a consistent increase in the degree of modification with increase in surface roughness and is related to the progressive degradation of the polymeric chain [11,30,32,94,127]. Hence, it has been observed that AFM images reflect the surface modifications in the polymeric specimen after ion implantation.

### 3.7.3 UV-Visible Spectroscopy

UV-Visible Spectroscopy has been performed to analyze the effect of nitrogen ion implantation on PP specimens. From the UV-Visible spectra of pre- and post-implanted specimens structural analysis and color examination has been investigated.

#### 3.7.3.1 Structural Analysis

UV-Visible absorption spectra of virgin and 100 keV nitrogen implanted (fluences of $1 \times 10^{15}$, $1 \times 10^{16}$, and $1 \times 10^{17}$ ions cm<sup>-2</sup>) polypropylene specimens are shown in Fig. 3.109. It is evident from the Fig. 3.109 that there is a gradual increase in the absorbance with increase in ion fluence. As it is well known that the absorption of light energy by polymeric materials in the UV-Visible region involves transition of electrons between occupied and unoccupied molecular orbitals [38,100]. In the present case, the UV-Visible absorption spectra for virgin specimen (curve ‘a’) show the presence of two absorption bands at 240 nm and 273 nm. These bands arise due to the electronic transitions between HOMO to LUMO. These transitions are likely to be associated with $\sigma-\sigma^*$ transitions due
to the presence of alkane group in the polypropylene matrix [37-38].

Fig. 3.109 show that the fundamental absorption edge of virgin PP polymer is smeared towards higher wavelength and simultaneous edge flattens with increasing ion implantation dose. This increased absorption can be attributed to the generation of some chromophoric groups having maximum absorption in the visible region [38,97]. These changes are due to the formation of a conjugated system of bonds as a result of the beam induced bond cleavage and reconstruction in the polymeric matrix [42,115]. Thus, it can be inferred from the UV-Visible spectra that nitrogen ion implantation produces significant changes in the polymeric matrix. Also, RBS and AFM studies of the same specimens as discussed above also confirmed the structural modifications in PP matrix by ion implantation.

3.7.3.2 Color Examination

The visual examination of specimens indicates towards the change in the color of the specimens as a result of ion implantation. The virgin sample was transparent and colorless. After implantation, the change in the color of the samples has been observed. The color changes to light brown for a dose of $1 \times 10^{15} \text{ N}^+ \text{ cm}^{-2}$. At the highest dose of
the color changes to grayish black. The color transformation is related closely to the structural change induced by ion implantation [2,8].

This color transformation may be attributed to the fact that ion implantation produces structural changes in the specimens [2,8,115,128]. This is because of the reason that ion beam treatment of polymers results in various processes viz. ionization, excitation which results in the rupturing of chemical bonds, cross-linking etc. This in turn results in the carbonization in the implanted surface layer of the specimen [34,10,75,116]. This increase in carbonization has also been observed through RBS studies.

3.7.4 Dielectric Spectroscopy

Dielectric measurements have been used to analyze the dielectric response of the N⁺ implanted PP specimens. Using these measurements dielectric constant, dielectric loss, dissipation factor, spreading factor, average relaxation time and molecular relaxation time have been calculated.

3.7.4.1 Dielectric constant and Dielectric loss

Fig. 3.110 and 3.111 show the variation of dielectric constant (ε’) and dielectric loss (ε”) respectively as a function of frequency for virgin and 100 keV nitrogen ion implanted PP samples to fluences 1x10^{15}, 1x10^{16} and 1x10^{17} ions cm⁻². The dielectric properties of pre- and post-implanted PP specimens have been studied in the frequency range of 100 Hz to 90 MHz. The value of dielectric constant (curves ‘a’, ‘b’, ‘c’, &‘d’, Fig. 3.110) increases with increase in frequency for all the PP specimens. In virgin PP (curve ‘a’, Fig 3.110) the value of dielectric constant increases from a value of 1.94 (at 100 Hz) to a maximum value of 7.68 (at 85.8 MHz). After implantation with 1x10^{15} N⁺ cm⁻² (curve ‘b’, Fig 3.110), the dielectric constant value increases from 1.24 (at 100 Hz) to a maximum value of 7.61 (at 85.8 MHz). For a dose of 1x10^{16} N⁺ cm⁻² (curve ‘c’, Fig 3.110), ε’ increases from 1.12 (at 100 Hz) to a maximum value of 7.5 (at 85.9 MHz) and at the highest implantation dose of 1x10^{17} N⁺ cm⁻² (curve ‘d’, Fig 3.110) ε’ increases from 1.07 (at 100 Hz) to a maximum value of 7.4 (at 85.9 MHz).

The value of dielectric constant (Fig. 3.110) shows a variation from low frequency region to high frequency region for all the PP specimens. It is discerned from the Fig. 3.110 that the value of ε’ increases up to the frequency of ~86 MHz. This observed behaviour in the polymeric matrix can be explained in terms of dipole orientation polarization mechanism. This polarization mechanism provides a reasonable explanation.
Fig. 3.110  Plot of dielectric constant vs. frequency for (a) virgin and implanted PP specimens at 100 keV to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^{-2}$ for the polarization as well as orientation of dipoles as a function of frequency [44,47]. As the frequency increases, the field tries to orient the dipoles along its direction and hence results in the increased value of the dielectric constant with increase in frequency.

However, after frequency of ~86 MHz, the value of dielectric constant falls. This change in the behaviour of $\varepsilon'$ can be explained in terms that the dipole orientation
polarization (which is predominant up to the frequency of ~86 MHz) changes to atomic polarization [54] with further increase in frequency. This variation in the dielectric constant value may be associated with the change in the polarization mechanism from dipole orientation to atomic. Hence, with increasing frequency, atomic polarization results in changes in the response of dipoles with applied field [54,102] which results in the decrease in the value of dielectric constant.

Fig. 3.111 shows the variation in the dielectric loss ($\varepsilon''$) as a function of frequency for pre- and post-implanted specimens.

**Fig. 3.111** Variation in dielectric loss vs. frequency for (a) virgin and implanted PP specimens at 100 keV to (b) $1\times10^{15}$, (c) $1\times10^{16}$, and (d) $1\times10^{17}$ N$^+$ cm$^{-2}$
The increase in $\varepsilon''$ is observed up to frequency range ~85 MHz which may be due to the polarization of dipoles with applied field [102]. However, with further increase in frequency, the dipoles in the polymeric chain get coupled to the adjacent dipoles of the same chain and hence results in the decrease in the value of dielectric loss after ~85 MHz.

3.7.4.2 Dissipation factor

It is also well known that in high frequency alternating fields there is always a phase difference between polarization and field, which gives the dissipation factor [55,58]. The plot of dissipation factor (tan $\delta$) as a function of frequency is shown in Fig. 3.112.

![Dissipation factor plot](image)

**Fig. 3.112** Variation in dielectric loss tangent with frequency for (a) virgin and implanted PP specimens to (b) $1\times10^{15}$, (c) $1\times10^{16}$ and (d) $1\times10^{17}$ N$^+$ cm$^{-2}$
It is clear from the Fig. 3.112 that dissipation factor of polypropylene specimen shows an increasing trend with increasing ion fluence as well as with frequency. It is also observed from the figure that the position of tan δ peak remains almost the same for virgin and implanted PP samples. It is observed that the behaviour of tan δ shows the similar trend and almost same peak position for unimplanted and implanted PP specimens. This peak is due to the vibrations of the main chain hence even after implantation the main sources of this loss peak remain almost unaffected [56,59].

It is observed from the figures (3.110, 3.111 & 3.112) that dielectric constant ($\varepsilon'$) decreases whereas dielectric loss ($\varepsilon''$) and dissipation factor (tan δ) increases with increasing ion fluence. This may be due to the fact that implantation generally induces disorder in the structure of polymeric specimens and leads to cross-linking, formation of free radicals, chain-scissioning etc. [34,52,61,116] as observed through RBS, AFM and UV-Visible results.

3.7.4.3 a.c. conductivity

The a.c. conductivity for pre- and post-implanted specimens at various frequencies has been calculated using equation (3.6). Fig. 3.113 shows the variation in a.c. conductivity of virgin and nitrogen ion implanted PP samples to fluences $1 \times 10^{15}$, $1 \times 10^{16}$ and $1 \times 10^{17}$ ions cm$^{-2}$ at various frequencies.

![Fig. 3.113 Plot of a.c. conductivity at various frequencies for virgin and implanted PP specimens at 100 keV to fluences of $1 \times 10^{15}$, $1 \times 10^{16}$ and $1 \times 10^{17}$ N$^+$ cm$^{-2}$]
Fig. 3.11 illustrate that the a.c. conductivity shows an increasing trend with increasing frequency and ion fluence. The increased conductivity of the PP specimens may be due to the increase in the carbon clusters in the implanted layers after implantation [34,52,58]. The formation of such clusters may be attributed towards the enhancement in the conductivity of implanted matrix. These modifications in the dielectric properties of the specimens reveal that implantation supports the formation of carbon enriched domains in the polymeric matrix as confirmed by the RBS results.

3.7.4.4 Cole-Cole Plot

Cole-Cole plot analysis has been used to study the dielectric relaxation occurring in virgin and nitrogen implanted polymeric specimens. Fig. 3.114 shows the Cole-Cole plots in the 100 Hz to 90 MHz frequency range for virgin and 100 keV N\(^+\) implanted PP specimens to fluences 1\(\times\)10\(^{15}\), 1\(\times\)10\(^{16}\) and 1\(\times\)10\(^{17}\) ions cm\(^{-2}\). The Cole-Cole plots are useful to confirm the distribution of relaxation time. Cole-Cole plots are used to determine the spreading factor (\(\alpha\)), average relaxation time (\(\tau_0\)) and molecular relaxation time (\(\tau\)).

**Fig. 3.114** Cole-Cole plot of (a) virgin and implanted PP specimens at 100 keV to (b) 1\(\times\)10\(^{15}\), (c) 1\(\times\)10\(^{16}\), and (d) 1\(\times\)10\(^{17}\) N\(^+\) cm\(^{-2}\)
It is clear from the Fig. 3.114 (curves ‘a’, ‘b’, ‘c’, &‘d’) that Cole-Cole plots are imperfect semicircular in nature. It has been observed that with increasing ion fluence, distortions in the shape and height of the curves in the Cole-Cole plots are increasing which indicates towards the polydisperse nature of the specimens. This polydisperse nature in polymers further increases owing to disorder due to ion implantation [67]. As the Cole-Cole plots are related to the relaxation phenomena [57,60,68] taking place in matrix, therefore, the changes observed in the nature of the curve after implantation also indicate towards the disorderness in the matrix and hence results in the formation of conjugated π-bonded clusters [37].

3.7.4.5 Spreading Factor (α)

The value of spreading factor (α) has been deduced from the expression for the maximum value of imaginary part of complex permittivity as given by the equation (3.7). The plot of variation of spreading factor of pre- and post-implanted PP specimens with ion fluence is shown in Fig. 3.115. The calculated value of α is listed in Table 3.23.

![Graph showing variation of spreading factor with ion fluence](image)

**Fig. 3.115** Variation of spreading factor (α) with ion fluences for virgin and nitrogen ion implanted PP specimen at 100 keV

It has been observed from the Fig. 3.115 along with Table 3.23 that the spreading factor value increase with increasing ion fluence. This indicates that there is a broad distribution of relaxation times [63,69] in the specimens and hence exhibit polydisperse nature. This increase in the value of α with increasing ion fluence may also be due to increase in disordering after implantation.
Table 3.23  Variation of spreading factor (\(\alpha\)), average relaxation time (\(\tau_0\)) and molecular relaxation time (\(\tau\)) at various ion fluences

<table>
<thead>
<tr>
<th>Ion fluence (N(^+) cm(^{-2}))</th>
<th>Spreading factor ((\alpha))</th>
<th>Average relaxation time (\tau_0) (s)</th>
<th>Molecular relaxation time (\tau) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin CR-39</td>
<td>1.43</td>
<td>1.27 \times 10^{-9}</td>
<td>2.52 \times 10^{-9}</td>
</tr>
<tr>
<td>(1 \times 10^{15})</td>
<td>1.46</td>
<td>0.83\times 10^{-9}</td>
<td>2.24\times 10^{-9}</td>
</tr>
<tr>
<td>(1 \times 10^{16})</td>
<td>1.53</td>
<td>0.76\times 10^{-9}</td>
<td>2.19\times 10^{-9}</td>
</tr>
<tr>
<td>(1 \times 10^{17})</td>
<td>1.60</td>
<td>0.63\times 10^{-9}</td>
<td>1.87\times 10^{-9}</td>
</tr>
</tbody>
</table>

3.7.4.6 Average relaxation time (\(\tau_0\))

The average relaxation time \(\tau_0\) for virgin and implanted PP specimens were calculated using the relation given by equation (3.8). Fig. 3.116 presents the plot of average relaxation time for virgin and implanted PP specimens at various doses. The measured values of \(\tau_0\) is listed in Table 3.23.

***Fig. 3.116 Variation of average relaxation time (\(\tau_0\)) with ion fluences for virgin and nitrogen ion implanted PP specimen at 100 keV***

From the Fig. 3.116, it is clearly observed that average relaxation time decreases with increasing ion fluence which may be due to the structural modification in the polymeric matrix and the formation of carbon enriched domains in the implanted layers.

3.7.4.7 Molecular relaxation time (\(\tau\))

The molecular relaxation time (\(\tau\)) for pre- and post-implanted specimens were calculated using the formula as given by equation (3.9). The plot of molecular relaxation
time for virgin and implanted PP specimens at various doses is shown in Fig. 3.117. The measured values of (τ) is listed in Table 3.23.

![Graph showing variation of molecular relaxation time (τ) with ion fluence for virgin and nitrogen ion implanted PP specimen at 100 keV](image)

**Fig. 3.117** Variation of molecular relaxation time (τ) with ion fluence for virgin and nitrogen ion implanted PP specimen at 100 keV

Fig. 3.117 depicts clearly that molecular relaxation time decreases with ion fluence. This is similar to the earlier trend of average relaxation time (Fig. 3.116). This may be due to the carbonization of the PP matrix due to nitrogen ion implantation as already seen from the RBS analysis.

It is clear from Table 3.23 that both the relaxation times (i.e. average and molecular) decreases with increasing nitrogen ion fluence. This decrease in relaxation times may be due the increase of disorderness in the matrix after ion implantation, thereby decreasing the relaxation time. Further, this decrease in the relaxation time may also be attributed to the improvement in the conductivity [58,73] of PP specimens as a result of implantation.

### 3.7.5 Dielectric Constant and Dielectric Loss using Optical Absorption and Reflection Studies

In the present work, the dielectric constant and dielectric loss have also been calculated using UV-Visible Spectroscopy. The data for optical absorption and reflection has been used for these calculations for virgin and argon ion implanted PP specimens in the frequency range of .42 - .75 PHz corresponding to the visible region wavelength (400-
In this frequency range, the response of the specimens to the applied field is mainly due to electronic polarization [44-45] which arises mainly due to the displacement of the outer electronic clouds with respect to the internal atomic cores by external fields. It is largely responsible for a number of optical properties of the materials [46-47,101]. In the present perspective the dielectric constant and dielectric loss are defined by equations (3.12) and (3.13) respectively. To study dielectric constant and dielectric loss in the visible region, the values of extinction coefficient and refractive index have been calculated using equations (3.14) and (3.15) respectively.

Fig. 3.118 shows the variation of extinction coefficient for virgin (curve a) and nitrogen ion implanted PP specimens (curves b, c, and d) as a function of wavelength in the range of 400-700 nm. It can be inferred from the Fig. 3.118 that the extinction coefficient remains constant for virgin PP whereas it shows a decreasing trend for all the implanted samples with wavelength. However, the value of extinction coefficient increases with increase in ion fluence.

![Graph showing variation in extinction coefficient with wavelength](image)

Fig. 3.118 Variation in extinction coefficient with wavelength of (a) virgin and implanted PP specimens to (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$, and (d) $1 \times 10^{17}$ N$^+$ cm$^{-2}$

Fig. 3.119 shows the reflectivity (%R) spectra in the visible region for virgin (curve a) and nitrogen implanted PP specimens (curves b, c & d). It is clear from the Fig. 3.119 that reflectivity decreases with increasing ion fluence. This may be due to the disordering created in the implanted specimens as a result of ion implantation.
The variation of refractive index as a function of wavelength for virgin and nitrogen ion implanted PP specimens is shown in Fig. 3.120. It is clear from the figure that refractive index decreases with increasing ion fluence.
This decrease in the values of refractive index (Fig. 3.120) in the implanted layers of the PP specimens is caused by the energy deposited by the ions during ion implantation. This leads to the destruction of initial chemical and physical structure by stripping of side group, chain scission and successive cross-linking [2,61]. These variations in the values of refractive index is associated with various physio-chemical changes, density and molecular weight variations taking place inside the PP matrix due to nitrogen ion implantation.

Exploiting the above calculated values of refractive index and extinction coefficient, the dielectric constant and dielectric loss of virgin and implanted specimens have been calculated. The variations of dielectric constant and dielectric loss with wavelength in the visible region are shown in Fig. 3.121 and 3.122 respectively.

![Fig. 3.121 Variation in dielectric constant with wavelength of (a) virgin and implanted PP specimens to (b) 1×10^{15}, (c) 1×10^{16}, and (d) 1×10^{17} N\textsuperscript{+} cm\textsuperscript{-2}](image)

It can be inferred from the Fig. 3.121 that the value of dielectric constant decreases with increasing ion fluence. However, the dielectric loss (Fig. 3.122) increases with increasing ion fluence for all the specimens. These observations can be explained by the fact that the dielectric properties are directly related to the polarization of the dipoles as a function of frequency. These modifications can be explained on the basis of polarization process in the polymeric samples [34]. The whole polarization in PP specimens is mainly

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contributed by the electronic polarization, which is governed by the orientation of the dipoles in response to applied field [54]. The electronic polarization resulting from orientation of dipoles and the subsequent alignment causes the observed modifications in the values of dielectric parameters.

3.7.6 Electrical Properties

Current–Voltage (I-V) characteristics for virgin as well as for implanted PP specimens with 100 keV N\(^+\) are shown in Fig. 3.123 (curves ‘a’, ‘b’, ‘c’ &‘d’). The I-V characteristics were recorded in the applied voltage range of 10-50 V.

For virgin PP specimen (curve ‘a’), the increase in current with applied voltage is less noticeable. After N\(^+\) implantation, the value of current increases (curves ‘b’, ‘c’ &‘d’) with increase in the ion fluence. However, at a low fluence of 1x10\(^{15}\) N\(^+\) cm\(^{-2}\) (curve ‘b’), there is slight increase in current with applied voltage. Also, for the fluences of 1x10\(^{16}\) and 1x10\(^{17}\) N\(^+\) cm\(^{-2}\) (curves ‘c’ and ‘d’), the current increases significantly as a function of applied voltage. The increase in current is found to be maximum for the highest implantation dose of 1x10\(^{17}\) N\(^+\) cm\(^{-2}\) (curve ‘d’) in comparison to virgin (curve ‘a’) PP specimen.
It is evident from the Fig. 3.123 (curves ‘a’, ‘b’, ‘c’ & ‘d’) that the increase in current is not proportional to the corresponding increase in voltage for all the specimens. Therefore, the possibility of Ohmic conduction mechanism is ruled out from the observed behaviour of I-V characteristics. Moreover, it can also be seen clearly from Fig. 3.123 (curves ‘b’, ‘c’ & ‘d’) that the current increases continuously with increasing nitrogen ion fluence. The changes observed in the values of current after ion implantation is due to the fact that the energy transferred from the incident ions to the polymer matrix results in the structural and chemical modifications. These modifications lead to the formation of carbon clusters with conjugated double and triple bonds. This is accompanied by the increased delocalization of charge carriers and hence leads to the formation of carbonaceous structure in the implanted specimens [37,74]. These carbonaceous clusters facilitate the flow of current and hence contribute towards the modification in the conductivity of implanted polymers. The possible conduction mechanism operating in the nitrogen implanted PP specimens can be studied using different conduction mechanisms.

To reveal the charge transport mechanism in virgin and implanted PP specimens, I–V data is plotted in the form $\ln(I)$ vs. $V^{1/2}$ (Fig. 3.124).
Fig. 3.124  Plot of ln (I) vs. V^{1/2} for (a) virgin and implanted PP specimens at 100 keV to (b) 1×10^{15}, (c) 1×10^{16}, and (d) 1×10^{17} N^+ cm^{-2}

Similar to the earlier cases of the present study, different conduction mechanisms have been used to describe the I-V characteristic measurements in the polymeric matrix. The experimental value of β i.e. β_{exp} for virgin and implanted PP specimens has been calculated using the equations (3.17) and (3.18) and are given in Table 3.24. The theoretical values of β for Schottky emission as well as for Poole-Frenkel emission are calculated by equations (3.19) and (3.20) and are also listed in Table 3.24.

Table 3.24 A comparison between the theoretical and experimental β coefficients of virgin and implanted PP specimens

<table>
<thead>
<tr>
<th>Ion Fluence (N^+ cm^{-2})</th>
<th>Theoretical values of conduction parameter</th>
<th>Experimental values of conduction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Schottky emission (β_{RS}) (eV⋅m^{1/2} V^{-1/2})</td>
<td>Poole Frenkel emission (β_{PF}) (eV⋅m^{1/2} V^{-1/2})</td>
</tr>
<tr>
<td>Virgin</td>
<td>2.68 × 10^{-5}</td>
<td>5.36 × 10^{-5}</td>
</tr>
<tr>
<td>1 × 10^{15}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 × 10^{16}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 × 10^{17}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It is clear from the table that, the experimental value ($\beta_{\text{exp}}$) for virgin PP has been found to be in good agreement with the theoretical value of $\beta_{\text{PF}}$. This leads to the conclusion that Poole–Frenkel mechanism is the dominating mechanism in case of the virgin PP specimen. However, after implantation, the values of $\beta_{\text{exp}}$ found to be close to the theoretical value of $\beta_{\text{RS}}$ leading to the conclusion that Schottky emission is the dominant charge transport mechanism operating in the nitrogen implanted PP specimens. The transition from Poole-Frenkel (for virgin PP) to Schottky emission (for implanted PP specimens) conduction mechanism may be due to the improvement in the conductivity of these specimens as a result of implantation [58,79-80]. This may be due to increase in the concentration of charge carriers with increase in ion fluence which results in the increase in the conductivity of the polymeric specimens. Moreover, Hopping mechanism has also contributed significantly towards the increase in the conductivity. The observed increase in the conductivity of the PP specimens also results from the hopping of charge carriers across the defect sites of the material.

Also for space charge linear conduction mechanism (SCLC) to occur, the slope of the I-V characteristic curve should be greater than or equal to 2, but in the present case the value of slope comes out to be less than 2 therefore, this conduction mechanism is ruled out [77].

Thus, it can be concluded that there are significant modifications in the surface properties of the polypropylene samples after nitrogen ion implantation. RBS measurements show that the structure and elemental composition of the virgin sample has been modified completely. Results yielded an increase in the concentration of carbon from 33 at.% to 42 at.% in implanted specimen in comparison to virgin specimen which indicate towards the formation of carbonization in implanted layers of PP specimens. The changes in surface morphology as well as structure have been confirmed by AFM and UV-Visible spectroscopy. The study of dielectric parameters results in the modifications in the values of dielectric constant, dielectric loss, dissipation factor. Also, the Cole-Cole analysis of virgin and implanted PP specimens indicates a deviation in the relaxation phenomena from the Debye relaxation phenomena. Moreover, the shapes of the Cole-Cole curves confirmed the structural disordering in implanted PP specimens. From I–V characteristic measurements, it has been observed that the Schottky emission is the dominant charge transport mechanism operating in implanted specimens. These
modifications in the specimens are due to the reason that ion beam treatment of polymers leads to the degradation of polymeric chains, cross-linking, creation of free radicals, molecular rearrangement which results in the formation of conjugated carbon-carbon double bonds and hence results in the carbonization of the surface layer with increasing ion fluence. This in turn induces structural disordering in the polymeric matrix [2,9,52,126]. Hence the results of different characterization techniques agree well with each other.

3.8 Comparison between the effects of argon ion implantation on CR-39, PC and PP polymers

The results of Ar⁺ implantation on various properties of CR-39, PC and PP polymers have been discussed in earlier sections: 3.2, 3.3 and 3.4 respectively. In order to analyze and understand the role of basic structure of CR-39, PC and PP polymers as an effect of 130 keV Ar⁺ implantation, a comparison has been made among the changes produced in different properties of these polymers.

The structural modifications and elemental composition in the specimens have been performed using RBS studies. RBS studies show an increment in the carbon concentration for all the Ar⁺ implanted specimens. It has been found that there is an increase in the concentration of carbon from 32 at.% (for virgin CR-39) to 51 at.% (at 1x10¹⁶ Ar⁺ cm⁻²). The carbon concentration increases from 48 at.% (virgin PC) to 74 at.% (at 1x10¹⁶ Ar⁺ cm⁻²). The enhancement in the concentration of carbon from 33 at.% (for virgin PP) to 46 at.% (at 1x10¹⁶ Ar⁺ cm⁻²) has been observed. This increase in the carbon composition indicates towards the formation of carbonaceous layer in the implanted specimens [3]. However, it has been observed that the calculated retained implanted dose and projected range was more accurate in case of implanted PP specimens.

XPS characterization has been carried out to examine the chemical states of various elements in the implanted specimens. It has been observed that the XPS spectra of C (1s), O (1s) and implanted Ar (2p) are all asymmetric [23]. The presence of one asymmetric peak at nearly 530 eV in Ar⁺ implanted PC and CR-39 specimens indicates the presence of oxygen in form of C=O bonds [24]. However, the asymmetric nature peak nearly centered at 283 eV of the C(1s) observed in the XPS spectra of Ar⁺ implanted PC and CR-39 specimens also suggests more than one bonding state of carbon present under this peak. This energy lies very close to the graphitic and amorphous carbon (C-C) states.
besides the C=C bond [23-24, 26]. Therefore, it also suggests the formation of a mixture of these three states during Ar\(^+\) ions implantation in PC and CR-39 matrix. The other bonding states would have been destroyed due to the emission of the hydrogen and oxygen gaseous molecules from the surface of these polymers during implantation. The XPS spectra of Ar\(^+\) implanted PC and CR-39 specimens clearly shows a weak peak present nearly at 243 eV of Ar(2p) indicating that the implanted argon may be sitting in isolated positions within the matrix or in small aggregates [25-27]. Therefore, the XPS analysis of all the implanted specimens point towards the formation of amorphous carbon containing graphitic structures in the near surface regions of PC and CR-39 as an effect of Ar\(^+\) ions implantation.

AFM studies show that the surface morphology of the specimens has been modified and the root mean square and average roughness values increase after implantation. It has been observed for pristine CR-39 samples, the root mean square roughness (R\(_{\text{rms}}\)) and average roughness values (R\(_{\text{av}}\)) were observed to be 8.34 nm and 5.57 nm respectively. These roughness values have been observed to be increased after implantation. At the fluence of 1x10\(^{16}\) Ar\(^+\) cm\(^{-2}\) the root mean square and average roughness values increase upto 19.12 nm and 12.56 nm respectively. The root mean square and average roughness values for virgin PC are 10.70 nm and 8.18 nm respectively. At the implantation dose of 1x10\(^{16}\) Ar\(^+\) cm\(^{-2}\), these values increase to 25.90 nm and 14.24 nm respectively. The calculated root mean square roughness (R\(_{\text{rms}}\)) and average roughness (R\(_{\text{av}}\)) values for virgin PP sample are 4.90 nm and 3.36 nm respectively. At the implantation dose of 1x10\(^{16}\) Ar\(^+\) cm\(^{-2}\), these values increases to 19.12 nm and 11.39 nm. Thus, it has been observed that there is more increase in the roughness values in the case of PC and PP specimens than that of CR-39.

UV-Visible Spectroscopy has been performed to analyze the existence of the absorption peaks; their shifts and broadening in PC, CR-39 and PP polymers as a result of ion implantation. It has been observed that there is an increase in the optical absorption in the all the specimens after Ar\(^+\) implantation. Also, there is a shift in the absorption edge with simultaneous flattening of edge for all the specimens. This increase in optical absorption and red shift of the absorption edge is due to the fact that as a result of implantation, the original bonds in the polymeric matrix got ruptured and leads to chain scission, cross linking, free radicals, and new bond formation etc. [34,61,115,117].
The visual examination of the specimens indicates that there is a change in the color of the CR-39, PC and PP specimens after Ar\textsuperscript{+} implantation. It has been observed that the color of the CR-39 and PC specimens changes from transparent (virgin) to dark brown (at fluence of 1x 10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}). However, in the PP specimens, there is a drastic change in the color after implantation. The color changes from transparent (virgin) to grayish black (at fluence of 1x 10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}). This color change in the specimens may be associated with the carbonisation taking place in the specimens as a result of implantation [8].

Dielectric spectroscopic studies revealed that there are variations in the values of dielectric constant. The dielectric constant decreases from 4.76 (for virgin CR-39) to 4.20 (at 1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}) at the low frequency value of 100 Hz. The dielectric constant value reduces from 2.48 (for virgin PC) to 2.12 at fluence of 1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}. The reduction in the dielectric constant value from 1.94 (for virgin PP) to 1.13 at fluence of 1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$} at 100 Hz was observed. Comparison shows that there is more reduction in the dielectric constant value in case of PP specimen as compared with PC and CR-39 polymer after Ar\textsuperscript{+} implantation.

The enhancement in the a.c. conductivity values for all the Ar\textsuperscript{+} implanted specimens has been observed. The a.c. conductivity value increases from -3.34 (for virgin CR-39) to -3.30 (at 1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}) at 30 MHz and from -2.31 (for virgin CR-39) to -2.18 (at 1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}) at 80 MHz for CR-39 specimens. For PC specimens, there is an increase in a.c. conductivity values from -3.83 (for virgin PC) to -3.75 (1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}) at 30 MHz and from -2.45 (for virgin PC) to -2.32 (1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}) at 80 MHz. The increase in the a.c. conductivity values from -3.94 (for virgin PP) to -3.39 (1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}) at 30 MHz and from -2.56 (for virgin PP) to -2.29 (1x10\textsuperscript{16} \text{Ar$^+$ cm$^{-2}$}) at 80 MHz has been observed. Comparison shows that there is more enhancement in the a.c. conductivity in case of PP specimen after Ar\textsuperscript{+} implantation.

Enhancement in the spreading factor value using Cole-Cole plot for all the Ar\textsuperscript{+} implanted specimens has also been observed. This indicates that there is a broad distribution of relaxation time and hence specimens exhibit polydispersive nature. This polydisperse nature indicates towards the disorderliness in the implanted specimens [53,58]. Moreover, It has been found that the increase in the value of spreading factor is more in case of PP specimens as compared to spreading factor values of PC and CR-39 specimens.
The reduction in the relaxation time has been observed for all the Ar\textsuperscript{+} implanted specimens. This indicates that with increasing implantation dose, disorderness in the polymeric matrix increases thereby decreasing the relaxation time. The average relaxation time decreases from 1.12 x 10\textsuperscript{-9} (for virgin CR-39) to 0.05 x 10\textsuperscript{-9} (at 1x10\textsuperscript{16} Ar\textsuperscript{+} cm\textsuperscript{-2}) for CR-39 specimen. The average relaxation time decreases from 2.20 x 10\textsuperscript{-9} (for virgin PC) to 0.15 x 10\textsuperscript{-9} at fluence of 1x10\textsuperscript{16} Ar\textsuperscript{+} cm\textsuperscript{-2}. There is reduction in the average relaxation time from 1.27 x 10\textsuperscript{-9} (for virgin PP) to 0.33 x 10\textsuperscript{-9} at fluence of 1x10\textsuperscript{16} Ar\textsuperscript{+} cm\textsuperscript{-2}. Comparison shows that there is more reduction in the average relaxation time in case of PC specimen as compared with PP and CR-39 polymer after Ar\textsuperscript{+} implantation.

The dielectric constant and dielectric loss in the frequency range of .42-.75 PHz corresponding to the visible region (400-700 nm) have also been studied using the data of optical absorption and reflection obtained from UV-Visible spectroscopy. It has been observed that the values of dielectric constant decrease whereas dielectric loss increases with increasing ion fluence for all Ar\textsuperscript{+} implanted specimens.

Current-Voltage measurements show an increase in the conductivity for all the Ar\textsuperscript{+} implanted specimens. It has also been found that, for virgin specimens, the experimental value (\(\beta_{\text{exp}}\)) has been found to be in good agreement with the theoretical value of Poole–Frenkel (\(\beta_{\text{PF}}\)). This leads to the conclusion that Poole–Frenkel mechanism is the dominating mechanism in case of the virgin specimen. However, after implantation, the values of \(\beta_{\text{exp}}\) was found to be close to the theoretical value of Schottky emission (\(\beta_{\text{sc}}\)) leading to the conclusion that Schottky emission is the dominant charge transport mechanism operating in all implanted specimens.

Thus, it can be concluded from the above discussion that there are more modifications in the surface characteristics and disordering in the structure in case of the PP and PC polymers than that of CR-39 polymer. These modifications may be correlated with the basic structure of the polymer as the polymers having the linear structure (PP and PC) proved to be more sensitive and got more affected by ion beams as compared with the polymer having the cross-linked structure (CR-39).
3.9 Comparison between the effects of nitrogen ion implantation on CR-39, PC and PP polymers

The results of N⁺ implantation on various properties of CR-39, PC and PP polymers have been discussed in earlier sections: 3.5, 3.6 and 3.7 respectively. To analyse and understand the role of basic structure of CR-39, PC and PP polymers as an effect of 100 keV N⁺ implantation, a comparison has been made among the changes produced in different properties of these polymers.

RBS studies has been performed to study the structural modifications and elemental composition in the specimens. The enhancement in the carbon concentration in all the specimens has been observed using RBS results. It has been found that there is an increase in the concentration of carbon from 32 at.% (for virgin CR-39) to 43 at.% (at 2x10¹⁶ N⁺ cm⁻²). The carbon concentration increases from 48 at.% (virgin PC) to 70 at.% at (1x10¹⁷ N⁺ cm⁻²). The enhancement in the concentration of carbon from 33 at.% (for virgin PP) to 42 at.% (at 1x10¹⁷ N⁺ cm⁻²) has been observed. RBS spectroscopic measurements confirm the formation of carbonization in the implanted layers of the specimens. Hence, the increase in the number of carbon atoms is responsible for the formation of carbonaceous network containing π-electron clouds in the implanted matrix [37,52]. Moreover, it has also been observed that the retained implanted dose and projected range was more accurate in case of implanted PP specimens.

XPS characterization was performed to do the elemental analysis in the N⁺ implanted PC and CR-39 specimens. The XPS spectra of N⁺ implanted PC and CR-39 specimens shows that the peaks of C(1s), O(1s) and implanted N(1s) are of asymmetric nature [23]. Thus, it is obvious from the XPS spectra that more than one bonding states are present under these peaks. The presence of one asymmetric peak at nearly 530 eV in all the implanted specimens indicates the presence of oxygen in form of C=O bonds in N⁺ implanted surfaces of PC and CR-39 [24]. The asymmetric nature spectra of the C(1s) peak nearly centered at 283 eV observed in the XPS spectra of N⁺ implanted specimens also suggests more than one bonding state of carbon present under this peak. This energy lies very close to the graphitic and amorphous carbon (C-C) states besides the C=C bond [23-24, 26]. Therefore, it also suggests the formation of a mixture of these three states during N⁺ ions implantation in CR-39 and PC matrix. The evolution of the gaseous molecules such as hydrogen and oxygen during implantation may have led to the scission
of other bonding states present on the surface of implanted polymers. Moreover the XPS spectra of N⁺ implanted PC and CR-39 specimens shows a weak and asymmetric peak nearly at 399 eV. This peak specifies the existence of most of the free state nitrogen [8,23] in N⁺ implanted PC and CR-39 specimens. Therefore, the XPS analysis of N⁺ implanted specimens also signifies the formation of amorphous carbon containing graphitic structures in the near surface regions of PC and CR-39 as an effect of N⁺ ions implantation.

AFM studies show that the surface morphology of the specimens has been modified and the rms and average roughness values increase after implantation. It has been observed for pristine CR-39 samples, the root mean square roughness (Rrms) and average roughness values (Rav) were observed to be 8.34 nm and 5.57 nm respectively. These roughness values have been observed to be increased after implantation. At the fluence of 1x10¹⁶ N⁺ cm⁻² the root mean square and average roughness values increase up to 13.67 nm and 10.92 nm respectively. The root mean square and average roughness values for virgin PC are 10.70 nm and 8.18 nm respectively. At the implantation dose of 1x10¹⁶ N⁺ cm⁻², these values increase to 16.41 nm and 12.76 nm respectively. The calculated root mean square roughness (Rrms) and average roughness (Rav) values for virgin PP sample are 4.90 nm and 3.36 nm respectively. At the implantation dose of 1x10¹⁶ N⁺ cm⁻², these values increase to 13.78 nm and 10.82 nm. Thus, it has been observed that there is more increase in the roughness values in the PP specimens.

The optical spectroscopy in the UV-Visible region has also been performed to analyze the existence of the peaks; their shifts and broadening as a result of ion implantation. An increase in optical absorption with a shift in the absorption edge with simultaneous flattening of edge for all N⁺ implanted specimens has been observed. These changes occurring in the optical absorption may be attributed to the chain scission, cross linking and formation of free radicals in implanted polymeric matrix [1,115,117] as an effect of N⁺ implantation.

A drastic change in the color of CR-39, PC and PP specimens has been obtained as a result of N⁺ implantation. The color of CR-39 and PC specimens transforms from transparent (virgin) to dark brown (at fluence of 1x 10¹⁶ N⁺ cm⁻²). However, in the PP specimens the color transforms from transparent (virgin) to grayish black (at fluence of 1x 10¹⁶ N⁺ cm⁻²). This color transformation may be correlated with the structural
modifications taking place inside the polymeric matrices as a result of N\(^+\) implantation [8,34].

It has been observed that there are variations in the values of dielectric constant as an effect of N\(^+\) implantation. The dielectric constant decreases from 4.76 (for virgin CR-39) to 4.28 (at highest fluence) at the low frequency of 100 Hz. The value of dielectric constant reduces from 2.48 (for virgin PC) to 2.13 at fluence of 1x10\(^{17}\) N\(^+\) cm\(^-2\) at 100 Hz. The dielectric constant reduces from 1.94 (for virgin PP) to 1.07 at fluence of 1x10\(^{17}\) N\(^+\) cm\(^-2\) at 100 Hz. Comparison shows that there is more reduction in the dielectric constant value in case of PP specimen after N\(^+\) implantation.

The enhancement in the a.c. conductivity values has also been observed for CR-39, PC and PP specimens as a result of nitrogen ion implantation. This increased conductivity of the specimens may be due to the formation of \(\pi\)-bonded carbon clusters in the implanted layers [34,58] which results in enhancement in conductivity of the implanted matrix. Moreover, it has been found that there is more enhancement in the a.c. conductivity in case of PP specimen as compared with PC and CR-39 polymers after N\(^+\) implantation.

The value of spreading factor using Cole-Cole plot has been found to be increased for all the N\(^+\) implanted specimens. Increase in the spreading factor indicates that there is a broad distribution of relaxation time in the specimens and hence they exhibit polydispersive nature [53,58]. This in turn points towards the disorderness in the implanted specimens. Moreover, the enhancement in the spreading factor value has been found to be more in case of PP specimens as compared to spreading factor values of PC and CR-39 specimens.

The reduction in the relaxation time has been observed for all the N\(^+\) implanted specimens. This indicates that with increasing implantation fluence, disorderness in the polymeric matrix increases thereby decreasing the relaxation time. The average relaxation time decreases from 1.12x10\(^{-9}\) (for virgin CR-39) to 0.07x10\(^{-9}\) (at 1x10\(^{16}\) N\(^+\) cm\(^-2\)) for CR-39 specimens. The average relaxation time decreases from 2.20x10\(^{-9}\) (for virgin PC) to 0.52x10\(^{-9}\) at fluence of 1x10\(^{16}\) N\(^+\) cm\(^-2\). There is reduction in the average relaxation time from 1.27x10\(^{-9}\) (for virgin PP) to 0.76x10\(^{-9}\) at fluence of 1x10\(^{16}\) N\(^+\) cm\(^-2\). Comparison shows that there is more reduction in the average relaxation time in case of PC specimen
as compared with PP and CR-39 polymer after N\(^+\) implantation. Moreover, the decrease in the values of relaxation time attribute towards the improvement in the conductivity.

The dielectric constant and dielectric loss of virgin and N\(^+\) implanted polymeric specimens have been studied in the frequency range of 0.42-0.75 PHz corresponding to the visible region (400-700 nm) using the absorption and reflection spectra recorded through UV-Visible spectroscopy. A decline in the value of dielectric constant and enhancement in the values of dielectric loss have been observed for all the polymeric specimens implanted with nitrogen ions.

I-V characteristics measurements show that the conductivity increases with increasing ion fluence in all the specimens. It has also been found that for virgin specimens the experimental value (\(\beta_{\text{exp}}\)) has been found to be in good agreement with the theoretical value of Poole–Frenkel (\(\beta_{\text{PF}}\)). This leads to the conclusion that Poole–Frenkel mechanism is the dominating mechanism in case of the virgin specimen. However, after implantation, the values of \(\beta_{\text{exp}}\) was found to be close to the theoretical value of for Schottky emission (\(\beta_{\text{RS}}\)) leading to the conclusion that Schottky emission is the dominant charge transport mechanism operating in all implanted specimens.

The above studies indicate that there are more alteration in the surface characteristics and properties of PP and PC polymers as compared with CR-39. These changes may be associated with the fundamental structure of the polymer as the polymers having the linear structure (PP and PC) have modified to greater extent by N\(^+\) ion beams as compared with the polymer having the cross-linked structure (CR-39).
References