Chapter - 3

Synthesis and Electrical Studies on PANI/ZnFe$_2$O$_4$ Free Standing Thin Films
3.1 Introduction

Conducting polymers have received much attention during recent years due to their promising technological applications [1-4]. Polyaniline (PANI) is one of the important classes of conducting polymers studied during the last decade for many applications, such as electromagnetic interference (EMI) shielding [5], rechargeable batteries [6], sensors [7] and Schottky devices [2,4,8].

Polymer semiconductor nanocomposites generate a field for the development of advanced material in science and technology [9]. The study of nanocomposites based conducting polymeric materials is the topic of great current interest due to its novel properties such as special doping mechanism, high environmental stability, ease of processability. The oxidative polymerization of aniline is the chosen method, because bulk quantity can be synthesized by this technique [10-12]. The properties of nanocomposites are quite different from the constituent materials due to interfacial interaction between nanostructure semiconductors and polymers. Polymer nanocomposite materials provide synergetic properties like mechanical strength, thermal stability of the inorganic materials and flexibility, processability of the organic polymers [13-14]. There are many studies in electrical properties of PANI nanocomposites. The conductivity of nanocomposites depends on factors such as concentration, shape, size, orientation of the fillers, and interfacial interaction between the filler and host matrix [15-18]. The geometrical shape of the dispersed filler governs conductivity network formation in the matrix. The dielectric properties of the nanocomposite are affected by the filler matrix interaction and agglomeration of the filler in the matrix [19-20].
There have been few literatures dealing with synthesis of PANI/ZnFe$_2$O$_4$ nanocomposites and dielectric properties of PANI/ ZnFe$_2$O$_4$ nanocomposite [21-25]. The reports deal with oxidative polymerization of aniline in presence of ZnFe$_2$O$_4$. Prasanna et al report the dc electrical conductivity measurement in 80-300 K temperature range. Patil et al., have reported the ac conductivity of the nanocomposite at room temperature. There is no report on the dc conductivity behavior of PANI/ ZnFe$_2$O$_4$ nanocomposite. The studies are focused on synthesis and characterization of the composites at room temperature. Most of the studies on PANI/ ZnFe$_2$O$_4$ nanocomposite have been carried out to study the dielectric behavior at room temperature. There is no literature on study of electrical property of PANI/ZnFe$_2$O$_4$ nanocomposite above room temperature up to 573 K. It is important to understand the properties of these composites at higher temperature because of its possible uses at elevated temperature.

Studies on electric properties of emeraldine base PANI have shown that the solvent used to cast PANI films affect the electrical properties of PANI [26]. The most commonly used solvents to dissolve PANI are N-methylpyrrolidinone (NMP) and dimethyl propyleneurea (DMPU) [27]. These are high boiling point solvents. Dielectric studies on PANI have shown that PANI film cast with NMP will have residual solvent even after evaporation. It is about 10-18% by weight. In addition, it is shown that the C=O of NMP that is attached with PANI interferes with the dopant diffusion and thus results in doping on the surface than the bulk [27]. This would give a lower conductivity PANI film, which is not desirable. The dielectric property of such film shows that there is phase separation oxidized and reduced phase when compared to PANI powder [28]. Dielectric relaxation in conducting polymers in absence of permanent dipoles is due to hopping of charge carriers.
The presence of two phases would present barrier for the charge movement. It was shown in previous dielectric study that DMPU would not cause microphase separation in PANI due to low solvent content in PANI [29]. The addition of nanoparticles would be the only barrier for charge transport in PANI films [30, 31].

The present work deals with the synthesis of ZnFe$_2$O$_4$ nanoparticles and ZnFe$_2$O$_4$ nanoparticles dispersed polyaniline composites and study of their electrical properties at various temperatures. Free standing thin films were fabricated by a solution casting method. The structural and morphological properties of polymer nanocomposites were characterized by FTIR, XRD, AFM and TEM. The dielectric properties of PANI/ ZnFe$_2$O$_4$ nanocomposites above room temperature were investigated. The dc conductivity of the PANI/ ZnFe$_2$O$_4$ nanocomposite was determined both at room temperature (by four probe method) and higher temperature (frequency dependent method). It is observed that the conductivity of the composite decreases with increase in loading of the ZnFe$_2$O$_4$ nanoparticles in PANI matrix. The effect of non-conducting nanoparticles in a conducting polymer matrix in its non-conducting form was studied.

3.2 Experimental Details

3.2.1 Materials

Aniline AR grade was purchased from Aldrich and was distilled under vacuum and stored below -10 °C. Ammonium persulphate (NH$_4$)$_2$S$_2$O$_8$ (APS) ZnSO$_4$.7H$_2$O, FeSO$_4$.7H$_2$O and FeCl$_3$ of analytic purity and used without further purification.
3.2.2 *Synthesis of polyaniline (PANI)*

PANI was synthesized by oxidative polymerization of aniline in the presence of hydrochloric acid and an oxidizing agent ammonium persulfate (APS) [32]. The solution of 4.5 mL of aniline and 1 M of HCl prepared in double distilled water. This mixture was stirred in a double wall flask at temperature 0±1 °C. The solution of ammonium persulfate (11.46 gm in 100 mL) was added drop wise into the above solution at constant stirring. After 6 h, green color precipitate was obtained; the obtained precipitate was filtered through Buchner funnel and washed 3-4 times with double distilled water. The resultant precipitate was dried at 20 mm Hg pressure using vacuum oven at 333 K for 20 h and grinded in pestle mortar to get powder form of HCl doped conductive PANI. The HCl doped conductive PANI powder was treated with 1 M ammonia solution to obtain undoped PANI in emeraldine base form.

*Figure. 3.1.* Flow chart of synthesized PANI by employing oxidative polymerization.
3.2.3 Preparation of ZnFe$_2$O$_4$ nanoparticles

Reagents used in this synthesis scheme are of analytical grade and used without further purification. Zinc ferrite nanoparticles were prepared by co-precipitation [33,34], using high purity ZnSO$_4$.7H$_2$O, FeSO$_4$.7H$_2$O and FeCl$_3$ materials. Equimolar (0.5 M) solution of all the reagents were prepared in de-ionized water mixed together and this cationic solution stirred to get complete dissolution. Further, the 1 M NaOH solution, which was kept at 333 K, was added drop wise into cationic solution with constant stirring and heating until precipitation occurs. Heating of the precipitate in its alkaline condition was continued to a soaking temperature of 373 K for 30 min in order to complete the reaction. The precipitated particles were filtered and washed with double distilled water and dried under 20 mm Hg at 333 K for 12 h. Free flowing nanoparticles were obtained by grinding co-precipitated ferrite agglomerates using pestle mortar. These particles were calcined in silica crucible at 673 K for further crystallization.

3.2.4 Preparation of freestanding thin film

Solution of ZnFe$_2$O$_4$ nanoparticles were prepared by dispersing in dimethyl propylene urea (DMPU) under sonication and quantitative amount of previously synthesized deprotonated PANI is added to above solution under vigorous stirring to get a good dispersion. Finally the resulting suspension is filtered through syringe filter of 50 μm and the suspension is cast on to cleaned glass plates, dried in 20 mm Hg at 323 K for 12 h to obtain free standing film of PANI/ZnFe$_2$O$_4$ nanocomposites. Free standing films of PANI/ZnFe$_2$O$_4$ nanocomposites with 25% weight fraction of ZnFe$_2$O$_4$ nanoparticles was named as sample P1 and subsequent composites with concentration of ZnFe$_2$O$_4$ nanoparticles at 37.5% and 50% as P2 and P3 respectively.
3.2.5 *Preparation of samples for dielectric characterization*

ZnFe$_2$O$_4$ nanoparticles pellet and P1 and P3 free standing thin films were used to measure dielectric properties. Silver paint was applied on the both sides of the thin films with connected probe to make a film as electrodes. The contact area of the thin film was 0.785 cm$^2$ with thickness being 0.087 mm. The contact area of the electrode with the P1 and P3 was 0.632 cm$^2$ and 0.812 cm$^2$ respectively. The thickness of the P1 and P3 film was 0.897 mm and 1.02 mm respectively.

![Figure 3.2](image.png)

*Figure 3.2. PANI/ZnFe$_2$O$_4$ nanocomposites free standing thin films for dielectric measurement.*

3.3 *Characterization techniques*

Fourier transform infrared spectroscopy (Thermo electron model Nicolet 5700 FTIR) was used to characterize the integrity of chemical composition of prepared free-standing thin films. FTIR spectra were recorded in the frequency range 4000 cm$^{-1}$ to 400 cm$^{-1}$. X-ray powder diffraction patterns (X-Pert PRO, Panalytical X-Ray diffractometer) were used to study the crystallinity of free-standing thin films. Atomic force microscopy (AFM-Nanosurf easy Scan 2), and transmission electron microscopy (TEM-Tecnai F-30) were used for morphological studies. Electrical conductivity was measured by four probe technique (Keithley 2182A nanovoltmeter, 6221 current source). Dielectric measurements were carried out using impedance analyzer (Novocontrol Alpha...
A) with $V_{\text{rms}}$ of 10 mV. The room temperature measurements were carried out at a frequency range of $10^2$-$10^6$ Hz. The high temperature measurements were carried out in the frequency range of $10^2$-$10^6$ Hz and temperature range of 303-573 K with a heating rate of 1 K/min.

3.4 Results and Discussion

3.4.1 XRD, FTIR, AFM, SEM and TEM analysis

X-ray diffraction patterns for neat PANI Emeraldine base form and samples P1, P2, P3 thin films with increasing loading of ZnFe$_2$O$_4$ nanoparticles, also the XRD of ZnFe$_2$O$_4$ nanoparticles powder are shown in Figure 3.3((a)-(e)). Diffraction pattern for ZnFe$_2$O$_4$ nanoparticles [Figure 3.3(e)] shows a cubic spinel phase with fcc structure (JCPDS card No. 82-1042) with no extra reflections and are well indexed to the crystallographic planes of spinel ferrite (220), (311), (400), (422), (511), and (440). Corresponding to the reflection plane (311) at $2\theta = 35.18^\circ$ the average particle size was calculated by Debye-Scherrer’s formula given by,

$$d = \frac{0.89\lambda}{\beta \cos \theta}$$

Where $d$ is the size of the particle, $\lambda$ the X-ray wavelength, $\beta$ the full width half maxima expressed in unit of $2\theta$, and $\theta$ is the Bragg’s angle, average particle size for neat ZnFe$_2$O$_4$ is found to be 10 nm and increases with decreasing content of ZnFe$_2$O$_4$ in PANI matrix. In the Figure 3.3(a) we can observe that, the neat polyaniline has broad peak (Figure 3.3(a)) in the region of 15–30°. For 25% loading of ZnFe$_2$O$_4$ nanoparticles in PANI matrix (P1) the peak has slightly shifted. Thereafter for higher loading –P2 (Figure 1(c)) and P3 (Figure 3.3(d)) characteristic peaks of ZnFe$_2$O$_4$ nanoparticles (shown in Fig 3.3(e)) begins to dominate. Hence, the broad peak of PANI (15–30°) disappears in Figure
3.3(d). With increasing ZnFe$_2$O$_4$ nanoparticles loading the characteristic peak of ZnFe$_2$O$_4$ nanoparticles were observed in the PANI/ZnFe$_2$O$_4$ nanocomposite along with the characteristic peak of PANI. It is interesting to note that the amorphous nature of the PANI decreases with the increase in the concentration of the ZnFe$_2$O$_4$ nanoparticles. This can be attributed to the presence of higher amount of nanoparticles in the PANI/ZnFe$_2$O$_4$ nanocomposite. The PANI/ZnFe$_2$O$_4$ nanocomposites however reveal broadening of the ferrite peaks with increase in doping level. This indicates that the crystal structure of ZnFe$_2$O$_4$ nanoparticles is not modified by the PANI in the composites. As the concentration of nanoparticles increased in PANI matrix, the characteristic peak of PANI slowly decreases, at 50% loading it completely disappears. Relative intensity of the characteristic peaks of PANI/ZnFe$_2$O$_4$ nanocomposites thin films increases in the ZnFe$_2$O$_4$ content. These results indicate that the addition of ZnFe$_2$O$_4$ nanoparticles induces the crystallinity in PANI.

Figure 3.3. XRD patterns of (a) neat PANI film, (b) P1 (c) P2 (d) P3 free standing films, (e) ZnFe$_2$O$_4$ nanoparticle.
Figure 3.4 shows the FTIR spectra of PANI and PANI/ZnFe$_2$O$_4$ nanocomposites thin films at various loadings. Figure 3.4(a) shows presence of the characteristic absorption bands of PANI such as C=C stretching deformation of the quinoid ring at 1567 cm$^{-1}$, benzoid ring at 1446 cm$^{-1}$, C-N stretching of secondary amine in PANI main chain at 1218 cm$^{-1}$ and C-H out-of-plane bending mode is observed at 775 cm$^{-1}$. From Figure 3.4(b)–(d) it is observed that, as the percentage loading of ZnFe$_2$O$_4$ nanoparticles in PANI matrix increases, the stretching vibration of C-N in benzoid ring and absorption, shift towards the lower wavelength region. At 50% loading of ZnFe$_2$O$_4$ nanoparticles ‘P3’ we observed the peak at 1218 cm$^{-1}$ for neat PANI is shifted to 1241 cm$^{-1}$ and also the C=C peak corresponding to benzoid ring at 1446 cm$^{-1}$ in PANI completely shifts towards 1486 cm$^{-1}$ in P3. These results indicate that there is a strong interaction between the secondary amine in polymer main chain and ZnFe$_2$O$_4$ nanoparticles due to the adsorption of PANI molecular chain onto surface of ZnFe$_2$O$_4$ nanoparticles [22].

![FTIR spectra](image)

*Figure 3.4. FTIR spectra of (a) neat PANI (b) P1 (c) P2 (d) P3 free standing films.*
AFM images (Figure 3.5) for PANI and PANI/ZnFe$_2$O$_4$ nanocomposite, show distinct characteristics morphology of PANI film, which is smooth and continuous with some pinholes. As the concentration of ZnFe$_2$O$_4$ nanoparticles increases, small and large islands adjacent to a smooth continuous film can be observed. As loading percentage augmented to 50%, the roughness of the surface enhances. AFM images shows, with increase in loading concentration of the free-standing films of PANI with nano-sized ZnFe$_2$O$_4$, change in morphology was observed. PANI/ZnFe$_2$O$_4$ nanocomposite films were observed to have a homogeneous morphology with very fine distribution of nanoparticles coated with PANI with various concentrations.

Figure 3.5. AFM images of a) neat PANI (b) P1 (c) P2 and (d) P3 free standing thin films.
SEM image for various loadings of ZnFe$_2$O$_4$ nanoparticles and their composites, P1, P2, and P3, in PANI matrix are shown in Figure 3.6. From this figure, it can be seen that the SEM image of neat conducting PANI film shows independent fine clear and smooth surface. Further, where the concentration of ZnFe$_2$O$_4$ is 25%, it observe that a very thin white layer of ZnFe$_2$O$_4$ in the surface of PANI film. As the concentration of ZnFe$_2$O$_4$ particles increases to 37.5%, the dispersion of ZnFe$_2$O$_4$ becomes thicker in PANI film. On further increasing the concentration of ZnFe$_2$O$_4$ to 50%, almost completely overcoats of the ZnFe$_2$O$_4$ particles. SEM studies reveals that, with higher concentration of ZnFe$_2$O$_4$ during the mechanical grinding of PANI with ZnFe$_2$O$_4$ nanoparticlecs, PANI undergoes interfacial interactions with ZnFe$_2$O$_4$ crystallites and loses its own morphology by its coating over ZnFe$_2$O$_4$ crystallites which evident from XRD study.

Figure 3.6. SEM micrographs of (a) neat PANI (b) P1 (c) P2 (d) P3 free standing films.
TEM images of ZnFe$_2$O$_4$ nanoparticles (shown in Figure 3.7) are in good agreement with the crystallite sizes obtained by Debye–Scherrer approximation. A phase corresponding to ZnO was observed in XRD pattern, which indicates the presence of ZnO as a separate phase. In TEM image shows a layer of ZnO around the single crystal domain of Fe$_2$O$_4$ nanoparticles [34].

![TEM image of Fe3O4ZnO nanocomposites](image)

**Figure 3.7.** TEM image of Fe3O4ZnO nanocomposites

The electrical conductivity of the free standing PANI film and various concentrations of ZnFe$_2$O$_4$ nanoparticles loaded PANI films doped with 1 M HCl solution were measured by the four–probe technique. The conductivity of PANI is 1.32 ± 0.006 S$	ext{cm}^{-1}$, P1 is 0.67±0.041, P2 is 0.79 ± 0.0051 S$	ext{cm}^{-1}$ and P3 is 0.79±0.0047 at room temperature. The increase in weight loading of nanoparticles into the PANI matrix reduces the conductivity from 1.32 ± 0.006 S$	ext{cm}^{-1}$ to 0.79 ± 0.004 S$	ext{cm}^{-1}$ in P3. Prasanna et al [22] have also observed decrease in conductivity of PANI/ZnFe$_2$O$_4$ nanocomposite with the incorporation of ZnFe$_2$O$_4$. The decrease in conductivity was attributed to increase in charge carrier scattering. However, other possibilities such as charge trapping due to nanoparticles themselves or due to morphological changes and defects produced by the
nanoparticles were not ruled out. In this work, the observed decrease in conductivity could be due to the partial blockage of charge carriers in conductive path of PANI matrix by ZnFe$_2$O$_4$ nanoparticles. This has been shown in dielectric study of the PANI/ZnFe$_2$O$_4$ nanocomposite in following section.

The dielectric properties of PANI/ZnFe$_2$O$_4$ nanocomposites were studied at both room temperature and up to 573 K. Figure 3.8 shows the variation of permittivity as a function of frequency of PANI, P1, P2 and P3 at room temperature. Although at lower frequencies, it shows that permittivity of PANI/ZnFe$_2$O$_4$ nanocomposite is lower than PANI, at frequencies greater than 100 Hz it is observed that permittivity of P1 is almost same as PANI and begins to increase for higher loadings. Figure 3.10 shows the variation of tan δ with frequency at room temperature. The value of loss tangent is less than PANI for all composites. This suggests that these materials act as lossless materials. The permittivity of PANI and nanocomposites with the ZnFe$_2$O$_4$ nanoparticles was compared. Figure 3.9 shows the variation of permittivity as a function of volume fraction of ZnFe$_2$O$_4$ nanoparticles in PANI at four selected frequencies. It may be noted that permittivity for 50% loading i.e., P3, is higher than permittivity of PANI, P1 and P2. At 1 MHz, permittivity of PANI and ZnFe$_2$O$_4$ nanoparticles is ~ 23 and for P3 it is ~ 51.

It can be observed that there is no much change in permittivity of P2 and P3 whereas in 50% loading of ZnFe$_2$O$_4$ in PANI has higher dielectric constant than PANI and ZnFe$_2$O$_4$ nanoparticles. This is may be due to the fact that 50% loading of ZnFe$_2$O$_4$ nanoparticles might have exceeded the critical concentration of nanoparticles in PANI matrix. The dielectric response of heterogeneous systems is usually given by Maxwell-Wagner-Sillars (MWS) polarization [35]. There are no permanent dipoles in conducting
polymers. The charge trapping and its localized motion when an alternating external field is applied, the trapped charge acts as dipole. The charges hop between localized sites in presence of alternating electric field. This will give rise to dielectric relaxation in conducting polymer [28]. In case of nanocomposites, the inclusions also act as charge trapping centers and thus affect the charge transport property of matrix. When charges encounter the inclusions in the nanocomposites, the different conductivity and dielectric constant of matrix and inclusion, will lead to accumulation of charges at the interface of inclusion and matrix. This will eventually lead to interfacial polarization and hence the permittivity increases [36]. Figure 3.8 indicates that P3 has higher permittivity ~ 68 at 103 kHz than PANI, P1 and P2. The ZnFe$_2$O$_4$ nanoparticles in PANI/ZnFe$_2$O$_4$ nanocomposites film act as charge trapping centers due to which the charge carrier would be localized and result in increase of polarization and therefore permittivity and Figure 3.11 shows the variation of tan δ with volume fraction of PANI/ZnFe$_2$O$_4$ nanocomposite. The loss tangent of P3 is less than that for ZnFe$_2$O$_4$. P3 is a low loss nanocomposite than ZnFe$_2$O$_4$ nanocomposite.

![Figure 3.8](image)

*Figure 3.8.* Variation of permittivity $\varepsilon'$ with log f for PANI, P1, P2, P3 at room temperature.
Figure 3.9. Variation of $\varepsilon'$ with weight fraction of ZnFe$_2$O$_4$ nanoparticles for PANI, P1, P2, P3 and ZnFe$_2$O$_4$ nanoparticles at selected frequencies at room temperature.

Figure 3.10. Variation of $\tan \delta$ with log $f$ for PANI, P1, P2, P3 at room temperature.
Figure 3.11. Variation of $\tan \delta'$ with weight fraction of ZnFe$_2$O$_4$ nanoparticles for PANI, P1, P2, P3 and ZnFe$_2$O$_4$ nanoparticles at selected frequencies at room temperature.

The effect of temperature on dielectric properties of PANI/ZnFe$_2$O$_4$ nanocomposites in DMPU are studied in this work. It has been shown in the previous work that PANI-DMPU films shows two relaxation processes above room temperature in loss tangent–temperature plot [29]. The microphase separation is absent in PANI film with DMPU as solvent due to low content of residual solvent. Thus in absence of microphase separation, ZnFe$_2$O$_4$ nanocomposites in PANI can change the relaxation processes occurring in PANI film. The dielectric properties of PANI/ZnFe$_2$O$_4$ nanocomposites with low loading P1 and higher loading P3 were analyzed up to 573 K. Figure 3.12 and 3.13 shows the variation of real part of the relative permittivity $\varepsilon'$ and loss tangent of the P1 as a function of temperature for selected frequencies. The permittivity increases slowly in the beginning with increasing temperature until ~373 K (Figure 3.12). At 100 Hz the permittivity shows a peak around 453 K. For higher frequencies $\varepsilon'(T)$ exhibits a shoulder at ~463 K and a peak at ~553 K. The maxima in the permittivity function of the sample are more clearly revealed in the temperature variation of loss tangent plot (see Figure 3.13). The inset in Figure 3.13 shows magnified plot. At 100 Hz, the loss tangent exhibits a peak
at ~423 K. As the frequency is increased (above 540 Hz), two maxima cannot be distinguished clearly. The decrease in loss tangent is smaller. The frequency corresponding to the two relaxation processes is a function of inverse of temperature as shown in Figure 4.5. The activation energy calculated from the Arrhenius relationship for the two relaxation processes is ~1.58 eV and ~1.52 eV. The activation energy for both relaxations was observed to be same. The activation energy for two relaxation processes in PANI was ~ 0.5 eV and ~ 1.5 eV [29]. Thus with increase in loading of ZnFe₂O₄ nanoparticles in PANI, the relaxation processes in PANI has been modified. For 25% of the loading of ZnFe₂O₄ nanoparticles, the activation energy has increased. Figure 3.14 shows the variation of real part of the relative permittivity ε' and loss tangent of the P3 as a function of temperature. At 100 Hz, ε' shows a peak at 503 K. At higher frequencies ε' increases with increase in temperature. A single peak in loss tangent plot was observed. The loss tangent peak temperature increases with increasing frequency. The frequency corresponding to this relaxation process was plotted as a function of inverse of temperature in terms of an Arrhenius plot (Figure 3.17) to obtain an estimate of the activation energy. The activation energy calculated is ~0.89 eV. The activation energy for 50% loading of ZnFe₂O₄ nanoparticles has decreased the activation energy than for 25% loading.

![Figure 3.12. Temperature variation of (a) relative permittivity ε' of P1 at selected frequencies.](image-url)
Figure 3.13. Temperature variation of loss tangent $\tan \delta$ of P1 at selected frequencies. The inset in shows magnified plot.

Figure 3.14. Temperature variation of relative permittivity $\varepsilon'$ of P3 at selected frequencies.

Figure 3.15. Temperature Variation of loss tangent $\tan \delta$ of P3 at selected frequencies. The inset shows magnified plot.
Figure 3.16. Arrhenius plot of the frequencies with temperature corresponding to the two peaks observed in Figure 4.1 for P1.

Figure 3.17. Arrhenius plot of the frequencies with temperature corresponding to the maxima observed in Figure 4.3 for P3.
The observed dielectric results indicated that the addition of ZnFe$_2$O$_4$ nanoparticles has altered the charge transport properties of PANI film. For 25% loading, the activation energy for charge hopping increases. This is because hopping sites are far apart. As loading increased to 50%, ZnFe$_2$O$_4$ nanoparticles would be closer and charge hopping to the neighboring sites would be with lesser energy than for 25% loading. This indicates that P3 acts as low loss nanocomposite than P1 and P2. Thus, the only additional barrier for the charge transport other than inherent disorder in PANI film is ZnFe$_2$O$_4$ nanoparticles added to the film.

The dielectric loss spectra for PANI/ ZnFe$_2$O$_4$ did not show any change with temperature. Well-defined peaks were not observed in the dielectric loss ($\varepsilon''$) spectra. In such case relaxation mechanism can be obtained from electric modulus representation.

The complex electric modulus is given as $M^* = \frac{1}{\varepsilon^*}$ where $\varepsilon^* = \varepsilon' + i\varepsilon''$

$$M^* = M' + M''$$

$$M' = \frac{\varepsilon'}{(\varepsilon' + \varepsilon''^2)} \quad (a)$$

and

$$M'' = \frac{\varepsilon''}{(\varepsilon' + \varepsilon''^2)} \quad (b)$$

The variation of $M'$ and $M''$ with frequency log $\omega$ is plotted. $M'$ and $M''$ were calculated using equations (a) and (b) respectively.

The plot of $M''$ with log $\omega$ (Figure 3.18 (a)-(c)) shows a peak at a particular relaxation frequency which increases towards higher frequencies with increase in temperature for PANI, P1 and P3. With increase in temperature there is increase in charge motion. Hence conductivity increases. It is also observed that with increase in loading of
ZnFe$_2$O$_4$ nanoparticles into emeraldine base PANI, the relaxation peak is shifted towards lower frequency. Theoretically, maximum of $M''$ shifts towards higher frequencies when conductivity of the material increases [37]. However in this case, there is shift towards lower frequency when there is increase in loading of nanoparticles. This suggests that the conductivity decreases for P1 and P3 than that for PANI. This can be confirmed from frequency dependent conductivity plot.

**Figure 3.18.** Plot of electric loss modulus ($M''$) versus log $\omega$ for (a) PANI (b) P1 and (c) P3.

Figure 3.19 (a)-(c) shows the variation of frequency dependent conductivity of PANI, P1 and P3. At lower frequencies, frequency dependent conductivity was found to be almost constant. Extrapolation of this line onto y-axis is taken as $\sigma_{dc}$. It is observed that the $\sigma_{dc}$ value of PANI decreased as the loading of ZnFe$_2$O$_4$ nanoparticles increased. The $\sigma_{dc}$ values for PANI, P1 and P3 at 30 °C are $1.29 \times 10^{-8}$ Scm$^{-1}$, $0.76 \times 10^{-8}$ Scm$^{-1}$ and $0.52 \times 10^{-6}$ Scm$^{-1}$, respectively (Figure 3.20). The dc conductivity obtained from four probe measurement also showed similar trend – conductivity decreases with increase in loading.
of ZnFe$_2$O$_4$ nanoparticles. Hence the ZnFe$_2$O$_4$ nanoparticles act as charge trapping center in PANI/ZnFe$_2$O$_4$ nanocomposite film.

**Figure 3.19.** Frequency dependent conductivity plot (log $\sigma$ vs log $\omega$) for (a) PANI (b) P1 and (c) P3.

**Figure 3.20.** DC conductivity in temperature range 303-423 K for (a) PANI (b) P1 and (c) P3.
3.5 Conclusion

PANI and ZnFe$_2$O$_4$ nanoparticles were successfully synthesized via oxidative polymerization of aniline methods and co-precipitation method, respectively; free-standing thin films were prepared by drop casting. The result of FTIR spectroscopy and XRD indicates an interaction between PANI back bone chain and ZnFe$_2$O$_4$ nanoparticles. The conductivity (obtained by four probe method) decreases from $1.32 \pm 0.006 ~\text{Scm}^{-1}$ to $0.79 \pm 0.004 ~\text{Scm}^{-1}$ with increase in loading of ZnFe$_2$O$_4$ particles in PANI matrix. Dielectric studies of PANI/ZnFe$_2$O$_4$ nanocomposites were carried out. The dielectric constant for 50% loading of ZnFe$_2$O$_4$ nanoparticles in PANI matrix is higher compared to PANI and other compositions. The higher dielectric constant for 50% loading may be due to ZnFe$_2$O$_4$ nanoparticles acting as charge trapping centre resulting in increase of polarization. The study of dielectric property at higher temperature indicates that the nanoparticles added to PANI have changed the dielectric property of PANI. Loss tangent of PANI had shown presence of two peaks at higher temperature. For 25% loading, PANI/ZnFe$_2$O$_4$ nanocomposite shows two small peaks which cannot be distinguished clearly. For 50% loading a single peak was observed in loss tangent which can be attributed to presence of ZnFe$_2$O$_4$ nanoparticles. The electric modulus and frequency dependent conductivity measurements also indicate that the conductivity of PANI/ZnFe$_2$O$_4$ nanocomposites decreases with the increase in loading of ZnFe$_2$O$_4$ nanoparticles. This suggests that ZnFe$_2$O$_4$ nanoparticles act as charge trapping center in PANI/ZnFe$_2$O$_4$ nanocomposites film.
References


