CHAPTER IX

EFFECT OF IONIC RADIATION ON PMMA/PS AND PMMA/PVC BLEND FILMS
9.1 Introduction

The interaction of ionizing radiation with polymers leads to a wide variety of property changes [1]. They are the consequence of irreversible modifications of the structure and the chemical composition including processes such as radical formation, main chain scission, inter molecular cross-linking, creation of unsaturated bonds, and loss of volatile fragments. Different set of experimental data is already available on changes induced by not only lone ionizing radiation such as photons and electrons but also by ionizing particle beams on some important polymers [2 - 7]. However, the information on effects induced by energetic ions in polymer blends is meager. In the present study the author prepared the blend films of PMMA/PS and PMMA/PVC and irradiated them with a $^{28}$Si ion beam. The induced structural changes were analyzed using infrared spectroscopic technique. The author selected one miscible blend (PMMA/PVC) and one immiscible blend (PMMA/PS). As these polymer blends offer tailor made properties, the author carried out the work on these two types of blends. Though the author's main aim was to irradiate the films of the blends presented from Chapter -III to Chapter -VIII in the thesis, owing to the limited beam time available, only two blend films were irradiated.
9.2 Materials and Methods

9.2.1 Sample Preparation

PMMA/PS blend films of compositions 100/0; 75/25; 50/50; 25/75 and 0/100 wt % were prepared by film casting technique by mixing solutions of PMMA and PS (in common solvent) in the appropriate proportions. PMMA/PVC blend films of compositions 25/75; 50/50 and 75/25 wt % were prepared by film casting technique. The films were dried under vacuum at 65 °C for 10 hrs in order to ensure the removal of the solvent. The films of PMMA/PS (with thickness of 30 μm) were mounted on metal frames, which in turn were fixed to the metal ladder (sample holder) of the accelerator chamber.

9.2.2 Irradiation Technique

The blend films of PMMA/PS were irradiated with a $^{28}$Si ion beam of 60 MeV in the General Purpose Vacuum Chamber (GPSC) at Nuclear Science Centre, New Delhi. This chamber is described in Chapter- II of the thesis. The vacuum was maintained at $\equiv 3 \times 10^{-6}$ mbar. The current was maintained at 2pna equivalent to $1.2 \times 10^{10}$ ions/s. The dose was kept at about $3 \times 10^{11}$ ions/cm$^2$ for each set of the blend films.

The films of PMMA/PVC were irradiated with a $^{28}$Si ion beam of 120 MeV in the fluence range of $10^{11}$ to $10^{13}$ ions/cm$^2$ in the Material Science Vacuum Chamber at the Nuclear Science Centre, New Delhi. The vacuum was maintained at $\equiv 2.25 \times 10^{-6}$ Torr. The current was maintained at 4pna equivalent to $2.5 \times 10^{10}$ ions/s. A brief
description of the Material Science Vacuum Chamber is already presented in Chapter -II. The dose was kept at about $3 \times 10^{13}$ ions/cm$^2$ for each set of the blend films.

### 9.2.3 Characterization

The polymer blend films under study were characterized by the infrared spectroscopy, light transmission, and solubility tests before and after irradiation. The films in the metal frames were directly used as the samples. Care was taken to see that the samples were free from moisture.

The infrared spectra of the samples under study were recorded before and after irradiation using an FT-IR, Perkin Elmer Model 10 PC graphics double beam infrared spectrophotometer in the region of 4400-450 cm$^{-1}$. For the PMMA/PS blend films the percentage of light transmitted through them was measured using a spectrophotometer at wavelength of 490 nm. For these films (PMMA/PS) the solubility was tested before and after irradiation by keeping them in fixed quantity of common solvent (toluene) for 24 hrs and un-dissolved part if any, was removed, dried, and weighed.

### 9.3 Results and Discussion

#### 9.3.1 PMMA/PS Blend

The percent transmission ($T$) of light at 490 nm through the polymer blend films before and after irradiation is presented in Table 9.1. The variation of $(\Delta T/T)^1$ with the blend composition ($\Delta T$ being the difference of the transmission of light through the
Table 9.1. Percent transmission of light (490nm) through PMMA/PS blend film before and after irradiation with a $^{28}$Si ion beam

<table>
<thead>
<tr>
<th>Blend Composition PMMA/PS (%)</th>
<th>Transmission of light (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before irradiation</td>
</tr>
<tr>
<td>100/0</td>
<td>90</td>
</tr>
<tr>
<td>75/25</td>
<td>48</td>
</tr>
<tr>
<td>50/50</td>
<td>34</td>
</tr>
<tr>
<td>25/75</td>
<td>23</td>
</tr>
<tr>
<td>0/100</td>
<td>88</td>
</tr>
</tbody>
</table>
samples after and before irradiation) is shown in Fig.9.1. From the figure it is evident that 
\((\Delta T/T)^1\) increased and reached a maximum at 25% of PS and then decreased. From 
Table 9.1 it is observed that on ion irradiation the light transmission increased for all the 
compositions except for PS. In fact it decreased slightly for PS on irradiation. This is 
understandable as cross-linking takes place in PS on irradiation [5]. The variation of 
\((1-T)\)% with the blend composition is presented in Fig.9.2. From this absorption of light 
curve, it is evident that when the PS content is 75% \((1-T)\)% is maximum, indicating the 
formation of maximum cross-linking. It is also observed that as the PMMA content 
increased in the blend composition the percentage transmission also increased on 
irradiation. This is in accordance with the expectation that PMMA undergoes scission [5] 
on irradiation, and as a result its density comes down. This trend is observed during other 
times of irradiation also. Further, the solubility test of the blend films in toluene was 
carried out before and after irradiation. It was observed that both PMMA and PS got 
dissolved readily in toluene before irradiation. But the irradiated sample of PS formed a 
gel in toluene whereas the irradiated PMMA dissolved quickly. This observation 
indicates that PS which is cross-linked on irradiation formed a three dimensional net 
work whose solubility is negligible and at the same time PMMA in which chain scissions 
were taking place readily dissolved. For other compositions, it was observed that the 
amount of gel formed was proportional to the PS content.

The IR spectra of the PMMA/PS (50/50) blend film before and after irradiation is 
presented in Fig.9.3. This reveals the characteristic peaks of both PMMA and PS. The 
peaks at 2999 and 2923 cm\(^{-1}\) belong to the CH\(_3\) group of both PMMA and PS. The peak
Fig. 9.1 Variation of $\Delta T/T$ % of PS/PMMA with composition of PS
Fig. 9.2 Variation of (1-T) % of PS/PMMA with composition of PS
Fig. 9.3 The IR spectra of PMMA/PS blend (50:50) films before (A) and after (B) irradiation with a $^{28}$Si ion beam.
at 2853 cm$^{-1}$ belongs to the CH stretching band of tertiary hydrogen atom of PS, 1729 cm$^{-1}$ to the ester group of PMMA; 1600 cm$^{-1}$ to the aromatic ring of PS; 1492 and 1450 cm$^{-1}$ to the CH$_2$ group of both PMMA and PS; 1240 and 1152 cm$^{-1}$ to C-C-O of PMMA; 1029 cm$^{-1}$ to the in-plane deformation of vibration of the ring in PS, and 751, 698 and 542 cm$^{-1}$ to the aromatic cycles of PS.

On irradiation, the intensity of all the characteristic bands was found to decrease. The decrease in the intensity of the peak at 1729 cm$^{-1}$ (ester group) indicates the degradation of PMMA moiety in the blend. Some additional bands were observed between 1600 and 1700 cm$^{-1}$ after irradiation of the sample, indicating the introduction of some unsaturated linkages in the sample. This also indicates the loss of ester pendant groups. The decrease in the intensity in the case of PS was found to be less when compared to that in the case of PMMA on irradiation, thereby indicating that PS remains intact whereas PMMA undergoes degradation. Further, the shift of the bands corresponding to PS towards a slightly lower frequency indicates the cross-linking on irradiation. The possible site for such cross-linking exists in the form of a a-carbon atom to which the phenyl group is attached, and the removal of a hydrogen atom facilitates the cross-linking at this site.

It was also observed that before and after irradiation the spectra showed the characteristic bands of the individual polymers (PMMA and PS) in the blend without any interaction. This indicates that the blend of PMMA and PS is immiscible
(incompatible). This confirms a similar observation made using ultrasonic velocity and viscosity measurements [8].

9.3.2 PMMA/PVC Blend

The author already studied the miscibility of the PMMA/PVC blend in solution by viscometric, ultrasonic, density, and refractometric methods. Basing on these studies the blend of PMMA/PVC was found to be miscible. These results are in Chapter-III of the thesis. The infrared spectra of the pristine and irradiated samples are presented for different compositions of the band in Figs. 9.4, 9.5, and 9.6. The intensity of the bands in the region of the 600-700 cm\(^{-1}\) corresponding to C-Cl stretching and C-Cl bond trans to CH bond (trans-gauche sequence) increased as per the content of PVC in the blend. However, the intensity of the band at 1740 cm\(^{-1}\) which is assigned to C=O stretching (ester group) of the PMMA in the blend did not vary much with the PMMA content. This may be due to the presence of plasticizer ester (Dioctyl phthalate) in the PVC as both PMMA and PVC taken are commercial samples. The intensity of the band at 1448 cm\(^{-1}\) (attributed to CH\(_2\) symmetric bonding) is also invariant with the variation of either the PMMA or PVC content in the blend. This is understandable as both PMMA and PVC have the same number of CH\(_2\) groups in their repeating unit, and as a result CH\(_2\) almost remains constant in the blends of these polymers for any composition. The peak positions and corresponding assignments are presented in Table 9.2. These spectra of the irradiated samples of the different compositions are discussed in the following sections.
Fig. 9.4 The IR spectra of PMMA/PVC blend (25:75) films before and after irradiation with a $^{28}$Si ion beam
Fig. 9.5 The IR spectra of PMMA/PVC blend (50:50) films before and after irradiation with a $^{28}$Si ion beam.
Fig. 9.6 The IR spectra of PMMA/PVC blend (75:25) films before and after irradiation with a $^{28}$Si ion beam.
Table 9.2. The characteristic peaks of PVC and PMMA in the blend of PMMA/PVC

<table>
<thead>
<tr>
<th>Peak position (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>CH₂ stretching vibrations</td>
</tr>
<tr>
<td>1740</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1470</td>
<td>CH₂ symmetric bending</td>
</tr>
<tr>
<td>1380</td>
<td>CH₂ asymmetric bending</td>
</tr>
<tr>
<td>1260,1150</td>
<td>C-O-C stretching</td>
</tr>
<tr>
<td>PVC</td>
<td></td>
</tr>
<tr>
<td>600-700</td>
<td>C-Cl stretching</td>
</tr>
<tr>
<td>603</td>
<td>C-Cl bond trans to C-H bond</td>
</tr>
<tr>
<td>605</td>
<td>Trans - gauche sequence</td>
</tr>
</tbody>
</table>
9.3.2.1 PMMA/PVC (25:75) Blend

In the spectra of the PMMA/PVC blend (25:75) for both pristine and irradiated samples (Fig. 9.4). The area of the bands in the 600-700 cm⁻¹ region decreases with fluence, indicating the abstraction of Cl and H and as a result possibly HCl gas evolves. The lowering of the area is more pronounced in the present case when compared to the other two compositions of the blends. The higher content of PVC in the blend may be the reason for this. The mechanism of HCl evolution from the PVC component of the blend on irradiation is presented below:

\[
\begin{align*}
\sim CH_2 - CH - ( -CH_2 - CH & \to )_n - CH_2 - CH - \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\downarrow & \quad \text{Electronic excitation} \\
\sim CH_2 - CH - ( -CH_2 - CH & \to )_n - CH_2 - H^\bullet + Cl^\bullet \\
\text{Cl} & \quad \text{Cl} \\
\downarrow & \quad \text{Electronic excitation} \\
\sim CH_2 - CH - ( -CH_2 - CH & \to )_n - CH = CH - + H^\bullet \\
\text{Cl} & \quad \text{Cl} \\
\downarrow & \quad \text{Electronic excitation} \\
H^\bullet + Cl^\bullet & \rightarrow \text{HCl}
\end{align*}
\]
The intensity of the bands around 3000 cm\(^{-1}\) decreased with fluence, indicating the cleavage of either CH\(_2\) or CH\(_3\) or both. Here there was no possibility of main chain scission for PVC as PVC cross-links. So the other possibility is either main chain scission of PMMA (as a result CH\(_2\) evolves) or its side chain scission (as a result CH\(_3\) or CH\(_4\) evolves) or both. The main chain scission can be confirmed by determining the molecular weight. But as the size of the irradiated portion of the samples was very small, it could not be undertaken. However, if we compare the spectra of unirradiated and irradiated samples of this composition, the intensity of the band at 1434 cm\(^{-1}\) (CH\(_2\) symmetric) is found to decrease with fluence indicating the elimination of some of CH\(_2\) groups. If side chain scissioning takes place, the gas evolution of H\(_2\), CO, CO\(_2\) and CH\(_4\) is possible [9]. If we compare the spectra of the blends of this composition for different fluence, the area of the band at 1732 cm\(^{-1}\) decreased with fluence, indicating the elimination of some of CO groups from the side chain of PMMA.
The possible side chain degradation of PMMA is presented below:

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\sim \text{CH}_2 - \text{C} - (\sim \text{CH}_2 - \text{C} \sim)_n \text{CH}_2 - \text{C} - \\
\text{C} = \text{O} \quad \text{C} = \text{O} \quad \text{C} = \text{O} \\
\text{OCH}_3 \quad \text{OCH}_3 \quad \text{OCH}_3
\]

\[\downarrow \text{Electronic excitation}\]

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \\
\sim \text{CH}_2 - \text{C} - (\sim \text{CH}_2 - \text{C} \sim)_n \text{CH}_2 - \cdot \text{C} - + \cdot \text{C} - \text{OCH}_3 \\
\text{C} = \text{O} \quad \text{C} = \text{O} \\
\text{OCH}_3 \quad \text{OCH}_3
\]

\[\downarrow \text{Electronic excitation}\]

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\sim \text{CH}_2 - \text{C} - (\sim \text{CH}_2 - \text{C} \sim)_n \text{CH} = \text{C} - + \text{H}^* \\
\text{C} = \text{O} \quad \text{C} = \text{O} \\
\text{OCH}_3 \quad \text{OCH}_3
\]

\[\downarrow \text{Electronic excitation}\]

\[
\text{O} \\
\cdot \text{C} - \text{OCH}_3 + \text{H}^* \rightarrow \text{H} - \text{C} - \text{O} - \text{CH}_3 \\
\text{Methyl formate}
\]
But as the samples are commercial in nature, the elimination of CO is also possible from the plasticizer of PVC.

9.3.2.2 PMMA/PVC (50:50) Blend

The intensity of bands of the blend of 50:50 composition before and after irradiation (Fig. 9.5) in the region of 600 – 700 cm\(^{-1}\) decreased, indicating the abstraction of HCl (area under the curve). The intensity decreased with fluence. The intensity of the band at 1727 cm\(^{-1}\) (attributed to the C=O of PMMA and also plasticizer of PVC) decreased over that of the pristine for \(10^{11}\) and \(10^{12}\) fluence. But for the fluence of \(10^{13}\) ions/cm\(^2\) the intensity increased, indicating the increase in the CO content (for higher fluence). This is possible only when C=O is formed at the site of hydrogen or chlorine abstraction due to the presence of trace oxygen in the chamber. The author in the case of the PS/PMMA blend also made similar observation.

9.3.2.3 PMMA/PVC (75:25) Blend

For the blend with 75:25 composition, the bands in the 600-700 cm\(^{-1}\) showed a decrease in the area (Fig. 9.6) indicating the abstraction of hydrogen and chlorine and as a result HCl evolves. The spectrum for the blend film of this composition exposed to \(10^{12}\) ions/cm\(^2\) could not be recorded as the sample got damaged in handling. For the fluence of \(10^{13}\) ions/cm\(^2\), the area slightly decreased. But the decrease in the area of these bands
was not as significant as in the case of 50:50 blend. This might have been due to the lower content of PVC here.

The bands at 1732 cm\(^{-1}\) did not show any significant change for fluence of 5\times10^{11} \text{ ions/cm}^2. However, it slightly got shifted to 1728 cm\(^{-1}\) at 1\times10^{13} \text{ cm}^2 with a decrease in the area (the spectrum is drawn for lower scale of % transmission). Here it may be attributed to the loss of C=O groups in the side chains of PMMA in the blend. But in the 50:50 blend such a thing was not observed. This might be due to the lower amount of PMMA in the 50:50 blend than in the present blend.

### 9.4 Conclusions

The transmission of light through the polymer blend films increased on irradiation by a \(^{28}\text{Si}\) ion beam, which may be attributed to the chain scission of PMMA. This was supported by solubility tests. The infrared spectra of the PMMA/PS blend after irradiation showed that PMMA was degraded whereas PS cross-linked.

The infrared spectra of PMMA/PVC showed some structural changes on irradiation by a \(^{28}\text{Si}\) ion beam of 5\times10^{11}, 5\times10^{12} and 1\times10^{13} \text{ ions/cm}^2. Abstraction of hydrogen, chlorine, C=O, CH\(_2\) and CH\(_3\) were indicated. Basing on this the possible mechanism of chemical modification is proposed. The abstraction of HCl increased with fluence in all the blends (PMMA/PVC).
As the infrared studies indicated controlled degradation of PMMA in the blend, the irradiated films can be utilized for the formation of ionic tracks by suitable chemical etching.
References


