CHAPTER 4
4.1. INTRODUCTION

Recently, material science has been shown to offer many effective methods for the preparation of conductive fibers based conducting polymers for several applications such as in light emitting diodes, supercapacitors, chemical sensors and nonlinear optics [1–4]. Electrospinning is a process by which fibers with sub-micron diameters can be obtained. Recently [5], we have prepared conductive fibers of polyaniline:polyacrylonitrile by stirring aniline and polyacrylonitrile solution with the help of magnetic bar. In this technique the conductivity of the fibrous material depends on the ratio of conducting polymer present in the fibrous material. It is difficult directly to form fibers of conducting polymers. Thus stirring process is applied to form fibers of conducting polyaniline and polyacrylonitrile. Electrically conducting polymers are an important and interesting class of new organic materials that have gained considerable attention in the recent years. These polymers have been used in many applications including sensors [6,7], switchable membranes [8], anticorrosive coatings [9,10], biosensors [11], electrochromic devices [12] and rechargeable batteries [13,14]. Most of the works in this area are focused on the dynamic reversible redox properties of the polymers. One of the most important class, ES of conducting polymers has been studied extensively [15]. Polyaniline can be doped and undoped on exposure to an acidic or alkaline environment without changing the number of $\pi$-electrons in the polymer [16]. This mechanism can be attributed to the presence of $-\text{NH}$ and $-\text{N}$– groups in the polymer backbone whose protonation and deprotonation brings a change in the electronic conductivity as well as in the color of the polymer [17]. It is believed that all or some of the nitrogen atoms (amines or imines) in any species can be protonated with protonic acids [18].
This aspect of doping and undoping makes polyaniline and its analogs highly suitable for industrial applications.

The electronically conductive polymeric filler can also have a strong effect on the electrical properties (DC conductivity and AC impedance) of the composite, but only when the fillers are highly conductive compared to the matrix [19,20]. Long, thin inclusions like fibers, which are insulating with respect to the matrix, have little effect on overall electrical properties [21], although they can affect mechanical properties. The electrical behavior of the fibers due to the presence of highly conductive filler is typically discussed with reference to the percolation threshold [22,23]. When enough conductive filler have been added to the matrix, the fibers are above the percolation threshold, which is defined as a characteristic volume or number fraction of filler at which continuous paths for electrical current exist in the composite. Some of these paths can occur through parts of the matrix where there is dielectric breakdown between filler tips, although most of the conduction is probably through touching fillers. PAN is one of the most important polymers for making fiber because of its high strength, high abrasion resistance and good insect resistance. In the present study, the fibers were made up of insulating polymer (polyacrylonitrile) with conducting polymer (polyaniline). These fibers are a new promising material from two perspectives; first the electrical conductivities are enough for a broad range of applications, secondly the formation of fibers using stirring technique in this study is superior to chemical synthesis given the consideration of time and cost parameters.
4.2. EXPERIMENTAL

4.2.1. Reagents and Chemicals

The following reagents and chemicals were used: Aniline, 99% (CDH, India), Polyacrylonitrile (from Research, Design and Standard Organization, India), Hydrochloric acid, 35% (E. Merck, India), Sulfuric acid (Qualigens), Perchloric acid (E. Merck, India), Ammonium persulphate, (CDH, India) and Tetrahydrofuran (CDH, India). All the experiments were conducted with double distilled water.

4.2.2. Preparation of Conductive Fibers

Conducting fibers of PANI:PAN composite were prepared in various volume ratios of aniline with polyacrylonitrile solutions by stirring vigorously at room temperature. 1gm of polyacrylonitrile was dissolved in 25 mL of tetrahydrofuran and different volumes (1, 3, 5 and 6 mL) of aniline were added to this polyacrylonitrile solution (Table 4.1). The solutions were well mixed with glass rod and then was poured drop wise in water with vigorous stirring to prepare the fibers. The prepared fibers were kept in 200 mL of 0.1M (NH₄)₂S₂O₈ solution and refrigerated overnight in order to oxidative polymerize aniline in the polyacrylonitrile matrix. The fibers were washed with doubly distilled water and acetone and were left overnight with 2% ammonia solution, it was again washed with doubly distilled water, resulting in base free and undoped fibers. These fibers were doped with 0.1M (HCl, H₂SO₄ and HClO₄) acid solutions to convert the polyaniline emeraldine base into electrically conducting fibers. The pellets of these fibers were made by hydraulic pressure machine (25 KN). DC conductivity measurements of the fibers were performed at room temperature using four in-line probes (DMV 001 Roorkee, India).
Table 4.1. Preparation details of polyaniline:polyacrylonitrile composite fibers.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>PAN (g)</th>
<th>THF (mL)</th>
<th>Amount of aniline in 1 g of PAN solution (mL)</th>
<th>Electrical conductivity $\sigma$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI:PAN–1</td>
<td>1</td>
<td>25</td>
<td>1</td>
<td>$\sim 10^{-3}$</td>
</tr>
<tr>
<td>PANI:PAN–2</td>
<td>1</td>
<td>25</td>
<td>3</td>
<td>$\sim 10^{-3}$</td>
</tr>
<tr>
<td>PANI:PAN–3</td>
<td>1</td>
<td>25</td>
<td>5</td>
<td>$\sim 10^{-1}$</td>
</tr>
<tr>
<td>PANI:PAN–4</td>
<td>1</td>
<td>25</td>
<td>6</td>
<td>$\sim 10^{-1}$</td>
</tr>
</tbody>
</table>
4.2.3. Characterization

The FTIR spectra of polyaniline and conducting fibers were recorded by Perkin Elmer-1725 instrument. The SEM studies were performed on a LEO-435 VP instrument to examine the surface morphology of the fibers and their components. The thermogravimetric analysis (TGA) were performed on the composite using Perkin Elmer (Pyris Dimond) instrument heating the materials from ~25 °C to 600 °C at the rate of 10 °C min⁻¹ in nitrogen atmosphere with the flow rate of 30 mL/min. The XRD patterns were recorded using CuKα radiation with the help of X-ray diffractometer 9 Philips PW 17290. The DC electrical conductivity of the differently doped fibers pellet was measured with increasing temperature (35 °C to 130 °C) using four-in-line probes, DC electrical conductivity measuring instrument.

DC electrical conductivity (σ) was calculated using the following equations—

\[ \rho = \frac{\rho_o}{G_\gamma(W/S)} \]  \hspace{1cm} (1)

\[ G_\gamma(W/S) = (2S/W)\ln 2 \] \hspace{1cm} (2)

\[ \rho_o = \frac{V}{I}2\pi S \] \hspace{1cm} (3)

\[ \sigma = \frac{1}{\rho} \] \hspace{1cm} (4)

Where \( G_\gamma(W/S) \) is a correction divisor which is a function of thickness of the sample as well as probe-spacing while I, V, W and S are current (A), voltage (V), thickness of the film (cm) and probe spacing (cm) respectively. The isothermal stability of the pellets in terms of DC electrical conductivity retention was carried out on the selected samples at 50 °C, 70 °C, 90 °C, 110 °C and 130 °C in an air oven. The electrical conductivity measurements were carried out at an interval of 15 min.

The sample to be tested was placed on the base plate of four-probe arrangement and the probes were allowed to rest in the middle of the sample. A very gentle pressure was applied on the probes and then it was tightened in that position so as to avoid piercing of the probes into the samples. This arrangement was placed
in electrically controlled oven. The current was passed through the outer probes and the floating potential across the inner pair of probes was measured. The power supply of the oven was then switched on and the temperature was allowed to increase gradually. The current and voltage were recorded simultaneously with rise in temperature.

4.3. RESULTS AND DISCUSSION

4.3.1. Electrical Properties

The electrical conductivity of the fibers having 1, 3, 5 and 6 mL of aniline increases from $10^{-5}$ to $10^{-1}$ S/cm after doping the fibers in hydrochloric acid for 24 h. The effect of aniline content on electrical conductivity of the PANi:PAN composite fibers is plotted in Fig. 4.1. When the volume fraction of aniline reaches to 5 mL, the conductivity increases from $10^{-6}$ to $10^{-1}$ S/cm. The saturation in conductivity also reached when amount of aniline reaches to 5 mL. The conductivity increases sharply when the volume ration of aniline is less than 4 mL, after that it gradually reached to $10^{-1}$ S/cm when amount of aniline reaches to 5 mL. It is evident that the percolation of the conductive fibers should be less than 5 mL of aniline volume. Hence, the threshold conductivity was reached with 5 mL of aniline loading. Fibers of PANi:PAN composite with 5 mL aniline has also shown better conductivity as compared to our previous reported work [24,25]. Therefore, the fibers (5 mL of aniline solution) were selected for the study of temperature dependence of electrical conductivity up to 100 °C with different doping agents’ viz. HCl, H$_2$SO$_4$ and HClO$_4$ (0.1 M). The fibers doped with H$_2$SO$_4$ and HClO$_4$ had lower magnitude of conductivity when compared to fibers doped with HCl (Fig. 4.1).
Fig 4.1. Conductivity versus HCl, H₂SO₄ and HClO₄ doped composite fibers with increasing temperature (30 to 100 °C).
4.3.2. FTIR Characterization

The interaction between polyaniline and the polyacrylonitrile matrix was investigated via fourier-transform infrared spectral analysis. Fig. 4.2 shows the FTIR spectra of polyaniline, polyacrylonitrile and hydrochloric acid doped fibers and the FTIR values are presented in Table 4.2. The band corresponding to out of plane bending vibration of C−H bond of p-disubstituted benzene rings appears at 824 cm$^{-1}$. The bands corresponding to stretching vibration of N−B−N and N=Q=N structures appeared at 1497 cm$^{-1}$ and 1587 cm$^{-1}$ respectively where −B− and =Q= stands for benzenoid and quinoid moieties in the polyaniline. These relative lower frequencies of benzenoid and quinoid ring stretching are due to the salt formation with HCl [26]. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C−N bond appears at 1143 cm$^{-1}$ and 1302 cm$^{-1}$. The FTIR spectrum supports the presence of benzenoid as well as quinoid moieties in the polyaniline [27]. The characteristic broad band for −CN groups in polyacrylonitrile appeared around 1995 cm$^{-1}$. The peaks at 3251, 3239 and 3280 cm$^{-1}$ were observed for PANI:PAN(1), PANI:PAN(2) and PANI:PAN(3) respectively. As the amount of polyaniline increased the intensities of these peaks also increased. Other characteristic peaks for conducting fibers of PANI:PAN composite were also observed at 2239 and 1162 cm$^{-1}$. Two characteristic bands for CH$_2$ appeared around 1451 cm$^{-1}$ and 750 cm$^{-1}$ for the bending and rocking vibrations, respectively. In the spectrum a broad band in the region at 3370 cm$^{-1}$ may be due to the presence of external water molecule, while a sharp peak in the region at 1644 cm$^{-1}$ is referred to the bending vibration of water. In the composite, the gradual increase in the intensities of the bands corresponding to PANI and decrease in the band corresponds to PAN supports the gradual change in the composition of the composite formulation as evident from FTIR spectra.
Fig 4.2. FTIR spectra of (a) PANI, (b) PAN, (c) PANI:PAN–1, (d) PANI:PAN–2 and (e) PANI:PAN–3
Table 4.2. FTIR peak positions (cm$^{-1}$) of polyaniline, polyacrylonitrile and fibers of polyaniline:polyacrylonitrile composite.

<table>
<thead>
<tr>
<th></th>
<th>PANI</th>
<th>PAN</th>
<th>PANI:PAN1–1</th>
<th>PANI:PAN1–2</th>
<th>PANI:PAN1–3</th>
</tr>
</thead>
<tbody>
<tr>
<td>3259</td>
<td>3969</td>
<td>3417</td>
<td>3439</td>
<td>3469</td>
<td></td>
</tr>
<tr>
<td>3035</td>
<td>3652</td>
<td>3251</td>
<td>3239</td>
<td>3280</td>
<td></td>
</tr>
<tr>
<td>2846</td>
<td>3555</td>
<td>2950</td>
<td>3004</td>
<td>3007</td>
<td></td>
</tr>
<tr>
<td>2358</td>
<td>3442</td>
<td>2230</td>
<td>2234</td>
<td>2239</td>
<td></td>
</tr>
<tr>
<td>1587</td>
<td>2950</td>
<td>2049</td>
<td>2049</td>
<td>2048</td>
<td></td>
</tr>
<tr>
<td>1497</td>
<td>2844</td>
<td>1965</td>
<td>1965</td>
<td>1959</td>
<td></td>
</tr>
<tr>
<td>1377</td>
<td>2653</td>
<td>1726</td>
<td>1736</td>
<td>1724</td>
<td></td>
</tr>
<tr>
<td>1302</td>
<td>2598</td>
<td>1603</td>
<td>1580</td>
<td>1580</td>
<td></td>
</tr>
<tr>
<td>1241</td>
<td>2414</td>
<td>1457</td>
<td>1427</td>
<td>1427</td>
<td></td>
</tr>
<tr>
<td>1143</td>
<td>2051</td>
<td>1387</td>
<td>1384</td>
<td>1387</td>
<td></td>
</tr>
<tr>
<td>1008</td>
<td>1995</td>
<td>1145</td>
<td>1267</td>
<td>1266</td>
<td></td>
</tr>
<tr>
<td>954</td>
<td>1726</td>
<td>1034</td>
<td>1104</td>
<td>1162</td>
<td></td>
</tr>
<tr>
<td>824</td>
<td>1637</td>
<td>988</td>
<td>1064</td>
<td>1064</td>
<td></td>
</tr>
<tr>
<td>728</td>
<td>1451</td>
<td>912</td>
<td>985</td>
<td>983</td>
<td></td>
</tr>
<tr>
<td>505</td>
<td>1387</td>
<td>841</td>
<td>911</td>
<td>913</td>
<td></td>
</tr>
<tr>
<td>1069</td>
<td>827</td>
<td>841</td>
<td>841</td>
<td>841</td>
<td></td>
</tr>
<tr>
<td>983</td>
<td>810</td>
<td>826</td>
<td>825</td>
<td>825</td>
<td></td>
</tr>
<tr>
<td>954</td>
<td>750</td>
<td>810</td>
<td>803</td>
<td>803</td>
<td></td>
</tr>
<tr>
<td>912</td>
<td>694</td>
<td>750</td>
<td>751</td>
<td>751</td>
<td></td>
</tr>
<tr>
<td>842</td>
<td>618</td>
<td>693</td>
<td>696</td>
<td>696</td>
<td></td>
</tr>
<tr>
<td>827</td>
<td>554</td>
<td>583</td>
<td>588</td>
<td>588</td>
<td></td>
</tr>
<tr>
<td>810</td>
<td>509</td>
<td>510</td>
<td>510</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>655</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>524</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.3. SEM Studies

Fig. 4.3(a,b) shows the photographs of conducting fibers of PANI:PAN composite and PAN fibers. Fig. 4.3(c,d) shows the SEM micrographs of fibers pellet and single conducting fiber. The cross section of the conductive fiber containing 5 mL of aniline in PAN solution can be seen to consist of some dark spots and bright grooves Fig. 4.3(d). The intensity of grooves becomes more intense at certain places, where the conductive particles are present in aggregated structure within the polymeric matrix. The dark region is related to conductive polyaniline phase, while the bright region is related to non conducting polyacrylonitrile phase. It is observed that polyaniline content is markedly localized in the polyacrylonitrile matrix. In the above SEM micrograph, an excellent dispersion between two components is seen in which about 15–20% dark phase of polyaniline can be observed clearly.

4.3.4. TGA Studies

As evident from Fig. 4.4 the TGA analysis showed that the small weight loss (~2%) upto 151 °C is due to the loss of water molecule and other volatile materials. There is extremely little weight loss (~6.1%) up to 301 °C, which may be due to the loss of low molecular weight oligomers, which strongly suggests that the fibers are thermally stable up to 300 °C under oxidative conditions. The thermo–oxidative degradation starts beyond this temperature, accompanied by a massive weight loss of the polymer. This weight loss in the last step is due to thermo–oxidative degradation of the polymer.
Fig 4.3. Photographs of (a) fibers of PANI:PAN and (b) PAN fibers.
SEM micrographs of (c) pellet of fibers of PANI:PAN and (d) PANI:PAN fiber.

Fig 4.4. TGA curve of PANI:PAN (3).
4.3.5. XRD Studies

The XRD of polyaniline base, salt and polyaniline:polyacrylonitrile composite fiber are shown in Fig. 4.5. The polyaniline base exhibits the main peak at $2\theta \sim 19.3^\circ$, while the salt exhibits diffraction peaks at $2\theta \sim 24.9^\circ$. These peaks indicate that polyaniline is a semicrystalline polymer as reported by Djurado et al. [28] and Laridjani et al. [29]. Its intrinsic crystallinity is due to the presence of a polar nitrogen atom in the main backbone chain, while in the salt the presence of polaron or charge defects enhances its crystallinity. The XRD pattern of the PANI:PAN fiber do not show any characteristic peaks and suggests an amorphous nature as shown in Fig 4.5.

![XRD pattern of PANI base, salt and fiber of PANI:PAN(3).](image)

**Fig 4.5.** XRD pattern of PANI base, salt and fiber of PANI:PAN(3).
4.3.6. Isothermal Stability in Term of DC Electrical Conductivity Retention

The fibers were observed to show enhanced electrical conductivity on exposure to HCl, due to the charge-transfer reaction between conducting fibers and doping agents, HCl [30,31].

\[ [\text{PANI(PAN)}] + n \text{HCl} \rightarrow [(\text{PANI}-n\text{H}^+(\text{PAN}))[(n\text{Cl}^-)] \quad (5) \]

The stability of electrical conductivity under isothermal conditions at 50°C, 70°C, 90°C, 110°C and 130°C of the differently doped fibers pellet has been conducted at different temperatures. The DC electrical conductivity was measured at an interval of 15 min in the accelerated ageing experiment as shown in Fig. 4.6. It has been observed that the electrical conductivity is stable at 50°C, 70°C and 90°C which support the fact that the fibrous materials are sufficiently stable under ambient conditions in terms of DC electrical conductivity retention below 90°C. The decrease in electrical conductivity with time in isothermal ageing at 110°C and 130°C may be attributed to the loss of dopant and the chemical reaction of dopant with polymer i.e. degradation of polymer composites.
Fig 4.6. DC electrical conductivity retention under isothermal conditions at 50 °C, 70 °C, 90 °C, 110 °C and 130 °C of (a) HCl, (b) H₂SO₄ and (c) HClO₄ doped fibrous PANI:PAN(3).
4.4. CONCLUSION

Electrically conductive and isothermally stable conducting fibers of PANI:PAN composite were prepared by stirring process. It was found that the fibers which contained 5 mL of aniline gave best results. From the above mentioned studies, it can be concluded that the electrical properties of fibers strongly depends on doping types and counter ion of the dopant which has an effective control on the mechanism of electrical conductivities of the fibers. The conducting fibers of PANI:PAN composite could be useful for many applications that require a combination of electrical conductivity with isothermal stability.
4.5. REFERENCES


