Chapter-4

PMMA-PAni (metal salt doped) Blends

After discussing the optical, electrical and structural behaviour of Poly(methyl methacrylate) (PMMA) on blending with acids (DBSA and CSA) doped Polyaniline (PAni) at different weight % (Chapter 3); in this chapter, the similar studies on blending PMMA with metal salts (Iron and Copper) doped PAni are presented. Like that in the previous chapter, the first part of this chapter deals with the characterization of synthesized Iron (Fe) and Copper (Cu) doped PAni while the second and third part highlight the induced changes in properties of PMMA after blending with PAni.Fe and PAni.Cu, respectively.

4.1 METAL SALTS (Fe and Cu) DOPED PANI

After the synthesis of Polyaniline doped with Fe and Cu metal ions adopting the method, as already discussed in Chapter 2, Section-2.2, the prepared PAni powders were characterized through UV-Visible-NIR absorption, FTIR and Raman spectroscopic techniques and finally, through V-I measurements.
4.1.1 UV-Visible-NIR Absorption Studies

To study the optical behaviour of the synthesized metal salts doped PANi, the same in the powder form were subjected to UV-Visible-NIR spectroscopy and the recorded spectra are presented in figure 4.1. In this figure, spectrum ‘a’, which corresponds to the absorption behaviour of PANi.Fe, clearly indicates the presence of two absorption bands. The first band peaking at 379 nm corresponds to the $\pi \rightarrow \pi^*$ transitions of electrons in benzenoid ring present in the PANi backbone [Ebrahim et al. 2009; Wallace et al. 2009] while the second absorption tail extended from visible to NIR region can be attributed to the delocalization of charge carriers, i.e. polarons, which are responsible for the conducting nature of PANi.Fe [Furukawa 1988; Izumi et al. 2007; Kumar et al. 2009].

![UV-Visible-NIR absorption spectra of Fe and Cu doped PANi](image)

**Figure 4.1: UV-Visible-NIR absorption spectra of Fe and Cu doped PANi**

The spectrum ‘b’ (figure 4.1), indicating the absorption behaviour for PANi.Cu, shows three bands centred at 339, 449 and 1019 nm. The band at 339 nm arises due to $\pi \rightarrow \pi^*$ transitions while the bands at
449 and 1019 nm are assigned to the benzenoid to quinoid excitonic transitions, i.e. polaron band transitions [Izumi et al. 2007].

### 4.1.2 FTIR Spectroscopy

To quantify the nature and strength of bonds present in synthesized PAni doped with Fe and Cu salts, the same were characterized through FTIR spectroscopy. Figure 4.2 presents the FTIR spectra of PAni.Fe (spectrum ‘a’) and PAni.Cu (spectrum ‘b’).

![FTIR Spectra of PAni](image)

**Figure 4.2: FTIR spectra of PAni doped with (a) Fe and (b) Cu salts**

The small bands observed at 3217 and 3039 cm$^{-1}$ in the spectrum of PAni.Fe and 3232 and 3062 cm$^{-1}$ in PAni.Cu, are attributed to hydrogen-bonded N–H stretching and aromatic C–H stretching, respectively. The broad absorption band observed at wavenumbers higher than 2000 cm$^{-1}$ in these spectra is due to the absorption of free charge-carriers generated in PAni due to doping and confirms the conducting nature [Epstein et al. 1987; Neoh et al. 1993; Ping 1996; Trchova and Stejskal 2011] of Fe and Cu doped PAni.
The strong peaks at 1574 and 1497 cm\(^{-1}\) in PAni.Fe (spectrum 'a') and at 1573 and 1489 cm\(^{-1}\) in PAni.Cu (spectrum 'b') may be attributed to quinoid (Q) and benzenoid (B) ring-stretching vibrations, respectively [Dey et al. 2004; Lee et al. 2005; Zhao et al. 2006; Yang et al. 2007; Yavuz and Gok 2007; Ding et al. 2010]. The band at 1303 cm\(^{-1}\) in PAni.Fe and at 1304 cm\(^{-1}\) in PAni.Cu may be assigned to the π-electron delocalization induced in the polymer on doping [Ping 1996; Trchova and Stejskal 2011]. The shoulder observed at 1265 cm\(^{-1}\) in both the PAni salts corresponds to C–N\(^{\neq}\) stretching vibration in the polaron structure [Boyer et al. 2000; Trchova and Stejskal 2011] and again indicates the confirmation of the conducting nature of PAni after doping. The peaks exhibited at 1149 and 1147 cm\(^{-1}\) in PAni.Fe and PAni.Cu, respectively are assigned to the vibration mode of –NH\(^{\neq}\)= structure, and associated with the vibrations of the charged polymer units Q=NH\(^{\neq}\)=B or B–NH\(^{\neq}\)=B [Boyer et al. 1998; Kang et al. 1998; Socrates 2001; Trchova and Stejskal 2011]. The peaks at 794 cm\(^{-1}\) in PAni.Fe and 795 cm\(^{-1}\) in PAni.Cu spectra are due to the C–H out-of-plane bending vibrations of two adjacent hydrogen atoms on a di-substituted benzene ring present in the PAni structure [Bellamy 1962; Vien et al. 1991; Boyer et al. 1998; Kang et al. 1998; Socrates 2001; Yang et al. 2007; Trchova and Stejskal 2011].

All the peaks/bands observed in the FTIR spectra, discussed above, are in line with those quoted in literature [Kang et al. 1998; Liu et al. 1999, 2002; Stejskal et al. 2001; Kumar et al. 2009; Yang et al. 2009] and confirm the characteristic bonds present in the emeraldine salt form of PAni.

### 4.1.3 Raman Spectroscopy

The chemical nature of PAni doped with Fe and Cu salts has been further investigated through Raman spectroscopic technique. Figure 4.3 presents the Raman spectra of PAni doped with both the metal salts. As depicted from the figure, the most intense peak at 1610 cm\(^{-1}\) and at 1636 cm\(^{-1}\) for PAni.Fe (spectrum 'a') and PAni.Cu (spectrum
‘b’), respectively is attributed to the C=C stretching mode of benzenoid rings present in PANi chains [Louarn et al. 1996; Izumi et al. 2007, 2009]. The small absorption at 1567 cm\(^{-1}\) for PANi.Fe, and at 1589 cm\(^{-1}\) for PANi.Cu, corresponds to the same stretching modes in quinoid rings of PANi chain [Quillard et al. 1994, 1995; Louarn et al. 1996; Izumi et al. 2007, 2009]. This peak is supressed and is not clear due to dominance of the peak of benzenoid C=C stretching mode. The band positioned at 1442 cm\(^{-1}\) in spectrum of PANi.Cu is assigned to the C=N stretching in the quinoid segments [Louarn et al. 1996].

![Figure 4.3: Raman spectra of PANi doped with (a) Fe and (b) Cu salts](image)

The band appearing at 1394 cm\(^{-1}\) in PANi.Fe is the signature of the C–C stretching mode of quinoid ring present in PANi backbone [Shakoor and Rizvi 2010]. Due to conformational difference of the polymer and the extent of doping, the shift for C–C stretching vibration may vary. The observed absorption band at 1333 cm\(^{-1}\) for PANi.Fe, and at 1320 cm\(^{-1}\) for PANi.Cu, is originated due to C-N\(^{+}\) stretching modes of delocalized polaronic charge carriers while the small absorption
observed at 1246 cm$^{-1}$ in PANi.Fe arises due to same stretching mode for delocalized bipolaronic charge carriers [Louarn et al. 1996; Shakoor and Rizvi 2010], which are characteristics of conducting form of PANi. This confirms the existence of both polaron and bipolaron in PANi.Fe and only polarons in PANi.Cu, which are responsible for the conduction.

The peak centred at 1187 cm$^{-1}$ for PANi.Fe, and 1177 cm$^{-1}$ for PANi.Cu, is assigned to the out of plane C–H bending in the polymer chain. The peak observed at 876 cm$^{-1}$ in PANi.Fe is attributed to the O-C(O)-O stretching mode in the PANi chain. The small bands at 607 and 616 cm$^{-1}$ in PANi.Fe and PANi.Cu, respectively are attributed to the benzene ring deformation present in PANi [Louarn et al. 1996; Cochet et al. 2000; Silva et al. 2005]. The bands observed at 572 cm$^{-1}$ in PANi.Fe and 582 cm$^{-1}$ in PANi.Cu are the signature of formation of phenazine like structure due to cross-linking among the polymer chains [Silva et al. 2000, 2005]. The other bands present in both the spectra also correspond to the quinoid or benzene rings deformation present in the main chain of PANi [Louarn et al. 1996]. Thus Raman spectroscopy confirms the various bonds present in the prepared PANi salts and verifies their conducting nature, which is also in line with the FTIR analysis.

From the above discussion, it is clear that the prepared PANi salts are conducting in nature. The presence of polaron band in UV-Visible-NIR absorption spectra extended from visible to NIR region, bands above 2000 cm$^{-1}$ and peaks at ~1303 and 1265 cm$^{-1}$ in FTIR spectra and bands at 1333 & 1246 cm$^{-1}$ in Raman spectra for PANi.Fe, and similar observations for PANi.Cu, confirms the existence of charge-carriers in metal salts doped PANi and are responsible for their conducting nature.

4.1.4 Conductivity Measurements

The electrical conductivity of PANi, doped with Fe and Cu metal salts, was determined from the V-I measurements in the voltage range -10 to 10 mV using the same method as for acid doped PANi, discussed in Chapter 3, Section-3.1.4.
Figure 4.4 presents the V-I characteristics for PAni.Fe (curve ‘a’) and PAni.Cu (curve ‘b’). From the figure it can be predicted that the observed voltage-current behaviour is linear, therefore, showing metal like conductivity response in these PAni salts. Electrical conductivity was calculated using Ohm’s law from these V-I characteristics and found to be $3.53 \times 10^{-2}$ S/cm for PAni.Fe and $1.58 \times 10^{-2}$ S/cm for PAni.Cu, positioning them in semi-conducting range on conductivity chart [Blythe 1979, 1984; Epstein 1997; Kohlman et al. 1997; Sze 2004; Jain et al. 2007].

![Figure 4.4: V-I characteristics of metal salts (Fe and Cu) doped PAni](image)

After synthesizing the conducting PAni salts, free standing films of blends of PMMA with different concentration of these salts have been prepared by adopting the same procedure as that for PMMA-PAni (acid doped) blends, discussed in Chapter 3, Section-3.1.4. These films were subjected to UV-Visible-NIR absorption studies to analyse the optical behaviour of the blends. FTIR and Raman spectroscopic techniques were used to reveal the structural changes in the blends on embedding different weight % of prepared PAni. Finally, electrical behaviour was scrutinized through V-I and dielectric measurements. The results of
our measurements and their interpretation are presented systematically in the following sections.

### 4.2 PMMA-PAni.Fe BLENDS

In the present section, variation in optical, electrical and structural properties of PMMA as an effect of embedding of PAni.Fe at different weight % is presented.

#### 4.2.1 UV-Visible-NIR Absorption Studies

Figure 4.5 presents the absorption spectra for PMMA and various PMMA-PAni.Fe blends at different concentrations (0.4, 1.0, 2.0, 6.0 and 10.0; % by weight) of PAni.Fe.

![Absorption spectra of PMMA and PMMA-PAni.Fe blends](image)

**Figure 4.5: UV-Visible-NIR absorption spectra of PMMA and PMMA-PAni.Fe blends**

Curve ‘a’ of this figure clearly indicates that PMMA exhibits two absorption peaks at 298 nm and 340 nm in UV-region while remains transparent in complete visible region [Jin et al. 1992]. These peaks correspond to $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of electrons, respectively [Sharma et al. 2007]. After embedding PAni.Fe in PMMA at a
concentration of 0.4% by weight, two additional new bands start originating. The first one, observed around 459 nm, corresponds to \( \pi \rightarrow \pi^* \) transitions of electrons in \( \text{PAni.Fe} \) chains [Lever 1968; Zidan and abu-Elnader 2005; Ebrahim et al. 2009; Wallace et al. 2009]. The another band, extended from visible to NIR region, corresponds to benzenoid to quinoid excitonic transitions or polaron band transitions, and is responsible for conduction in the blends [Furukawa 1988; Izumi et al. 2007; Kumar et al. 2009]. The intensity of these bands is very small at low concentrations and become apparent at higher concentrations of \( \text{PAni.Fe} \) (above 1% by weight) in PMMA.

It is also evident from this figure that there is a continuous shift in the fundamental absorption edge corresponding to PMMA towards the longer wavelengths with increasing concentration of \( \text{PAni.Fe} \) in PMMA. The observed shift in absorption edge can be explained in terms of the formation of new energy levels within the band gap of PMMA by the addition of \( \text{PAni.Fe} \). Due to generation of these levels in band gap, lower energy transitions become feasible and improvement in optical properties is obtained.

**Determination of Optical Energy Gap**

In order to determine the values of optical energy gap of PMMA and its blends with varying concentration of \( \text{PAni.Fe} \), the values of \( (\alpha h\nu)^{1/2} \) as a function of photon energy (\( h\nu \)) have been plotted corresponding to the fundamental absorption edge in the respective UV-Visible absorption spectra (figure 4.5), in light of the Tauc’s relation [Tauc 1974; Fink 2004; Mighad and Zidan 2006; Sharma et al. 2007; Kumar et al. 2011]. The linear fitted lines in these plots have been extrapolated and their intercepts on \( h\nu \) axis (figure 4.6) provide the values of optical energy gap. The values of optical energy gap, so obtained, for pure PMMA and its blends are appended in table-4.1.

It is clearly observable from table-4.1 that the value of optical energy gap, which was found to be 2.72 eV for pure PMMA, has been found to decrease continuously with increase in the concentration of \( \text{PAni.Fe} \) in PMMA and finally, achieves a value of 1.81 eV at 10%
concentration (by weight) of PAni.Fe in PMMA. Such a reduction in the values of optical energy gap may be correlated to the structural

![Figure 4.6: Plots for the determination of optical energy gap for PMMA and PMMA-PAni.Fe blends](image)

**Table 4.1: Optical energy gap values for PMMA and PMMA-PAni.Fe blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical Energy Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PMMA</td>
<td>2.72 ± 0.02</td>
</tr>
<tr>
<td>PMMA+0.4% PAni.Fe</td>
<td>2.52 ± 0.01</td>
</tr>
<tr>
<td>PMMA+1% PAni.Fe</td>
<td>2.14 ± 0.01</td>
</tr>
<tr>
<td>PMMA+2% PAni.Fe</td>
<td>1.98 ± 0.02</td>
</tr>
<tr>
<td>PMMA+6% PAni.Fe</td>
<td>1.91 ± 0.02</td>
</tr>
<tr>
<td>PMMA+10% PAni.Fe</td>
<td>1.81 ± 0.03</td>
</tr>
</tbody>
</table>
rearrangements in PMMA apprehended due to formation of some kind of chemical network between the embedded PANi.Fe particles with PMMA chains. Same is also revealed through FTIR and Raman spectroscopic studies, discussed in proceeding sections of the chapter.

Due to formation of chemical conjugation, localized states are formed between the HOMO and LUMO bands of PMMA, which are responsible for the modification in their extended electronic states, thus, contributing to the formation of charge transfer complexes (CTCs) [Devi et al., 2002; Mamunya et al. 2002; Laska 2004; Ebrahim et al. 2009]. These CTCs are responsible for the optical transitions feasible at lower energies leading to the observed change in optical energy gap.

4.2.2 FTIR Spectroscopic Studies

In order to divulge the induced structural changes in PMMA after blending it with PANi.Fe at different concentrations by weight, FTIR spectra of PMMA and its blends have been recorded and are presented in figure 4.7. The various absorption peaks/bands observed in spectrum ‘a’ of this figure correspond to the various functional groups present in pure PMMA, as already described in Chapter 3, Section-3.2.2 [Jo et al. 1989; Balamurugan et al. 2004; Saikia and Kumar 2005; Wang et al. 2006; Khan et al. 2008; Choudhury and Misra 2010; Tomar et al. 2011].

After embedding PANi.Fe (0.4% by weight) in PMMA, the recorded spectrum (spectrum ‘b’) indicates that the intensity of almost all the bands/peaks present in pure PMMA has been reduced considerably indicating the rearrangements in the structure of PMMA on adding PANi.Fe. As the concentration of PANi.Fe is increased (1% and 2% by weight), the intensity of the peaks/bands at higher wavenumber side (above 2500 cm\(^{-1}\)) becomes negligibly small while the decrease in the intensity of other peaks continues (spectra ‘c’ and ‘d’). With increase in concentration of PANi.Fe to 6% by weight in pure PMMA (spectrum ‘d’), only certain peaks corresponding to CH bonds (2949 cm\(^{-1}\)), carbonyl group (1734 cm\(^{-1}\)), bending vibration of CH\(_3\) (1446 cm\(^{-1}\)) and ester
(C-O) vibrations (1300-1100 cm$^{-1}$) are retained, but with small intensities, and the other peaks/bands are eliminated.

Finally, at 10% concentration by weight of PANi.Fe (spectrum 'e'), almost similar trend as that in spectrum 'd' has been noticed except for the more reduction in the intensity of the remaining peaks.

Thus, the observed behaviour of FTIR spectra of PMMA-PANi.Fe blends in comparison to that for pure PMMA clearly indicates that some structural rearrangements have taken place after blending PMMA with PANi.Fe.

4.2.3 Raman Spectroscopic Studies

In order to understand the induced structural rearrangements in PMMA after blending with PANi.Fe completely, another complementary technique, i.e. Raman spectroscopy, was employed. Figure 4.8 shows the Raman spectra of PMMA and its blends with varying concentration by weight of PANi.Fe. In this figure, spectrum 'a' depicts the presence of various bonds present in PMMA, as already discussed in detail in
Chapter 3, Section 3.2.3 [Ward and Mi 1999; Tagowska et al. 2004; Silva et al. 2005; Lu et al. 2009; Kumar et al. 2010; Shakoor and Rizvi 2010; Tomar et al. 2012].

After adding PAni.Fe (0.4% by weight) in PMMA (spectrum ‘b’), new peaks at 1646, 1596 and 1238 cm\(^{-1}\) start originating. These peaks correspond to C=C stretching mode of benzenoid ring, same stretching mode in quinoid ring and delocalized charge carriers in PAni.Fe, respectively. Further, the band positioned at 1178 cm\(^{-1}\), corresponding to C–O–C stretching mode of PMMA [Quillard et al. 1994, 1995; Louarn et al. 1996; Izumi et al. 2007, 2009], becomes narrower.

With increase in concentration of PAni.Fe in PMMA to 2% by weight (spectrum ‘c’), the intensity of the peaks/bands corresponding to PAni.Fe increases while decrease in intensity of peaks/bands corresponding to PMMA has been observed. In addition, more new bands/peaks at 2316-2573, 2154-2242, 1736-2153, 1829 and 1401 cm\(^{-1}\) are observed and the positions of the peaks/bands at 1646 and 1596 cm\(^{-1}\) in spectrum ‘b’ are found to be red shifted slightly. The
small absorption at 1401 cm\(^{-1}\) is due to C–C stretching mode of quinoid ring of PANi.Fe while the other new peaks/bands originated are due to formation of new bonds in the PMMA-PANi.Fe structure and indicate the formation of chemical conjugation between PMMA and PANi.Fe chains.

With further increase in concentration of PANi.Fe in PMMA to 6% by weight (spectrum ‘d’), the same trend as that in spectrum ‘c’ continues and the new peaks/bands originated due to blending with PANi.Fe dominate over the characteristic peaks/bands observed in spectrum ‘a’ for pure PMMA. Moreover, additional new peaks at 1570 and 1510 cm\(^{-1}\) are observed, which may be attributed to the formation of further conjugation in PMMA and PANi.Fe chains. For 10% PMMA-PANi.Fe blends, the peaks/bands corresponding to PANi.Fe and those generated due to conjugation dominate with elimination of most of the peaks/bands corresponding to PMMA.

From the above discussion, it can be concluded that when PANi.Fe is embedded in PMMA at different concentrations, it penetrates in the PMMA chains resulting in the formation of an interpenetrating network of both PMMA and PANi.Fe. As a result, chemical conjugation occurs between the functional groups of PMMA and PANi.Fe, which is also confirmed through FTIR analysis.

After confirming the formation of chemical network between PMMA and PANi.Fe in blends, the induced changes in electrical behaviour of PMMA as an effect of embedding of PANi.Fe, revealed through V-I and dielectric measurements, have been presented in the following sections.

4.2.4 V-I Measurements

In order to study the dc conductivity and charge transportation mechanism in PMMA-PANi.Fe blends, Voltage-Current measurements have been carried out in the voltage range 0-100 V, adopting the same procedure as that for PMMA-PANi (acids doped) blends, discussed in Chapter 3, Section-3.2.4. The observed V-I characteristics of PMMA and PMMA-PANi.Fe blends are shown in figure 4.9.
From this figure, it is clearly observable that current increases continuously with increase in the applied voltage for PMMA. On adding 0.4 weight % of PANi.Fe in PMMA, a significant change in the current is apparent in the entire voltage range. This may be due to the generation of charge carriers in PMMA as an effect of embedding of conducting PANi.Fe particles. With further increase in concentration of PANi.Fe to 1% by weight, a slight decrease in the current is noticed. This decrease in current may be attributed to the presence of percolation threshold in this region [Jachym 1982; Boudenne et al. 2011].

![Figure 4.9: V-I characteristics of PMMA and PMMA-PAni.Fe blends](image)

For still higher concentrations of PANi.Fe in PMMA (2% by weight and above), an appreciable increase in the current has been observed. This enhancement in the current is due to the increase in conducting islands of PANi.Fe in insulating PMMA matrix, which makes the hopping of charge carriers easier [Kaiser et al. 2001; Veluru et al. 2007; Amrithesh et al. 2008].
(a) DC Conductivity

DC conductivity ($\sigma_{dc}$) for PMMA and PMMA-PAni.Fe blends at varying concentration of PAni.Fe by weight was determined from V-I characteristics using the same procedure as that for PMMA-PAni (acid doped) blends, discussed in Chapter 3, Section-3.2.4. The values of dc conductivity for PMMA and its blends with different concentration of PAni.Fe are tabulated in table-4.2. It can be clearly depicted from the table that the value of dc conductivity for PMMA, which was found to be $8.8 \times 10^{-16}$ S/cm, increases to $1.12 \times 10^{-13}$ S/cm after adding 0.4% by weight of PAni.Fe in it. This may be attributed to the creation of charge transfer complexes (CTCs) inside the polymer matrix, which in turn generate the charge trapping sites within the band gap of PMMA. These newly created energy levels promote the charge carriers to migrate easily through the polymer matrix [Jachym 1982; Devi et al. 2002; Boudenne et al. 2011]. Also, the creation of the conducting PAni.Fe regions in insulating PMMA matrix increases the electronic tunnelling probability through the PMMA chains [Kaiser et al. 2001; Amrithesh et al. 2008].

As the concentration of PAni.Fe is increased to 1% by weight, a decrease in the conductivity is observed. This may be due to the presence of percolation threshold in this region [Jachym 1982; Boudenne et al. 2011]. With further increase in PAni.Fe content in PMMA (2% and above), the density of CTCs is increased proportionally in the blends. As a result, the barrier strength of insulating PMMA regions decreases resulting in the increase in $\pi$ electron mobility through the blends. The increased electron mobility leads to the increased tunnelling probability and hence, the dc conductivity [Kaiser et al. 2001; Amrithesh et al. 2008]. At 10% by weight concentration of PAni.Fe in PMMA, dc conductivity attains the value $4.17 \times 10^{-10}$ S/cm, which is about 6 orders of magnitude higher in comparison to that for pure PMMA.
(b) Charge Conduction Mechanism

In order to understand the conduction process in PMMA and its blends with PAni.Fe, different charge conduction mechanisms are considered. As already discussed in Chapter 1, Section 1.4 and the observed behaviour of ln(I) versus ln(V), the applicability of Ohmic and SCLC conduction behaviour is ruled out. Furthermore, the linear behaviour of plots of ln(I) versus $V^{1/2}$ (figure 4.10) with positive slope, like that in PMMA-PAni (acid doped) blends (Chapter 3, Section 3.2.4), endorse the applicability of Poole-Frenkel or Schottky-Richardson mechanism in the present case.

Figure 4.10: Plots of $V^{1/2}$ versus ln (I) for PMMA and PMMA-PAni.Fe blends

To identify the dominating mechanism among these two, the experimental values of $\beta$ ($\beta_{exp}$) for PMMA and PMMA-PAni.Fe blends have been determined from the slopes of ln(I) versus $V^{1/2}$ plots. These values are compared with those corresponding to Poole-Frenkel ($\beta_{PF}$) and Schottky-Richardson mechanism ($\beta_{SR}$), calculated following the method as discussed in Chapter 1, Section 1.4.
The values of $\beta_{\text{exp}}$ for PMMA and its blends with varying concentration of PAni.Fe along with the calculated values of $\beta_{\text{PF}}$ and $\beta_{\text{SR}}$ are appended in table-4.2. From the table, it can be deduced that for pure PMMA, the value of $\beta_{\text{exp}}$ lies closer to $\beta_{\text{SR}}$ validating the applicability of Schottky-Richardson mechanism as the dominating charge transportation mechanism in pure PMMA [Devi et al. 2002; Deshmukh et al. 2007]. On adding 0.4% by weight of PANi.Fe in PMMA, an increase in the value of $\beta_{\text{exp}}$ is observed but remains closer to $\beta_{\text{SR}}$. This indicates that at this concentration, the induced charge carriers are too less in number that the major role is played by the injected charges only.

**Table-4.2: DC conductivity and values of $\beta$ for PMMA and PMMA-PAni.Fe blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{dc}$ (S/cm)</th>
<th>$\beta_{\text{PF}}$ (eV) ($\times 10^{-5}$)</th>
<th>$\beta_{\text{SR}}$ (eV) ($\times 10^{-5}$)</th>
<th>$\beta_{\text{exp}}$ (eV) ($\times 10^{-5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PMMA</td>
<td>8.80$\times 10^{-16}$</td>
<td></td>
<td></td>
<td>1.53</td>
</tr>
<tr>
<td>PMMA+0.4% PAni.Fe</td>
<td>1.12$\times 10^{-13}$</td>
<td></td>
<td></td>
<td>1.88</td>
</tr>
<tr>
<td>PMMA+1% PAni.Fe</td>
<td>2.14$\times 10^{-14}$</td>
<td>3.77</td>
<td></td>
<td>1.97</td>
</tr>
<tr>
<td>PMMA+2% PAni.Fe</td>
<td>8.24$\times 10^{-13}$</td>
<td>1.89</td>
<td></td>
<td>2.24</td>
</tr>
<tr>
<td>PMMA+6% PAni.Fe</td>
<td>9.52$\times 10^{-11}$</td>
<td></td>
<td></td>
<td>2.41</td>
</tr>
<tr>
<td>PMMA+10% PAni.Fe</td>
<td>4.17$\times 10^{-10}$</td>
<td></td>
<td></td>
<td>2.63</td>
</tr>
</tbody>
</table>

On increasing the concentration of PAni.Fe in PMMA, the increase in the value of $\beta_{\text{exp}}$ is retained. The increase in value of $\beta_{\text{exp}}$ may be ascribed to the generation of charge transfer complexes (CTCs) in PMMA on blending with PAni.Fe [Devi et al. 2002; Deshmukh et al. 2007]. These CTCs increase with increase in concentration of PAni.Fe and lead to the production of localized states in the matrix. These localized states, in turn, increase the hopping probability of charge carriers in the matrix. At the lower concentrations of PAni.Fe in blends, the conducting regions remain far apart and the hopping of the charges is difficult. Therefore, a very few number of charge carriers
Chapter 4: PMMA-PAni (metal salt doped) Blends

are generated in bulk and majority of the charge carriers responsible for conduction are injected from the electrodes retaining the Schottky-Richardson conduction mechanism as the dominating mechanism for conduction. With increasing concentration of PAni.Fe in these blends, the conducting islands of PAni.Fe come closer favouring the charges to hop through these regions and lead to increased conduction.

In the light of the above, it seems that upto a concentration of 1% by weight of PAni.Fe in PMMA, the value of $\beta_{exp} = 1.97 \times 10^{-5}$ eV, being closer to $\beta_{SR}=1.89 \times 10^{-5}$ eV, the conduction through Schottky-Richardson mechanism is dominated. The continuous increasing trend in $\beta_{exp}$ at still higher concentrations suggests the contribution in conduction by the Poole-Frenkel mechanism also. As is evident from the table that the value of $\beta_{exp}=2.63 \times 10^{-5}$ eV at 10% concentration of PAni.Fe lies in between $\beta_{SR}$ and $\beta_{PF}$, but still nearer to $\beta_{SR}$ than $\beta_{PF}$; thus, migration of charges can be assumed to be through both the mechanisms simultaneously yet the Schottky-Richardson mechanism dominates over the Poole-Frenkel mechanism.

From the above discussion, it can be inferred that the conduction, which is through Schottky-Richardson conduction mechanism for pure PMMA and its blends with lower concentrations of PAni.Fe also starts taking place through Poole-Frenkel mechanism as the concentration of PAni.Fe is increased in PMMA-PAni.Fe blends.

4.2.5 Dielectric Measurements

In the present section, the dielectric behaviour (dielectric constant, dielectric loss and ac conductivity) of PMMA and PMMA-PAni.Fe blends, as a function of frequency of the applied electric field, has been discussed.

(a) Dielectric Constant and Dielectric Loss

Figure 4.11 shows the variation in frequency dependent dielectric constant ($\varepsilon'$) for PMMA and PMMA-PAni.Fe blends at different concentration of PAni.Fe by weight at room temperature. It can be clearly seen from the figure that $\varepsilon'$ decreases with increase in
frequency for PMMA and PMMA-PAni.Fe blends. At low frequency, the induced dipoles in polymeric samples orient easily along with the alternating field \cite{Mardare2004} and polarization increases leading to the high value of dielectric permittivity. Also, the interfacial polarization and electrode effect in the sample plays a wide role in increasing $\varepsilon'$, as discussed in Chapter 3, Section-3.2.5.

Figure 4.11: Variation of dielectric constant with frequency for PMMA and PMMA-PAni.Fe blends

With increase in frequency, the observed decrease in the value of $\varepsilon'$ may be due to the contribution of orientation relaxation of dipoles and conduction of charge carriers at higher frequency \cite{Dyre1988}. This is because, at high frequency, field reversal becomes so fast that dipoles are unable to orient themselves with the field and intrawell hopping probability of charge carriers dominates resulting in decrease in polarization and hence, dielectric constant.

As also depicted from figure 4.11 that with increase in concentration of PAni.Fe (curves 'b'-'f') in PMMA-PAni.Fe blends, the value of $\varepsilon'$ decreases in the complete frequency range. This decrease can be elucidated on the basis of increased conduction in blends by
means of increasing concentration of PANi.Fe in PMMA. It is well known that the polarons/bipolarons, charge carriers in PANi.Fe, are mobile and free to move along the chain and thus, account for the observed conductivity in the samples while the dipoles, present in all polymeric systems, have only restricted mobility and are responsible for the strong polarization in the system. Therefore, the presence of conducting islands of PANi.Fe in insulating PMMA matrix is responsible for the conduction of charge carriers (polaron/bipolaron and dipoles of PANi.Fe) through hopping in PMMA chains [Joo et al. 1998; Pinto et al. 2000; Gmati et al. 2008; Afjal 2010].

At low concentrations of PANi.Fe in PMMA, the PANi.Fe clusters are far apart and conduction is restricted by the presence of the dielectric matrix in between. However, with increase in the conductive phase content, PANi.Fe islands come closer and a physical path is formed through which the current can flow percolating the whole system [Veluru et al. 2007], thus, increasing the conduction and supporting the observed decrease in $\varepsilon'$ with increasing the concentration of PANi.Fe in PMMA. The values of dielectric constant at various frequencies are tabulated in table-4.3.

**Table-4.3: Values of dielectric constant for PMMA and PMMA-PANi.Fe blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dielectric Constant at 100 kHz</th>
<th>500 kHz</th>
<th>1 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PMMA</td>
<td>4.28</td>
<td>4.08</td>
<td>4.06</td>
</tr>
<tr>
<td>PMMA+0.4% PANi.Fe</td>
<td>3.94</td>
<td>3.84</td>
<td>3.80</td>
</tr>
<tr>
<td>PMMA+1% PANi.Fe</td>
<td>3.54</td>
<td>3.44</td>
<td>3.40</td>
</tr>
<tr>
<td>PMMA+2% PANi.Fe</td>
<td>3.38</td>
<td>3.26</td>
<td>3.21</td>
</tr>
<tr>
<td>PMMA+6% PANi.Fe</td>
<td>2.71</td>
<td>2.59</td>
<td>2.54</td>
</tr>
<tr>
<td>PMMA+10% PANi.Fe</td>
<td>2.33</td>
<td>2.18</td>
<td>2.12</td>
</tr>
</tbody>
</table>
It is evident from the table that at the frequency of 1 MHz, the value of dielectric constant decreases from 4.06 (pure PMMA) to 2.12 on embedding of 10% by weight of PANi.Fe in PMMA.

The variation in imaginary part of dielectric constant $\varepsilon''$ (dielectric loss) with frequency for pure PMMA and its blends at different concentration of PANi.Fe is shown in figure 4.12. It is obvious from this figure that $\varepsilon''$ decreases with increase in frequency for PMMA and all PMMA-PANi.Fe blends. At low frequency, the high value of dielectric loss $\varepsilon''$ is usually associated with dipole polarization or interfacial polarization, as discussed in Chapter 3, Section 3.2.5.

Figure 4.12: Variation of dielectric loss with frequency for PMMA and PMMA-PANi.Fe blends

With increase in frequency, periodic field reversal becomes too fast that there is no excess ion diffusion in the direction of electric field and thus, charge accumulates and forms the space charge [Dyre 1988; Mardare 2004]. Due to the screening produced by this space charge, polarization decreases leading to the decrease in $\varepsilon''$. Further, dielectric loss increases with increase in the concentration of PANi.Fe in PMMA.
(curve ‘b–f’), which can be understood in terms of increased electrical conductivity, which is associated with the dielectric loss.

(b) AC Conductivity

Figure 4.13 represents the variation in ac conductivity ($\sigma_{ac}$) for pure PMMA and PMMA-PAni.Fe blends with increasing filler concentration at different frequencies. From this figure, an increase in ac conductivity in the blends has been observed up to a concentration of 2% by weight of PAni.Fe, due to the generation of the conducting regions of PAni.Fe in PMMA, at all frequencies. This can be explained on the basis of the Random free energy barrier (RFEB) model [Dyre 1988], as described in Chapter 3, Section-3.2.5. At higher concentrations of PAni.Fe in PMMA, the conducting regions are large enough that charges can be migrated easily percolating through the matrix, and hence, ac conductivity becomes nearly uniform, as depicted in figure 4.13.

Figure 4.13: Variation of ac conductivity with concentration of PAni.Fe in PMMA at different frequencies
From the above discussion, it can be conferred that an appreciable modifications in the optical, electrical and structural behaviour of PMMA have been observed as an effect of embedding of PANi.Fe (at different concentrations) in PMMA.

4.3 PMMA-PAni.Cu BLENDS

In the present section, the variation in optical, electrical and structural behaviour of PMMA-PAni.Cu blends, as an effect of embedding of PAni.Cu at different weight %, have been studied utilizing the same characterization tools and methods as those for PMMA-PAni.Fe blends, discussed in Section-4.2.

4.3.1 UV-Visible-NIR Absorption Studies

Figure 4.14 presents the UV-Visible-NIR absorption spectra of PMMA and its blends with varying concentration (0.4, 1.0, 2.0, 6.0 and 10.0; % by weight) of PAni.Cu.

![UV-Visible-NIR absorption spectra of PMMA and PMMA-PAni.Cu blends](image)

Figure 4.14: UV-Visible-NIR absorption spectra of PMMA and PMMA-PAni.Cu blends
Curve ‘a’ of this figure clearly indicates the existence of two absorption peaks in UV-region, i.e. at 298 nm and 340 nm in pure PMMA, while it exhibits high transparency in complete visible region [Jin et al. 1992], as already discussed in Section-4.2.1. On blending PMMA with PAni.Cu (curve ‘b’), two additional new bands, one around 459 nm, corresponding to $\pi \rightarrow \pi^*$ transitions [Lever 1968; Zidan and abu-Elnader 2005; Ebrahim et al. 2009; Wallace et al. 2009], and another extended tail from visible to NIR region, corresponding to benzenoid to quinoid excitonic transitions [Furukawa 1988; Izumi et al. 2007; Kumar et al. 2009], start emerging. With further increase in the concentration of PAni.Cu in PMMA (curve ‘c’ to ‘f’), the increase in the intensity of these newly originated bands is clearly observable, confirming the presence of PAni.Cu in the blends.

Moreover, a continuous shift in the fundamental absorption edge corresponding to PMMA towards the higher wavelengths has been observed with increase in the concentration of PAni.Cu in PMMA and can be explained in the similar way as that for PMMA-PAni.Fe blends, as already discussed in Section-4.2.1.

**Determination of Optical Energy Gap**

The change in optical energy gap values for PMMA on addition of different weight % of PAni.Cu can be determined by plotting the values of $(\alpha h\nu)^{1/2}$ as a function of photon energy (h$\nu$), corresponding to the fundamental absorption edge of the respective UV-Visible-NIR absorption spectra (figure 4.14), in light of the Tauc’s relation [Tauc 1974; Fink 2004; Mighad and Zidan 2006; Kumar et al. 2011]. Such plots are presented in figure 4.15. The linear fitted lines in these plots have been extrapolated to $h\nu$ axis and the intercepts on this axis provide the respective values of optical energy gap. These values for pure PMMA and its blends with varying concentration of PAni.Cu are appended in table-4.4.
Table 4.4: Optical energy gap values for PMMA and PMMA-PAni.Cu blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical Energy Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PMMA</td>
<td>2.72 ± 0.02</td>
</tr>
<tr>
<td>PMMA + 0.4% PAni.Cu</td>
<td>2.50 ± 0.01</td>
</tr>
<tr>
<td>PMMA + 1% PAni.Cu</td>
<td>2.35 ± 0.01</td>
</tr>
<tr>
<td>PMMA + 2% PAni.Cu</td>
<td>2.23 ± 0.03</td>
</tr>
<tr>
<td>PMMA + 6% PAni.Cu</td>
<td>2.09 ± 0.01</td>
</tr>
<tr>
<td>PMMA + 10% PAni.Cu</td>
<td>1.97 ± 0.02</td>
</tr>
</tbody>
</table>
From the figure 4.15 and table-4.4, it can be deduced that the value of optical energy gap, which comes out to be 2.72 eV for pure PMMA, decreases continuously with increasing concentration of PANi.Cu in PMMA and attains a value of 1.97 eV, when concentration of PANi.Cu is reached to 10% by weight in PMMA. Such a reduction in the optical energy gap values may be correlated to the induced structural rearrangements causing generation of trap levels between HOMO and LUMO of PMMA on blending it with different amounts of PANi.Cu [Devi et al. 2002; Mamunya et al. 2002; Laska 2004; Ebrahim et al. 2009] and can be explained in same way, as those for PMMA-PAni.Fe blends in Section-4.2.1.

4.3.2 FTIR Spectroscopic Studies

Figure 4.16 presents the FTIR spectra for PMMA and its blends at different concentration by weight of PANi.Cu. The various peaks/bands observed in spectrum ‘a’ of this figure correspond to the functional groups present in pure PMMA, as already described in Chapter 3, Section-3.2.2 [Jo et al. 1989; Balamurugan et al. 2004; Saikia and Kumar 2005; Wang et al. 2006; Khan et al. 2008; Choudhury and Misra 2010; Tomar et al. 2011].

On adding PANi.Cu in PMMA, a continuous decrease in the intensity of all the peaks/bands has been observed with increasing concentration (curve ‘b’ to ‘e’) of PANi.Cu with complete elimination of certain bands (above 2500 cm\(^{-1}\)) at 10% by weight of concentration (curve ‘f’) of PANi.Cu in blends. Such a behaviour can be attributed due to increased screening between PMMA chains and degree of conjugation between the host PMMA and embedded PANi.Cu, as already discussed in Chapter 3, Section-3.2.2.

Thus, FTIR spectroscopic analysis, like that in PMMA-PAni.Fe blends, confirms the formation of chemical network between functional groups of PMMA and PANi.Cu chains leading to the induced structural rearrangements in the PMMA-PAni.Cu blends.
4.3.3 Raman Spectroscopic Studies

In order to quantify the detailed analysis of induced structural changes in PMMA on embedding different weight % of PAni.Cu, another spectroscopic technique, i.e. Raman spectroscopy, has been employed. Figure 4.17 presents the Raman spectra for PMMA and different PMMA-PAni.Cu blends at varying concentration of PAni.Cu. In this figure, spectrum ‘a’ illustrates the various chemical bonds present in PMMA, as already discussed in detail in Chapter 3, Section-3.2.3 [Ward and Mi 1999; Tagowska et al. 2004; Silva et al. 2005; Lu et al. 2009; Kumar et al. 2010; Shakoor and Rizvi 2010; Tomar et al. 2012].

It is apparent from spectrum ‘b’ of the figure that with the addition of 0.4% by weight of PAni.Cu, no appreciable change in the peaks/bands of PMMA has been observed rather a small peak at 1342 cm\(^{-1}\), corresponding to C-N\(^{+}\) stretching mode of delocalized polaronic charge carrier, and two bands at 1763-2180 and
2318-2777 cm\(^{-1}\), corresponding to the formation of conjugation between PMMA and PANi.Cu chains, start originating. On increasing the content of PANi.Cu in PMMA to 1% by weight (spectrum ‘c’), in addition to the increase in the intensity of the bands originated in spectrum ‘b’, two more peaks at 1596 and 1646 cm\(^{-1}\) start appearing. These are attributed to the C=\(\text{C}\) stretching mode of quinoid ring and N–H bending vibrations, respectively, which are characteristic peaks in doped PANi [Quillard et al. 1994, 1995; Louarn et al. 1996; Izumi et al. 2007, 2009].

Further, appreciable change in the characteristic band of PMMA at 1031-1281 cm\(^{-1}\) and newly originated bands in spectrum ‘b’ has been observed. These may be correlated to the formation of new bonds between PMMA and PANi.Cu chains. As the concentration of PANi.Cu is further increased (spectra ‘d’ and ‘e’), considerable change in the Raman spectra have been observed. Some additional new bands/peaks, along with those observed in PANi.Cu spectrum, discussed in Section-4.1.3, appear to emerge. These may be allocated...
to the presence of PAni.Cu in blends in addition to creation of new bonding between PMMA and PAni.Cu chains.

Thus, the observed changes in the recorded spectrum of pure PMMA and origination of new peaks/bands in PMMA-PAni.Cu blends predict the formation of chemical network between the PMMA and PAni.Cu chains, which is further enhanced with increase in concentration of PAni.Cu in blends.

4.3.4 V-I Measurements

To determine the dc conductivity and understand the charge conduction mechanism in PMMA-PAni.Cu blends, Voltage-Current measurements have been carried out in the voltage range 0-100 V and are represented in figure 4.18.

![Figure 4.18: V-I characteristics of PMMA and PMMA-PAni.Cu blends](image)

From the figure, it can be deduced that the magnitude of the current is an increasing function of applied voltage for all the samples. On adding 0.4% by weight of PAni.Cu in PMMA (curve ‘b’), an
appreciable increase in the current has been observed. This can be explained on the similar basis as that for PMMA-PAni.Fe blends, discussed in Section-4.2.4. As the concentration of PAni.Cu is increased to 1% (curve ‘c’), current is found to decrease slightly due to attainment of percolation threshold in the region. With further increase in content of PAni.Cu (curve ‘d’ to ‘f’), a continuous increase in current has been observed. These results are consistent with those for PMMA-PAni.Fe blends, as explained in Section-4.3.4.

(a) DC Conductivity

The dc conductivity ($\sigma_{dc}$) of PMMA and its blends with different weight % of PAni.Cu have been determined using the three terminal guard ring electrode method, following the same procedure as that for PMMA-PAni.Fe blends, as described in Section-4.2.4. These calculated values are averaged in entire voltage range (0-100 V) and appended in table-4.5. It is evident from the table that dc conductivity is found to increase with increasing concentration of PAni.Cu in PMMA, except for a concentration of 1% by weight of PAni.Cu. This increase can be attributed to the generation of charge transfer complexes (CTCs) in PMMA matrix on embedding PAni.Cu in it. Due to these CTCs, trap levels are generated in the band gap of PMMA. The density of the CTCs is enhanced with increase in concentration of PAni.Cu in the blends [Quillard et al. 1994, 1995; Louarn et al. 1996; Izumi et al. 2007, 2009]. As a result, interwell barrier strength decreases leading to increase in tunnelling probability, which is responsible for the increased dc conductivity [Kaiser et al. 2001; Amrithesh et al. 2008]. The decrease in dc conductivity at 1% concentration has been observed due to presence of percolation threshold in the region [Jachym 1982; Boudenne et al. 2011]. As is observable from the table-4.5, the value of dc conductivity, which comes out to be $8.8 \times 10^{-16}$ S/cm for pure PMMA attains a value $6.04 \times 10^{-10}$ S/cm, after embedding 10% by weight concentration of PAni.Cu in PMMA, resulting in an increase by about 6 orders in dc conductivity.
(b) Charge Conduction Mechanism

Like that for PMMA-PAni.Fe blends (figure 4.10), the linear behaviour with positive slope of the plots between ln(I) and $V^{1/2}$, as presented in figure 4.19 for PMMA and PMMA-PAni.Cu blends, recommend the applicability of Poole-Frenkel or Schottky-Richardson mechanisms. To understand the actual mechanism involved among these two, the values of $\beta_{\text{exp}}$ for PMMA and PMMA-PAni.Cu blends have been determined from the slopes of ln(I) versus $V^{1/2}$ plots.

Figure 4.19: Plots of $V^{1/2}$ versus ln (I) for PMMA and PMMA-PAni.Cu blends

These experimentally determined values of $\beta$ ($\beta_{\text{exp}}$) have been compared with those corresponding to Poole-Frenkel ($\beta_{PF}$) and Schottky-Richardson ($\beta_{RS}$) mechanisms, calculated using the procedure as already discussed in Chapter 1, Section-1.4. The value of $\beta_{\text{exp}}$ for PMMA and PMMA-PAni.Cu blends at different concentrations of PAni.Cu along with the calculated values of $\beta_{PF}$ and $\beta_{RS}$ are appended in table-4.5.
From the table, it is quite evident that the value of $\beta_{\text{exp}}=1.53\times10^{-5}$ eV, for pure PMMA, in comparison to $\beta_{\text{SR}}=1.89\times10^{-5}$ eV, clearly validates the applicability of Schottky-Richardson mechanism as the dominating charge transportation mechanism in this polymer. On embedding of 0.4% by weight of PAni.Cu in PMMA, an increase in the value of $\beta_{\text{exp}}$ is observed and reaches to $2.21\times10^{-5}$ eV but still remains closer to $\beta_{\text{SR}}$. This specifies that the charge carriers induced upto this concentration are too less in number to govern the conduction and the dominant role is played by the electrode injected charges only.

The further increase in the concentration of PAni.Cu in PMMA (1% by weight) results in the value of $\beta_{\text{exp}}$ to $2.56\times10^{-5}$ eV, which lies in between $\beta_{\text{SR}}$ and $\beta_{\text{PF}}$ and gives a signature of the initiation of conduction through Poole-Frenkel mechanism also. The increase in the value of $\beta_{\text{exp}}$ may be ascribed to the generation of localized charge states and increase in hopping probability of charge carriers in the PMMA matrix by means of increase in PAni.Cu concentration, similar to that for PMMA-PAni.Fe blends. With further increase in content of PAni.Cu (2% by weight), the resulting increased value of $\beta_{\text{exp}}$ to $2.56\times10^{-5}$ eV signifies the increase in the contribution of Poole-Frenkel conduction in charge transportation process, simultaneously with Schottky-Richardson conduction.
As the concentration of PANi.Cu is further raised (6% by weight) in blends, the increase in the value of $\beta_{\text{exp}}$ continues and becomes $3.09 \times 10^{-5}$ eV, which lies closer to $\beta_{\text{PF}} = 3.77 \times 10^{-5}$ eV than $\beta_{\text{SR}} = 1.89 \times 10^{-5}$ eV indicating the prominence of the number of induced charge carriers than those injected from the electrodes for conduction. At this situation, the conduction in the PMMA-PANi.Cu blend is mainly governed by Poole-Frenkel conduction mechanism, dominating over the Scottky-Richardson mechanism. At 10% concentration by weight, the value of $\beta_{\text{exp}}$ is further increased and attains a value $3.39 \times 10^{-5}$ eV, more close to $\beta_{\text{PF}}$, thus, inferring the major conduction through induced charge carriers and Poole-Frenkel mechanism becomes the dominant conduction mechanism.

From the above discussion, it can be concluded that the conduction, which is through Schottky-Richardson conduction mechanism for pure PMMA and its blends with lower concentrations of PANi.Cu, shifts towards the Poole-Frenkel mechanism as the concentration of PANi.Cu is increased in PMMA-PANi.Cu blends.

4.3.5 Dielectric Measurements

To understand the frequency dependent electrical response of PMMA and different PMMA-PANi.Cu blends, dielectric constant, dielectric loss and ac conductivity have been determined as a function of frequency.

(a) Dielectric Constant and Dielectric Loss

The variation in frequency dependent dielectric constant ($\varepsilon'$) of PMMA and PMMA-PANi.Cu blends with varying concentration of PANi.Cu has been shown in figure 4.20. From the figure, it can be seen clearly that the similar behaviour has been observed for PMMA-PANi.Cu, as that for PMMA-PANi.Fe blends. The values of dielectric constant reduce continuously with increase in frequency for all the samples. This may be due to the pronounced nature of dipolar polarization at lower frequencies and increase in intrawell hopping at higher frequencies.
Figure 4.20: Variation of dielectric constant with frequency for PMMA and PMMA-PAni.Cu blends

Table-4.6: Value of dielectric constant for PMMA and PMMA-PAni.Cu blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dielectric Constant at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 kHz</td>
</tr>
<tr>
<td>Pure PMMA</td>
<td>4.57</td>
</tr>
<tr>
<td>PMMA+0.4% PAni.Cu</td>
<td>3.92</td>
</tr>
<tr>
<td>PMMA+1% PAni.Cu</td>
<td>3.51</td>
</tr>
<tr>
<td>PMMA+2% PAni.Cu</td>
<td>3.12</td>
</tr>
<tr>
<td>PMMA+6% PAni.Cu</td>
<td>2.39</td>
</tr>
<tr>
<td>PMMA+10% PAni.Cu</td>
<td>2.09</td>
</tr>
</tbody>
</table>
Further, dielectric constant decreases with increase in the concentration of PANi.Cu in the blends in complete frequency range. This can be understood in terms of increased conductivity on increasing the conductive phase content in insulating PMMA matrix. The values of dielectric constant at different frequencies for PMMA-PANi.Cu blends are also included in table-4.6. From the table, it can be depicted that at 1 MHz, the value of dielectric constant, which is 4.06 for pure PMMA, attains a value of 1.98 on embedding 10% by weight of PANi.Cu in PMMA.

Figure 4.21 depicts the variation in dielectric loss ($\varepsilon''$) with frequency for pure PMMA and PMMA-PANi.Cu blends at varying concentration of PANi.Cu. It is obvious from this figure that $\varepsilon''$ decreases with increase in frequency. However, the values of dielectric loss at the same frequency increase continuously with increase in concentration of PANi.Cu. The observed behaviour of $\varepsilon'$ and $\varepsilon''$ for PMMA-PANi.Cu blends is consistent with that observed for PMMA-PANi.Fe blends, as presented in Section-4.2.5.

![Figure 4.21: Variation of dielectric loss with frequency for PMMA and PMMA-PANi.Cu blends](image-url)
(b) AC Conductivity

Figure 4.22 represents the variation in ac conductivity ($\sigma_{ac}$) plotted as a function of the concentration of PANi.Cu in PMMA at different frequencies. It is clearly observable from the figure that the value of ac conductivity increases with increase in the content of PANi.Cu up to a concentration of 2% by weight and afterwards, saturates at all frequencies indicating the attainment of percolation threshold. It is also evident from figure 4.22 that the values of ac conductivity have been found to increase consistently with increase in frequency at all concentrations. This may be attributed due to the reason that due to the fast reversal of applied time varying electric field, dipoles remain polarized and the charge carriers are able to hop from one dipolar conducting region to another, which is responsible for the enhanced conductivity of the PMMA-PANi.Cu blends with increase in frequency.

![Figure 4.22](image)

Figure 4.22: Variation of ac conductivity with concentration of PANi.Cu in PMMA at different frequencies

From the above discussion, it is apparent that the similar trends related to dielectric constant, dielectric loss and ac conductivity have
been observed for PMMA-PAni.Cu blends, as those for PMMA-PAni.Fe blends. Therefore, the variation in the values of these parameters for PMMA-PAni.Cu blends can be understood in the similar manner as that explained in detail for PMMA-PAni.Fe blends (Section-4.2.5).

4.4 A RELATIVE COMPARISON

As already discussed in Section-4.2 and 4.3 in this chapter, a systematic study related to the variation in the optical, electrical and structural behaviour of PMMA on blending it with different concentration of PAni doped with Fe and Cu salts, respectively has been carried out. This section is devoted to a comparison related to the induced variation in the properties under study of PMMA on embedding PAni.Fe and PAni.Cu at different concentrations.

Figure 4.23 presents the relative comparison of the values of optical energy gap of PMMA after blending with increasing concentration of PAni.Fe (curve ‘a’) and PAni.Cu (curve ‘b’).

![Figure 4.23: Variation in optical energy gap versus concentration of PAni.Fe/PAni.Cu in PMMA](image)
The figure clearly depicts the clear cut decrease in optical energy gap of PMMA with increasing filler concentration. However, the effect is more pronounced with about 34% reduction in optical energy gap after embedding PAni.Fe than 28% for PAni.Cu, at the maximum filler concentration of 10% by weight in both the cases.

Further, the dc conductivity has also been found to be increased considerably from $8.8 \times 10^{-16}$ S/cm (for virgin sample) to $4.17 \times 10^{-10}$ and $6.04 \times 10^{-10}$ S/cm after embedding PAni.Fe and PAni.Cu, respectively at a concentration of 10% by weight. This clearly indicates an increase in the conductivity of PMMA by 6 orders of magnitude on blending with PAni.Fe or PAni.Cu (10 weight %).

As far as dielectric behaviour is concerned, table-4.7 clearly shows a decrease in dielectric constant from 4.03, for pure PMMA, to 2.12 and 1.98 on embedding PAni.Fe and PAni.Cu (at 10 weight % concentration), respectively at frequency 1MHz; indicating the effect being more pronounced for PAni.Cu. Regarding dielectric loss, a considerably large increase from about 1.21 to about 6.03 (PAni.Fe) and 6.26 (PAni.Cu) has been noticed indicating almost the similar behaviour.

**Table-4.7: Comparison of frequency dependant electrical parameters for blends of PAni.Fe/PAni.Cu with PMMA (at 1 MHz frequency)**

<table>
<thead>
<tr>
<th>PAni content in PMMA (% by weight)</th>
<th>Dielectric Constant</th>
<th>Dielectric Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAni.Fe</td>
<td>PAni.Cu</td>
</tr>
<tr>
<td>0</td>
<td>4.06</td>
<td>4.06</td>
</tr>
<tr>
<td>0.4</td>
<td>3.80</td>
<td>3.77</td>
</tr>
<tr>
<td>1</td>
<td>3.40</td>
<td>3.38</td>
</tr>
<tr>
<td>2</td>
<td>3.21</td>
<td>3.01</td>
</tr>
<tr>
<td>6</td>
<td>2.54</td>
<td>2.28</td>
</tr>
<tr>
<td>10</td>
<td>2.12</td>
<td>1.98</td>
</tr>
</tbody>
</table>
From the above, it is apparent that a considerable reduction in optical energy gap, significantly large increase in conductivity, decrease in dielectric constant and increase in dielectric loss have been observed on blending PMMA with PANi.Fe/PANi.Cu at varying concentrations.

CONCLUSION

On embedding PANi (metal salts doped) in PMMA, a continuous change in optical, electrical and structural properties of this polymer with increasing filler concentration has been observed. About 30% reduction in optical energy gap, by about 6 orders of magnitude enhancement in dc conductivity and considerably large change in dielectric parameters have been observed at 10% concentration by weight of the embedded PANi.Fe/PANi.Cu in PMMA.
REFERENCES


Chapter 4: PMMA-PAni (metal salt doped) Blends


Chapter-4: PMMA-PAni (metal salt doped) Blends


