CHAPTER - 7

Microstructural Studies on FeCl₃ and Chalcone doped PVA/PVP blend
7.1 Introduction

The chapters 3, 4, 5 and 6 dealt with the investigation of microstructural changes induced by 8MeV electron beam irradiation on pure Poly(vinyl alcohol) (PVA) and monovalent, divalent and trivalent salts (KCl and BaCl₂ and FeCl₃) doped PVA respectively. In this chapter, the author has undertaken the work on blending of PVA with one of the commercially important miscible polymer Poly(vinylpyrrolidone) (PVP) and investigating the microstructural changes on doping the blend with trivalent transition metal chloride (FeCl₃). In addition, an organic Non-linear optical (NLO) active chromophore 1-(4-methyl phenyl)-3-(4-N, N, dimethyl amino phenyl)-2-propen-1-one (MPDMAPP) has been prepared and doped with PVA/PVP blend for different concentrations. The microstructural changes due to doping have been investigated.

It is known that the blending of different polymers or inorganic compounds with polymers represents a strategic route to improve the performance of a material. This tailoring of the macroscopic properties by the process of polymer blending is the result of modifying the composite structure at the microscopic scale. As seen from other chapters, the polymer PVA has the carbon chain backbone with hydroxyl groups attached to methane carbons. These -OH groups can be a source of hydrogen bonding and hence assist in the formation of polymer blends. PVP is another important synthetic polymer which has a wide variety of applications in the biomedical field because of its properties including adhesion, excellent physiological compatibility, low toxicity, and reasonable solubility in water and in most organic solvents. Furthermore, PVP has been investigated in blends with, cellulose and polymethacrylates where hydroxyl-bonding appears to be a major factor in inducing miscibility. In view of this, PVA and PVP are perfectly compatible and miscible polymers via the hydrogen bond interactions between the –CO groups of PVP and –OH groups in PVA, in the amorphous zones of the blends.

From various studies it is known that, in ferric chloride doped polymers, the interaction between dopant and polymer is complex in nature and it takes...
place via acceptor–donor mechanism (each Fe ion receives an electron from the polymer matrix). This is mainly because of the fact that the ferric chloride contains high spin trivalent metal ion and a half filled $d$-sub shell is having a stabilizing effect on the electron density. Hence doping a polymer with FeCl$_3$ is expected to alter the properties of that polymer via charge transfer reaction process. The author has selected this transition metal halide as the dopant and doped in to the polymer blend. Here in blend preparation a widely accepted method is used for preparing materials with well-controlled morphological and microstructural properties.

In addition, the blend of PVA and PVP is also been doped with organic Non-linear optical (NLO) active chromophore 1-(4-methylphenyl)-3-(4-N, N, dimethyl amino phenyl)-2-propen-1-one (MPDMAPP). When this NLO compound is doped to PVA and it is also expected to form complex with the polymer. It has been demonstrated that the blends doped with various metal salts forms complex system and microstructural modifications are mainly attributed to the presence of lone pair electrons on the side chain of polymer blends where metal salts are solvated [4]. In such a complex system, it is very interesting to know the positron behavior. In the present study, an attempt is made to understand the effect of FeCl$_3$ and MPDMAPP doping on the microstructure of PVA+PVP polymer blend and positron behaviour using different techniques explained in chapter 2.

7.2 Microstructural Studies on FeCl$_3$ doped PVA/PVP blend

7.2.1 FTIR Studies

The FTIR spectra of the pure PVP, pure PVA, pure and FeCl$_3$ doped PVA/PVP blend with different concentrations of 2.5, 5 and 10 wt% are shown in the Figure 7.1.

The IR spectrum of the pure PVA has been shown in Figure 7.1, for which the peak assignments are similar to the assignments in chapter 3. For the polymer PVP, the peak assignments of IR spectrum are assigned as follows: The peak at 3432 cm$^{-1}$ is attributed to O—H stretching of hydroxyl groups, 2924
cm\(^{-1}\) to C–H asymmetric stretching vibration and 2862 cm\(^{-1}\) to C–H symmetric stretching vibration [1,2]. The other characteristic peaks are observed at 1660 cm\(^{-1}\) represents the acetyle C=O stretching vibrations, 1496 cm\(^{-1}\) represents the O–H and C–H bending and 1372 cm\(^{-1}\) represents the C–H symmetric stretching respectively. The peak at 1081 cm\(^{-1}\) corresponds to C–H as well as C–O stretching and O–H bending. The peaks at 647 cm\(^{-1}\) and 470 cm\(^{-1}\) are assigned to ferrous Fe–O stretching bands.

Figure 7.1: FTIR spectra of pure PVP, PVA, PVA/PVP blend and blend doped with different concentrations of FeCl\(_3\).

The IR spectrum of the pure PVA+PVP blend has been shown in Figure 7.1, for which the peak assignments are as follows. The observed characteristic
IR peaks at 3445 cm\(^{-1}\) is attributed to O–H stretching of hydroxyl groups, 2922 cm\(^{-1}\) to C–H asymmetric stretching vibration, 2851 cm\(^{-1}\) to C–H symmetric stretching vibration, 1470 cm\(^{-1}\) to O–H and C–H bending, and 1085 cm\(^{-1}\) to O–H bending and also C–O stretching of acetyl group present on the PVA backbone. The faint absorption peaks corresponding to C=C stretching vibrations occur around 1652 cm\(^{-1}\) and acetylene C=O stretching vibrations around 1742 cm\(^{-1}\). The peak at 1559 cm\(^{-1}\) assigned to C=C stretching (aromatic) and C–N stretching. which was not present in PVA [1, 2].

Table 7.1: FTIR spectral assignments of pure PVA, PVP, PVA+PVP blend and PVA+PVP doped with FeCl\(_3\)

<table>
<thead>
<tr>
<th>Wavenumbers (cm(^{-1}))</th>
<th>(\text{Peak Assignments})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PVA</strong></td>
<td><strong>PVP</strong></td>
</tr>
<tr>
<td>3425</td>
<td>3432</td>
</tr>
<tr>
<td>2928</td>
<td>2924</td>
</tr>
<tr>
<td>2853</td>
<td>2862</td>
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<tr>
<td>1640</td>
<td>1660</td>
</tr>
<tr>
<td>----</td>
<td>1565</td>
</tr>
<tr>
<td>1432</td>
<td>1496</td>
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<tr>
<td>1382</td>
<td>1372</td>
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<tr>
<td>----</td>
<td>1285</td>
</tr>
<tr>
<td>1089</td>
<td>1081</td>
</tr>
<tr>
<td>794</td>
<td>647</td>
</tr>
<tr>
<td>472</td>
<td>470</td>
</tr>
</tbody>
</table>

After doping the blend with FeCl\(_3\) for different concentrations, the resulting FTIR spectra show shift in the peaks and change in the intensity of peaks. This data shows that the stretching frequency of O–H group at 3425 cm\(^{-1}\) has got shifted to 3445 cm\(^{-1}\) with variation in intensity. The intensity of C=O
(PVP) stretching frequency at 1660 cm\(^{-1}\) increases with increase in FeCl\(_3\) doped blend. These changes in the IR spectra are understood using inter/intra molecular interaction between polymer blend PVA/PVP and the dopant. The dopant FeCl\(_3\) may be considered as an efficient electron acceptor. In other words, it forms charge transfer complex with blend through OH/C=O groups via inter/intra molecular hydrogen bonding [2, 3].

These formed complexe acts as cross-links for PVA/PVP chains making the doped films insoluble in water. Accordingly in the present case PVA/PVP/FeCl\(_3\) polymer films are casted with water and in this aqueous medium the Fe\(^{3+}\) is expected to interact strongly with –OH/C=O groups of blend. Because of the relatively high electropositivity of the Fe\(^{3+}\) ions the extensive dissociation of Cl\(^-\) ions takes place within the solvent. As the PVA/PVP blend contains electron donor –OH and carbonyl oxygen in the side chain, they form stable complex with the Fe\(^{3+}\) ions. This interaction involves both inter and intra molecular type and this complexation cross-links the polymer chains. Thus most of the ferric ions are acting as cross-linking agents, which increase the stiffness of the composite and make it to be insoluble in water.

These interactions and complex formation of PVA/PVP blend with FeCl\(_3\) are reflected in the band intensities and wavenumbers in the FTIR spectra of doped blend (Figure 7.1). The observed fluctuation in intensity with wave number shift of Fe–O stretching bands at 460 cm\(^{-1}\) for FeCl\(_3\) doped PVA/PVP suggesting that the interaction of Fe\(^{3+}\) with blend. Hence, the main stretching frequency of -OH group at 3425 cm\(^{-1}\) has been shifted towards higher wavenumber side to 3445 cm\(^{-1}\) with a variation in intensity. Due to these interactions the affected band is the stretching frequency of carbonyl group C=O whose intensity increases after doping. This suggests that, the interaction and complex formation decreases the number of C=O groups within the doped blend, as C=O attached to the Ferric ions (Fe\(^{3+}\)) leads to crosslinking reaction [2, 3]. In other words, there are no other carbonyl groups of PVA left for
providing further chemical cross-linking for higher doping level. This complex formation also affects the other stretching, wagging, bending, skeletal, out of plane, in-plane vibrations like the stretching frequencies of acetylene C–O group present in the blend around 1085 cm\(^{-1}\), C–H in-plane bending frequency at 1470 cm\(^{-1}\) and the bending frequency at 1382 cm\(^{-1}\) of O–H. Hence the complex formation due to doping of FeCl\(_3\) modifies the microstructural properties of the blend PVA/PVP [4].

7.2.2 UV - Visible Studies

The UV-Vis optical absorption spectra of pure PVA+PVP blend and doped with FeCl\(_3\) with 0.5, 2.5, 5, 7.5 and 10 wt% concentrations are shown in the Figure 7.2. For the pure PVA+PVP blend, we observe two absorption bands at 207-230 nm, 255-285 nm and small hump at 375-505 nm due to carbonyl group containing segments. These are assigned to localized \(n\rightarrow\pi^*\), \(n\rightarrow\pi^*\) inter band and \(\pi\rightarrow\pi^*\) transitions respectively. These transitions in the polymeric material arise due to the charge transfer groups [1].

![Figure 7.2: UV-Visible absorption spectra of pure and FeCl\(_3\) doped PVA/PVP blend.](image)

After the doping of FeCl\(_3\) to the PVA/PVP blend it is observed drastic changes in the optical behaviour of the blend. Here the position of the
maximum absorption is found to be shifted from 250nm to 375nm as the concentration of the dopant is increased to 10wt%. On the basis of these observations, it may be concluded that the optical absorption increases with increase of doping concentration. The above observations can be explained as follows: It has been demonstrated that the polymer blends doped with various metal salts forms complex system. The microstructural modifications within the blend due to doping are mainly attributed to the presence of lone pair electrons on the side chain of polymer blends. The dopant FeCl$_3$ may be forms charge transfer complex with blend through OH/C=O groups via inter/intra molecular hydrogen bonding. The optical behaviour of the blend matrix may also be attributed to the change of the mode of chelation of the dopant FeCl$_3$ dopant with in the PVA/PVP blend. As the FeCl$_3$ doping concentration is increases the number of charged species due to Fe$^{3+}$ ions interactions with –OH/C=O groups of PVA/PVP blend (via inter/intra molecular interaction) increases and hence the crosslinking density [5,1]. This increase in complex formation in turn enhances the defect level. Thus most of the ferric ions are acting as cross-linking agents in the blend.

Table 7.2: Optical absorption maximum wavelength, peak assignments, band edges and optical band gap energies of pure and FeCl$_3$ doped PVA/PVP blend.

<table>
<thead>
<tr>
<th>FeCl$_3$ concentration (wt%)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Peak Assignment</th>
<th>$\lambda_{\text{edg}}$ (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>207-230</td>
<td>$n\rightarrow\pi^*$</td>
<td>294</td>
<td>4.25</td>
</tr>
<tr>
<td></td>
<td>255-295</td>
<td>$n\rightarrow\pi^*$</td>
<td>293</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>360</td>
<td>$\pi\rightarrow\pi^*$</td>
<td>422</td>
<td>2.75</td>
</tr>
<tr>
<td>2.5</td>
<td>360</td>
<td>$\pi\rightarrow\pi^*$</td>
<td>440</td>
<td>2.62</td>
</tr>
<tr>
<td>5</td>
<td>352</td>
<td>$\pi\rightarrow\pi^*$</td>
<td>446</td>
<td>2.56</td>
</tr>
<tr>
<td>7.5</td>
<td>345</td>
<td>$\pi\rightarrow\pi^*$</td>
<td>448</td>
<td>2.52</td>
</tr>
<tr>
<td>10</td>
<td>362</td>
<td>$\pi\rightarrow\pi^*$</td>
<td>461</td>
<td>2.35</td>
</tr>
</tbody>
</table>
7.2.3 Optical energy band gap

Using the observed UV-Vis spectra, the optical energy band gap $E_g$ is determined for the FeCl$_3$ doped blend by translating the spectra into Tauc’s plots (Figure 7.3) (using equation 1.4), which is explained in chapter 1.

![Figure 7.3: The dependence of $(\alpha h \nu)^{1/2}$ on photon energy ($h\nu$) for pure and FeCl$_3$ doped PVA/PVP for various concentrations.](image)

The calculated $E_g$ for pure and FeCl$_3$ doped PVA/PVP blend for different concentration are presented in the Table 7.2. The variation of optical energy gap as a function of dopant concentration is given in Figure 7.4. The estimated optical band gap of pure FeCl$_3$ doped PVA/PVP blend is 4.25 eV and as the dopant concentration is increases, this value decreases and reaches to 2.35eV for the dopant concentration of 10 wt%. The variation of optical energy gap $E_g$ may be explained by invoking the presence of complex moieties which affects the molecular environment around the blend. That means to say that the presence of dopant perturb original band structure of PVA/PVP blend by creating new molecular dipoles, which could be a result of point defects created within the band gap [1,2].
7.2.4 X-ray Diffraction Studies

The X-ray diffraction pattern of the pure PVA, pure PVP, PVA/PVP blend and FeCl$_3$ doped PVA/PVP blend with different concentrations of 2.5, 5 and 10 wt% are shown in the Figure 7.5. Similar to earlier chapters the XRD pattern of pure PVA has a broad peak at 2$\theta$ =21° indicates the semi crystalline behavior of the polymer corresponding to the orthorhombic lattice structure. The XRD pattern of PVP has peaks at 11.73° and 22.2° indicates the amorphous behavior.

The XRD pattern of pure PVA/PVP blend shows a broad amorphous region centered at 2$\theta$=20.2° with d=4.3982Å. As the concentration of the dopant increases, the spectrum peak is broadened along with a significant decrease in its intensity. These observed changes indicate that the distribution of the dopant FeCl$_3$ in the polymer blend matrix became random and the amorphous nature of the film increases with dopant concentration. This behaviour may be attributed to the change of the mode of chelation of the FeCl$_3$
dopant within the PVA/PVP blend. These modified chelation leads to a formation of complex via inter/intra molecular interaction resulting into a crosslinking network within the blend chains. This crosslinking network helps in structural repositioning of the blend segments as a result the amorphous nature increases [1,4].

Figure 7.5: Wide angle X-ray diffractogram of pure PVA, pure PVP and pure and FeCl₃ doped PVA/PVP blend with various concentrations.

Here the presence of dopant, more space should be provided for its entering into the layered structures. Correspondingly, the rotation of the polymeric backbone about its chain axis occurs and resulted into a conformational change. These change resulting in dramatic variations in the interlayer spacing within the semicrystalline regions of the polymer [3, 4]. At
the same time the interaction between neighboring main chains should become strong, resulting in the decrease in the spacing between the adjacent side-chains. It is known that the dopant ions within the amorphous structure lies between the chains and the neighboring C=O group [4]. In this way the formed complex via inter/intra molecular interaction results into crosslinking network within the blend chain segments (here the chain segments become more rigid) as a result the amorphous nature increases.

7.2.5 Positron Annihilation Lifetime Studies

The positron lifetime spectra were measured using the spectrometer explained in chapter 2 and measured spectra were resolved into three components. Figure 7.6 shows the variation of intensities $I_1$, $I_2$ and lifetime $\tau_2$ as a function of FeCl₃ doping concentration in PVA/PVP blend. It shows that the first component (p-Ps) intensity $I_1$ and lifetime (trapped positron) of intermediate component $\tau_2$ decreases and intensity $I_2$ increases with doping concentration. The decrease in $I_1$, $\tau_2$ and increase in $I_2$ with increase in FeCl₃ dopant concentration indicates an increase in number of trapped positron annihilation at the defect sites within the polymer matrix as well as decrease in the positronium formation probability.

Figure 7.7 depicts the variation of o-Ps lifetime $\tau_3$ and intensity $I_3$ as a function of FeCl₃ doping level in the PVA/PVP blend. It is observed that the o-Ps lifetime ($\tau_3$) decreases from 1.61 to 0.92 ns and its intensity $I_3$ decreases from 18.83 % to 5.25 % with doping level. The observed positron parameters in this complex system cannot be useful to understand the free volume related microstructure study but corresponding variation of $\tau_3$ and $I_3$ may be understood based on the spur model [5, 6] as explained in Chapter 1.
According to this model, the Ps formation in polymers is described as a reaction between the thermalized positron and one of the excess electrons.
created in the terminal positron spur, when the positron loses its last part of kinetic energy during thermalization ($e^+ + e^- \rightarrow Ps$).

In order to understand this behaviour further, $I_3$ is phenomenologically fitted with the inhibition relation for different dopant concentrations $C$ (FeCl$_3$) and is given by $I_3(C) = I_3(0)/ (1+\alpha C)$, where $I_3(0)$ is the o-Ps intensity at additive concentration $C=0$, $\alpha$ is the inhibition constant = 0.27809 Mol$^{-1}$ and is obtained from the slope of the linear fitting of the above equation (Figure 7.8). This linear ($I_3(0)/I_3(C)$ v/s FeCl$_3$) behaviour confirms the strong inhibition characteristics of FeCl$_3$ for the Ps formation within the composite film [5-7].

![Figure 7.8: Variation of $I_3(0)/I_3(C)$ verses FeCl$_3$ doping concentrations level in the PVA/PVP blend.](image)

Besides the inhibition process explained above, the quenching of Ps due to FeCl$_3$ or Fe$^{3+}$ ions could also be observed on account of spin conversion process. FeCl$_3$ being a metal salt possesses paramagnetic properties and the Fe$^{3+}$ ion is a high spin ion with half filled d-sub shell and is expected to affect the Ps formation to a greater extent [6]. However, it is known that the Fe$^{3+}$ interaction with Ps promotes oxidation reaction which leads to the quenching of Ps in the polymer matrix [6-8]. In order to understand the Ps reaction behaviour, the o-Ps reaction rate is expressed using the equation, $\lambda_3 = \lambda_3^0 + kC$ where $\lambda_3$ and $\lambda_3^0$ are the o-Ps annihilation rates at concentration $C$ of the dopant.
and in pure matrix respectively and \( k \) is the reaction rate constant. The value \( k \) is the slope of the \( \lambda_3 \) (=1/\( \tau_3 \)) v/s concentration (C) as shown in Figure 7.9.

**Figure 7.9:** Variation of \( 1/\tau_3 \) as a function of FeCl\(_3\) doping level in PVA/PVP blend.

The estimated value of \( k \) in the present case is 0.04803mol\(^{-1}\)ns\(^{-1}\), which is slightly smaller than the values reported in literature [7] for FeCl\(_3\) in liquid (0.065mol\(^{-1}\)ns\(^{-1}\) for Fe\(^{3+}\) in water). This result suggests that the quenching process is taking place in the FeCl\(_3\) doped PVA/PVP blend and FeCl\(_3\) is a strong chemical quencher.

Apart from above inhibition and quenching of Ps, the dopant creates local lattice distortion in such a way as to create a local negatively charged domain that traps the positrons. These positron trapping site are the defect regions due to formed charged species like complex formation and crosslinking process. As the FeCl\(_3\) doping concentration increases, the number of charged species due to Fe\(^{3+}\) ions interactions with \(-\text{OH}/\text{C}=\text{O}\) groups of PVA/PVP blend (via inter/intra molecular interaction) increases and hence the crosslinking density [5,8]. This increase in complex formation in turn enhances the defect level or number of positron trapping sites and this is reflected in I\(_2\) variation.

### 7.3 Studies on Fluorescent PVA+PVP+MPDMAPP Composite Films

To understand the effect of NLO active compound doping on the Microstructural and florescent properties of the blend is studied using different
technique. In this case also the techniques explained are used for the present study.

7.3.1 FTIR Spectroscopic analysis

To understand the nature of interaction of the chalcone chromophore (MPDMAPP) and the PVA/PVP blend, the FTIR spectra were taken using the method explained in chapter 2. The FTIR spectrum of pure PVP, pure PVA, pure MADMAPP and MADMAPP doped PVA/PVP blend with different concentrations of 0.01, 0.025, 0.05, 0.1, 0.5, 1 wt% has been shown in Figure 7.10 and the peak assignments are given in the Table 7.3.

![FTIR spectra of pure PVP, pure PVA, pure MPDMAPP, pure PVA+PVP blend and MPDMAPP doped PVA+PVP blend with various concentrations.](image)

Figure 7.10: FTIR spectra of pure PVP, pure PVA, pure MPDMAPP, pure PVA+PVP blend and MPDMAPP doped PVA+PVP blend with various concentrations.
Table 7.3: FTIR spectral assignments of pure PVA, PVP, PVA+PVP blend, pure MPDMAPP and PVA+PVP +MPDMAPP composites

<table>
<thead>
<tr>
<th>Wavenumbers (cm⁻¹)</th>
<th>PVA</th>
<th>PVP</th>
<th>PVA+PVP</th>
<th>MPDMAPP</th>
<th>Composite</th>
<th>Peak Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3425</td>
<td>3432</td>
<td>3445</td>
<td>-----</td>
<td></td>
<td>3435-3442</td>
<td>O–H stretching</td>
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<td>2928</td>
<td>2924</td>
<td>2922</td>
<td>2905</td>
<td></td>
<td>2924-2928</td>
<td>C–H asymmetric stretch (m)</td>
</tr>
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<td>2853</td>
<td>2862</td>
<td>2851</td>
<td>2803</td>
<td></td>
<td>2848-2853</td>
<td>C–H symmetric stretch (m)</td>
</tr>
<tr>
<td>1733</td>
<td>-----</td>
<td>1742</td>
<td>-----</td>
<td></td>
<td>1745-1750</td>
<td>C=O stretching (chalcone)</td>
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<td>1640</td>
<td>1660</td>
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<td>1565</td>
<td>1559</td>
<td>1575</td>
<td>1562-1570</td>
<td></td>
<td>1562-1570</td>
<td>C=C stretch (aromatic, s), C–N stretch</td>
</tr>
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<td>1432</td>
<td>1496</td>
<td>1470</td>
<td>1435</td>
<td></td>
<td>1465-1470</td>
<td>C–H def (m) &amp; O–H bending</td>
</tr>
<tr>
<td>1382</td>
<td>1372</td>
<td>1370</td>
<td>1370 &amp; 1340</td>
<td></td>
<td>1372-1426</td>
<td>C–H def (m)</td>
</tr>
<tr>
<td>1285</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td></td>
<td>CH₂ def</td>
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<tr>
<td>1089</td>
<td>1081</td>
<td>1085</td>
<td>-----</td>
<td></td>
<td>1075-1085</td>
<td>C–H and C–O stretch, O–H bending</td>
</tr>
<tr>
<td>794</td>
<td>647</td>
<td>785,650</td>
<td>815 &amp; 799</td>
<td></td>
<td>785,669,595</td>
<td>C–H def</td>
</tr>
<tr>
<td>472</td>
<td>470</td>
<td>466</td>
<td>-----</td>
<td></td>
<td>465-478</td>
<td>Out of plane vibrations</td>
</tr>
</tbody>
</table>

The band assignments for the blend sample are similar to the one given in 7.2.1. From Figure 7.10 it is noticed that the after doping the blend with MPDMAPP with different concentrations, the resulting FTIR spectra show following changes [9,10]. The IR bands positions corresponding to C–N stretching vibrations for pure MPDMAPP (1575cm⁻¹) has been shifted to the wavelength range 1562-1570cm⁻¹ along with a variation in intensity. The band at 1565cm⁻¹ corresponding to pure PVP and at 1559cm⁻¹ (not seen for pure PVA) is shifted to wavelength range 1562-1570cm⁻¹ along with variation in intensity. The appearance of new peaks along with a change in existing peaks (and/or their disappearance) in IR spectra of the composites reflects the
complexation of PVA+PVP+MPDMAPP. All these modifications are understood based on various types of interactions associations using the reaction schemes given in the Figure 7.11.

Figure 7.11: Reaction scheme of MPDMAPP doped PVA/PVP blend.

Here the carbonyl bonds of the composites, which are attached to the pyrrolidone rings of PVP, results in the shift in stretching modes as seen with the peaks at 1654-1658cm\(^{-1}\) and C—N stretching vibrations at 1562-1570cm\(^{-1}\). These two peaks represent the free and hydrogen bonded carbonyl stretching...
modes for the PVA/PVP blend respectively (Figure 7.11a). Here the complex formation occurs in a cooperative way, leading to compact structures. During complexation and hence the blending, four main types of polymer-polymer interactions can be expected: Van der Waals, hydrophobic, electrostatic, and hydrogen bonding. Hence the complexation/blending will modify structure of the polymeric systems and changes its physical and chemical properties. Accordingly, it is assumed that a hydrogen bonded carbonyl is an indication of an intermolecular secondary interaction between the carbonyl oxygen on a PVP chain and a hydroxyl group along a PVA chain [8,9,10]. The observed shifts and variation in intensities of the composites also suggests the hydrophobic interactions between PVA and PVP as shown in Figure 7.11b.

Generally PVP contains a lactam unit (without any symmetry) as well as a nitrogen atom in planar configuration. This lactam unit is considered to be an active site to form charge transfer complex with C=O group of MPDMAPP in the bulk state or in solution [9, 10]. In the presence of hydrogen donor, the mesomerism of the peptide linkage, which is the tautomeration form of the interaction in PVP as shown in the Figure 7.11e. On the other hand the interaction of dimethylamino as well as the carbonyl groups of MPDMAPP with the O–H groups of PVA in the composite is also expected to takes place at different positions of PVA main chain [1,2]. Particularly the hydrogen-bonding and hydrophobic interactions between the N atoms of dimethylamino group and carbonyl O atoms of MPDMAPP with the O–H groups of PVA (as shown in the reaction scheme (Figure 7.11c – 7.11f)) and form the CTC [10]. All these modifications explained above are reflected in the FTIR spectra in the form of shifting of characteristic band positions and variations in the band intensities, suggests that the chalcone chromophore MPDMAPP is strongly interacting with the PVA+PVP blend.

7.3.2 UV-Visible Studies

The UV-Vis optical absorption spectra of pure PVA+PVP blend; pure MPDMAPP and PVA+PVP+MPDMAPP composite films with 0.01, 0.05, 0.1,
0.25, 0.5 and 1wt% concentration of MPDMAPP are shown in the Figure 7.12. Observed spectra and band assignment for pure blend is similar to 7.2.2.

The UV-Vis spectrum of pure MPDMAPP shows the maximum absorption at 405nm with the range of absorption lying in 335-480nm [9]. Generally it is known that the chalcone derivative compound absorbs light in the UV region and transmits in the remaining region. Good transparency and short cut-off wavelength in UV range are the important properties for any nonlinear optical crystal, which is useful for NLO applications. Accordingly, the spectrum of pure MPDMAPP shows transparency in the entire visible region and the absorption takes place only in the UV range.

From the Figure it is observed that both absorption peak and absorption edges changes with concentration of MPDMAPP for the composite films.
These are understood based on CTC formation. The chalcone derivative MPDMAPP contains both electron acceptor-donor groups \(\text{CH}_3\text{-N(CH}_3)_2\) and electron-donor C=O groups, when it is doped to PVA+PVP blend it forms CTC as seen in FTIR results. These CTC modifies the band structure as well as band gaps, as a result both intensity and absorption band edge shifts [9, 10-12].

The measured refractive index for pure MPDMAPP crystal is 1.466, whereas for the composite films the refractive indices are in the range of 1.4937-1.5398 and 1.5165-1.5516 for Red (\(\lambda=632.8\text{nm}\)) and Green (\(\lambda=543.5\text{nm}\)) He-Ne Lasers respectively. These changes in refractive index are also thought to be due to the presence of CTC within the doped blend matrix.

**7.3.3 Fluorescence Studies**

The steady state fluorescence spectra of the PVA+PVP+MPDMAPP composite films are measured using the method given in chapter 2 and same is given in Figure 7.13. The Figure shows that the fluorescence emission peak wavelengths and fluorescence emission intensity increases with MPDMAPP doping level in the PVA/PVP blend.

The data shows that the fluorescence emission wavelength (\(\lambda_{\text{max}}\)) shifts towards higher wavelengths from 509 to 550 nm for 273 nm excitation wavelength. Similarly, \(\lambda_{\text{max}}\) shifts towards higher wavelengths from and 510 to 539 nm for 427nm excitation wavelength. In addition, a small emission peak appears around 426nm. In these blends complex the energy transfer or fluorescence emission is expected to occur with the complex. This is provided with the emission spectrum of the donor component overlaps with the absorption spectrum of the acceptor, and the dipoles are sufficiently close to each other. The emission of fluorescence is understood by invoking the complex formation due to the interaction of MPDMAPP with the blend.
Figure 7.13: Fluorescence emission spectra of pure MPDMAPP, PVA/PVP blend and PVA+PVP+MPDMAPP composite films doped with different concentrations of MPDMAPP.

In this case the chalcone contains donar N(CH₃)₂ group and blend contains acceptor groups, during the complexation the charge transfer in the excited state resulting from the transfer of electron upon excitation from the donor (−N(CH₃)₂) to the acceptor (−CH₃) connected through benzene ring [13, 14]. That means the lone pair of nitrogen in the donor is transferred to the acceptor group to form a highly polar charge transfer state. Therefore in the presence of relative energy levels due to complexation, the photo-induced charge transfer or excitation energy transfer may become the predominant process. Hence in the present case the reasoning behind the incorporation of fluorescent chromophores within a polymer blends is to get the possibility of
charge transport and light-emission processes. Generally it is known that the optimum blend should combine complementary charge transport, with efficient energy transfer from the higher to the lower energy gap component of chromophore molecule with spatial confinement of the complex within the acceptor chains. Here our conceptual view of the fluorescence is similar to that of fluorescence resonance energy transfer (FRET) in which the excited state molecule (donor molecule) “sees” a nearby molecule (acceptor molecule) if the acceptor is within a few nanometers of the donor [12-16]. In the FRET mechanism, the donor molecule nonradiatively transfers its energy to the acceptor molecule, which subsequently emits fluorescence in its typical excitation spectral region. The strong fluorescence emission is probably because of no or weak energy transfer between the excited fluorescent chromophore unit.

Figure 7.14: Variation of (a) fluorescence emission peak wavelength, (b) peak intensity, (c) fluorescence anisotropy and (d) luminescence polarization P of composite films for \( \lambda_{ex} = 273 \) nm and \( \lambda_{ex} = 427 \) nm.
The fluorescence anisotropy or the degree of polarization is another property, which is defined as the ratio of the difference between the emission intensity parallel to the polarization of the electric vector of the exciting light and perpendicular to that vector. These polarized fluorescence measurements can provide useful insight into the effects of inter and intramolecular excitation, energy transfer on the degree of polarization and the role of film morphology in controlling emissive properties [17,18]. The fluorescence anisotropy is estimated using the equation 2.6 given in Chapter 2.

The estimated fluorescence anisotropy of pure chalcone is found to be 0.086 for λ<sub>ex</sub> = 273 nm excitation and 0.081 for λ<sub>ex</sub> = 427 nm excitation (figure 7.14c). This low value of anisotropy for pure chalcone explains the fast molecular motion of chalcone molecules in solution at room temperature. For the PVA+PVP+MPDMAPP composite films, it is varying from 0.21 to 0.31 for 273 nm excitation and from 0.34 to 0.14 for 427 nm excitation. These relatively enhanced values suggest that the chalcone molecular motion is suppressed with in the solid blend composite film. The luminescence polarization P is estimated using 2.7 given in Chapter 2, which is a very effective and sensitive parameter in the evaluation of chromophore molecular alignment in polymer films, and the variation is shown in the figure 7.14d.

The fluorescence microscopic image (Figure 7.15) of these composite films shows a bright green emission under blue wide band pass excitation (450-480 nm) and red emission under green wide band pass excitation (510-550 nm) sources. This property of emission under excitation sustaining for long time, may be due to the aromatic C=C and phenyl groups present in the chalcone chromophore [18,19]. Therefore the photo-induced fluorescence imaging of the exposed area results strong fluorescent images implying that the intramolecular hydrogen bond plays a key role in chalcone doped PVA+PVP blend. This type of material where the fluorescence emissions takes place upon exposure to the light of different wavelengths is known as photochromic material.
Hence this fluorescence microscopic imaging study on MPDMAPP doped PVA+PVP shows the films are photochromic in nature and varies with dopant concentration. Thus the observed photochromic reaction mechanism in the present MPDMAPP doped PVA leads to the changes of chemical bond or the motion of molecular segments within the polymer matrix [18,19]. These modifications are probably due to the intra and intermolecular interactions, such as the hydrogen bonding and hydrophobic interactions between the OH/C=O groups of PVA+PVP and CO, CH₃ and N(CH₃)₂ groups of the chalcone derivative. The larger fluorescence suggest that the electron-donating properties of substituted groups have a great influence on the fluorescence emission with substituted groups which exhibit stronger emission than those with electron-accepting substitute groups [20].

7.4 Conclusions

The microstructural modifications in PVA/PVP (50:50) blend upon doping of transition metal chloride FeCl₃ as well as Chalcone chromophore MPDMAPP have been studied extensively. The positron behaviour in the transition metal chloride FeCl₃ doped PVA/PVP blend were studied. This study shows that the doping increases the amorphous nature of the film and both inhibition and quenching of Ps formation occurs within the blend. Because the
Fe$^{3+}$ ion is known to promote oxidation of Ps, the intensity ($I_3$), of Ps pick-off annihilation is decreased to a great extent. The linear behaviour of Ps trapping rate ($1/\tau_3$) with FeCl$_3$ doping indicates that the quenching process also takes place in this complex system and quenching rate constant has been estimated.

The UV-Vis study on chalcone chromophore MPDMAPP doped PVA/PVP composite films shows that optical responses depend strongly on the dopant concentration. These absorption results indicate that the MPDMAPP interacts with PVA/PVP matrix via intermolecular hydrogen bonding and hydrophobic interaction and forms the charge transfer complex or charge cluster groups. The observed increase in the fluorescence emission intensities and emission wavelengths indicates that the chalcone molecules in a crystalline state are less fluorescent but strongly fluorescent in the polymeric matrix due to the specific intermolecular interactions. The fluorescence polarization $P$ and anisotropy $r$ for the composite films were measured and these values are low for pure chalcone and these parameters increases for composites films. The fluorescence microscopic images of the composite films show that the composite films are photochromic in nature. Thus doping can effectively modify the macroscopic properties of the blends and they can be tuned for particular applications by controlling the dopant concentration.
7.5 References


