5.1. INTRODUCTION

Conducting polymers are very versatile materials with potential applications in various evolving technologies such as electrodes in primary and secondary batteries [1, 2], energy storage devices [3, 4], microelectronics [5], photocatalysts [6], optoelectronic devices [7, 8], sensors and actuators [9] etc.

Among all conducting polymers, polyaniline (Pani) drew widespread attention because it possesses unique properties such as low cost, high environmental stability, reversible and tailorable electrical properties by controlled charge-transfer processes [10-12]. Polyaniline can experience changes on adsorption and desorption of chemical species onto its surface, making it a potential sensing material for humidity, toxic solvents [13-16], organic vapours such as methanol, ethanol, chloroform, dichloromethane and hexane [17, 18].

Silk fibroin (SF) is an attractive scaffold biomaterial because of its excellent mechanical properties, biocompatibility, biodegradability, tissue regeneration and various other biomedical applications [19]. Natural silk fibroin fibers (a filament core protein) are obtained by removing the outer sericin (glue-like coating of a nonfilamentous protein) from silk fibres with anhydrous sodium carbonate solution at appropriate temperature [20].

A number of composites of silk fibroin have been reported for various potential applications. Yahya A. Ismail et. al. [21] reported Fibroin/Polyaniline composite for electrochemical characterization as reactive sensor. Youyi Xia et. al. [22] reported silk fibroin/polyaniline (core/shell) coaxial fiber for the application in cell proliferation. Developments of gas sensors by conducting composite materials have drawn more attention over the last few years [23].

Among various toxic compounds, acetaldehydes and ammonia are classified as potentially dangerous to the environment even at low concentration. Thus, the development of new materials for the detection and determination of these toxic volatile compounds in the atmosphere are of the immediate concern to environmental researchers. Herein we have tried to explore the ammonia and acetaldehyde sensing capabilities of Pani by modifying the non conducting silk fibroin into Pani coated conducting composite fibers (Pani/SF). To the best of our knowledge, the sensing
application with Pani modified SF fibers (Pani/SF) has not been yet reported elsewhere.

5.2. EXPERIMENTAL

5.2.1. Materials

In the preparation of Pani and Pani/SF composite fibers, the chemicals used were: aniline 99% (E.Merck, India), CSA (camphor sulphonic acid) ≥98% (TCI, Tokyo), Cocoons for silk (Banaras, India), potassium persulphate (E.Merck, India) and methanol. Double distilled water was used throughout the experiments.

5.2.2. Preparation of Silk Fibroin

Cocoons were degummed twice for 1.5 h in aqueous solution of 0.02 M Na₂CO₃ and then rinsed thoroughly with double distilled water to extract the silk fibroin (SF). The extracted SF was then dried at 40°C for 24 h.

5.2.3. Preparation of Pani and Pani/SF Composites

Aniline (2.0 mL) was mixed with 100 mL of 0.1 M camphor sulphonic acid (CSA) under constant stirring for 1 hr. A solution of potassium persulphate (PPS) was added dropwise and the mixture was allowed to react for 24 h. The final dark green coloured reaction mixture was then filtered, washed several times with double distilled water and methanol and then dried in an air oven at 70°C for 10 h.

The Pani/SF composite fibers were prepared by in situ oxidative polymerization of aniline in the presence of CSA modified SF fibers using potassium persulphate as an oxidizing agent. The extracted silk fibroin fibers were dipped in 100 mL of 0.1 M CSA aqueous solution and stirred for 1 h. The resultant SF fibers were filtered and dried at 40°C. Thus the CSA modified SF fibers (300 mg) each were added to different amounts of aniline solutions prepared in 0.1 M CSA and stirred for 1 hr. A solution of K₂S₂O₈ (6 g) in 100 mL of 0.1 M CSA was then poured dropwise into the mixture at room temperature with constant stirring. The colour of the SF fibers changed from light yellow to greenish black indicating the polymerization of aniline on silk fibroin fibers. The fibrous reaction mixture was then stirred for further 24 h.
The final Pani/SF composite fibers was then filtered, washed thoroughly with double distilled water and methanol to remove excess acid, potassium persulphate and Pani oligomers. Thus prepared Pani/SF composite fibers were dried at 50°C for 20 h in an air oven and were stored in desiccators for further experiments. For electrical conductivity measurements, 250 mg material from each sample was pelletized at room temperature with the help of a hydraulic pressure machine at 80 kN load for 15 min. The preparation details of are given in Table 5.1.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Aniline (mL)</th>
<th>K$_2$S$_2$O$_8$ (g)</th>
<th>SF Fibers (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pani</td>
<td>2.0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Pani/SF-1</td>
<td>1.0</td>
<td>6</td>
<td>300</td>
</tr>
<tr>
<td>Pani/SF-2</td>
<td>2.0</td>
<td>6</td>
<td>300</td>
</tr>
<tr>
<td>Pani/SF-3</td>
<td>3.0</td>
<td>6</td>
<td>300</td>
</tr>
<tr>
<td>Pani/SF-4</td>
<td>5.0</td>
<td>6</td>
<td>300</td>
</tr>
</tbody>
</table>

5.3. CHARACTERIZATION

In order to investigate the morphology, structure and chemical composition of Pani/SF fibers, a variety of methods were used including the Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The spectra were recorded using Perkin-Elmer 1725 instrument. Scanning electron microscope (SEM) studies were carried out by JEOL, JSM, 6510-LV (Japan). Thermogravimetric analysis (TGA) was done by using a Perkin Elmer instrument in the temperature range from 35 to 700°C.

The thermal stability in terms of DC electrical conductivity of Pani and Pani/SF composite fibers under isothermal and cyclic ageing conditions was also studied. For this study, a four-in-line probe with a temperature controller, PID-200 (Scientific Equipments, Roorkee, India) was used to measure the DC electrical
conductivity and its temperature dependence. The equation used in calculation of DC electrical conductivity was:

\[ \sigma = \frac{\ln(2S/W)}{2\pi S(V/I)} \]  \hspace{1cm} (5.1)

where I, V, W and S are the current (A), voltage (V), thickness of the pellet (cm) and probe spacing (cm) respectively and \( \sigma \) is the conductivity (S/cm) [24]. In testing of isothermal stability, the pellets were heated at 50°C, 70°C, 90°C, 110°C and 130°C in an air oven and the DC electrical conductivity was measured at particular temperature at an interval of 10 min in the accelerated ageing experiments. In testing of the stability under cyclic ageing condition, DC conductivity measurements were taken 5 times within the temperature range of 50-130°C.

5.4. RESULTS AND DISCUSSION

5.4.1. Mechanism of Preparation of Pani/SF Composite Fibers:

The mechanistic view of the polymerization process seems to involve the anilinium cations (phenyl-NH\(_3^+\)) getting hooked up by Coulombic attraction between anilinium cations and the sulphonate group of camphor sulphonic acid adsorbed on the surface of silk fibroin. Thus the SF fibers get uniformly surrounded by anilinium cations. This arrangement comes in contact with K\(_2\)S\(_2\)O\(_8\), the anilinium cations get polymerized on the surface of SF fibers forming uniform smooth layer of Pani (emeraldine salt). The uniform deposition of Pani on the CSA modified surface of silk fibroin may be supported by the interaction between negatively charged sulphonate groups and polarons of Pani.

The similar mechanism is mentioned by Youyi Xia et. al. in which SF fibers were modified by methyl orange (MO) and then aniline was polymerized on the surface of MO modified SF fibers [22]. The schematic presentation of coulombic attraction is given in Fig. 5.1.
5.4.2. ATR-FTIR Analytical Studies

ATR-FTIR spectra of the SF and Pani/SF-4 composite fibers are shown in Fig. 5.2. Fig. 5.2a shows the spectra of pure SF fibers in which the peaks observed at 1636 cm\(^{-1}\) and 1540 cm\(^{-1}\) correspond to amide I and amide II vibrations which may be attributed to the \(\beta\) sheet structure of silk fibroin [25].

In the spectra of Pani/SF-4 composite fibers, the four major peaks are observed. The peaks observed at 1569 cm\(^{-1}\) and 1488 cm\(^{-1}\) may be due to C=C stretching mode of quininoid and benzenoid rings respectively. The peaks at around 1292 cm\(^{-1}\) and 800 cm\(^{-1}\) may be attributed to C-N bond stretching and C-H bond out of plane bending respectively as shown in Fig. 5.2b [26]. There are some extra peaks observed in Pani/SF-4 spectra which may be related to presence of camphor sulphonic acid in Pani. The peak at around 1726 cm\(^{-1}\) may be attributed to the characteristic peak of CSA due to stretching of C=O bond, also the peak at 620 cm\(^{-1}\) may be related to S-O bond stretching of sulphonate group [27]. All these results indicated and supported the presence of CSA doped Pani coated on the SF fibers.
5.4.3. Thermogravimetric Analysis (TGA)

The thermal stability of the Pani/SF-4 composite fibers was investigated and shown in Fig. 5.3. The initial weight loss may be due to removal of low weight oligomers of Pani and absorbed water on the surface of Pani. Afterward, the sharp degradation of the Pani/SF-4 composite fibers is observed at about 295.4°C [22], which is higher than that of pristine SF fibers (281.3°C) [28]. This degradation pattern of Pani/SF-4 fibers suggesting that Pani layer resists the degradation thermo oxidative conditions.
5.4.4. Scanning Electron Micrograph (SEM) Studies

The morphology of SF fibers and Pani/SF-4 composite fibers were studied by SEM at different magnifications as presented in Fig. 5.4. Fig. 5.4a and Fig. 5.4b represent the SEM image of SF fibers which seems to be very rough surfaced. The change in rough surfaced SF fibers to smooth surfaced Pani/SF-4 composite fibers observed in Fig. 5.4c and Fig. 5.4d indicating the growth of smooth Pani layer on SF fibers. The SF fibers were modified by CSA helping in uniformly adsorption of anilinium molecules on the fibers providing uniform coating on SF fibers. Thus the Pani/SF-4 composite fibers exhibit smooth surfaced morphology.

Fig. 5.4 SEM micrographs of: (a and b) SF fibers, (c and d) Pani/SF-4 composite fibers at different magnifications.

5.4.5. Digital Photographic Studies

Fig. 5.5a and Fig. 5.5b show the digital photographs of SF and Pani/SF-4 composite fibers respectively. Evidently, it may be seen that the light yellow colour of SF fibers changed into deep green suggesting that the SF fibers has been successfully covered with Pani.
5.5. ELECTRICAL CONDUCTIVITY

For the electrical conductivity measurements and sensing experiments, 250 mg material from each sample was pelletized at room temperature with the help of a hydraulic pressure machine at 80 kN force for 15 min. The initial DC electrical conductivity Pani and Pani/SF composite fibers were measured by standard four-inline probe method. The variations in DC electrical conductivity in Pani/SF composites with loading of different amounts of aniline monomer are shown in Fig. 5.6.
In Pani/SF-4 composite fibers, the highest electrical conductivity was found with highest loading (5mL) of aniline monomer [24]. The electrical conductivity of CSA doped Pani/SF composite fibers increases with increase in aniline monomer content in the composites materials varied from $10^{-6}$ to $10^{-2}$ S/cm. Therefore, Pani/SF-4 was selected for temperature dependence of electrical conductivity studies and as sensing material.

The DC electrical conductivity in CSA doped Pani/SF composite fibers was found to be lower than that of pristine CSA doped Pani. In all Pani/SF composite fibers, the silk fibroin was functionalised by CSA having negatively charged functional sulphonate group (SO$_3^-$) which interacts strongly with positively charged nitrogen of polyaniline which induce the formation of conductive polymer. Based on this mechanism involved in the formation, the SO$_3^-$ group interrupt the polarons of the Pani thus decreasing the mobility of polarons resulting into decrease in electrical conductivity in Pani/SF composite fibers.

5.5.1. Stability under Isothermal Ageing Conditions

**Fig. 5.7** Relative electrical conductivity of: (a) Pani, (b) Pani/SF-4 composite fibers under isothermal ageing conditions.

The stability of Pani and Pani/SF-4 composite fibers in terms of DC electrical conductivity was studied under isothermal ageing conditions as shown in **Fig. 5.7**. The representation of relative electrical conductivity was calculated by the equation:
where $\sigma_{t,t}$ is the relative electrical conductivity, $\sigma_t$ = electrical conductivity at time $t$, $\sigma_o$ = electrical conductivity at time zero. The comparative study of relative electrical conductivity with respect to time at different temperatures was done by analysing the stability of prepared materials in terms of DC electrical conductivity. The electrical conductivity of each of the samples was measured for temperature (50, 70, 90, 110, 130°C) versus time at an interval of 10 min upto 40 min.

It can be understood From the Fig. 5.7a that the stability of relative DC electrical conductivity of Pani is very fair at 50 and 70°C and from 90 to 130°C seems to be unstable. In Fig. 5.7b the relative DC electrical conductivity of Pani/SF-4 composite fibers is seems to be very stable at 50, 70, and 90°C. Thus it is inferred that the fibrous Pani/SF-4 material is sufficiently stable under ambient conditions in terms of DC electrical conductivity retention upto 90°C under isothermal ageing condition.

### 5.5.2. Stability under Cyclic Ageing Conditions

The stability in the term DC electrical conductivity retention of Pani and Pani/SF-4 composite fibers was also studied by cyclic ageing method within the temperature range of 50 to 130°C as shown in Fig. 5.8. The electrical conductivity was recorded for successive cycles and observed to be gradually increased in Pani while decreased in Pani/SF-4 composite fibers for each of the cycle. The relative electrical conductivity was calculated using the following equation:

$$\sigma_t = \frac{\sigma_T}{\sigma_{50}}$$

where $\sigma_t$ is relative electrical conductivity, $\sigma_T$ is electrical conductivity at temperature $T$ (°C) and $\sigma_{50}$ is electrical conductivity at 50°C.
As cycle runs from temperature 50 to 130°C the relative electrical conductivity of Pani seems to be increased may be due to the increment of number of charge carriers which may be attributed to the formation of greater number of polarons/bipolarons. From Fig. 5.8a it may observed that the electrical conductivity of Pani for all of the cycles is similar and following the same trend with gain in the conductivity.

In Pani/SF-4 composite fibers just opposite trend of Pani relative electrical conductivity is observed. The relative DC electrical conductivity found to decrease as temperature increases as shown in Fig. 5.8b. The decrease in electrical conductivity may be attributed to the removal of moisture, loss of low molecular weight oligomers of aniline and earlier degradation of coated polyaniline on silk fibroin under cyclic ageing conditions.

**5.6. SENSING STUDIES**

Acetaldehyde is a highly reactive volatile organic compound which may be responsible for dizziness, headache and even cancer if someone exposed for prolonged periods. Although, ammonia solutions does not usually cause problems for humans and other mammals but it is highly toxic to aquatic animals even at very low concentration.
Thus the both compounds are classified as dangerous for the environment and the detection of acetaldehyde and ammonia vapours are important in environmental monitoring and chemical control. The acetaldehyde and ammonia vapours sensitivity of Pani/SF-4 fibers was monitored by measuring the changes in the electrical conductivity at room temperature by using a four-in-line probe electrical conductivity device as shown in Fig. 5.9.

![Schematic representation of acetaldehyde and ammonia vapours sensor unit by four-in-line probe technique.](image)

**Fig. 5.9** Schematic representation of acetaldehyde and ammonia vapours sensor unit by four-in-line probe technique.

The electrical conductivity of 250 mg pelletized Pani/SF-4 composite fibers showed significant response on exposure to different concentrations (0.1, 0.2, 0.3, and 0.5 M) of aqueous acetaldehyde at room temperature as shown in Fig. 5.10.

The sensitivity of material was investigated on the two parameters; response time and sensing intensity. The pellet fabricated was attached with four probes and placed in a closed chamber of acetaldehyde vapours for 60 seconds and after that the pellet was removed from chamber and exposed to air for next 60 seconds. It can be seen that the electrical conductivity decreased for first 60 seconds for all of the different concentration of solutions of acetaldehyde and recovered in next 60 seconds on exposing with fresh air. Relatively good changes in electrical conductivity and fast recovery observed in the atmosphere of 0.5 M aqueous acetaldehyde vapours.
Fig. 5.10 Effect on the DC electrical conductivity of Pani/SF-4 on exposure to different concentrations (0.1 M, 0.2 M, 0.3 M, 0.5 M) of acetaldehyde with respect to time.

The reversibility response of Pani/SF-4 composite fibers towards 0.5 M aqueous acetaldehyde was investigated as shown in Fig. 5.11. The reversibility was determined by first keeping sample in acetaldehyde vapours environment for 10 sec followed by 10 sec in open air for a total duration of 120 seconds. The conductivity after each cycle never recovered upon exposure to air due to two process occurring simultaneously, i.e. electrical neutralization of Pani backbone and the desorption of acetaldehyde.

Fig. 5.11 Reversible electrical conductivity response of Pani/SF-4 composite fibers for 0.5 M acetaldehyde solution.
The similar experiment was done in presence of different concentrations (0.1, 0.2, 0.3, and 0.5 M) of ammonia solution at room temperature as shown in Fig. 5.12. It may be seen that the electrical conductivity decreased on exposure to ammonia solutions (0.1, 0.2, 0.3, and 0.5 M) for first 60 seconds and regained in next 60 seconds on exposing with fresh air. The electrical conductivity response of Pani/SF-4 in 0.5 M ammonia solution is found to be better than other ammonia solutions.

**Fig. 5.12** Effect on the DC electrical conductivity of Pani/SF-4 composite fibers on exposure to different concentrations (0.1 M, 0.2 M, 0.3 M, 0.5 M) of ammonia with respect to time.

The reversibility response of Pani/SF-4 composite fibers towards 0.5 M ammonia solution was also investigated as shown in Fig. 5.13. The similar experiment was done in absence and presence of ammonia vapours for total 120 sec by first keeping the sample in ammonia vapours for 10 sec followed by 10 sec in fresh air. It is observed that the conductivity after each cycle never reverted upon exposure to air. The reason for not recovering electrical conductivity of Pani/SF-4 composite fibers is same as was in case of acetaldehyde. If the air exposing time is increased, the conductivity may regain due to complete desorption of ammonia from the polymer surface.
Fig. 5.13 Reversible electrical conductivity response of Pani/SF-4 composite fibers for 0.5 M ammonia solution.

5.6.1. Proposed Mechanism for Sensing

The sensing mechanism of ammonia and acetaldehyde vapours was explained through DC electrical conductivity response by simply adsorption and desorption mechanism of vapours at room temperature. In Pani/SF-4 composite fibers, the DC electrical conductivity decreases after exposure to acetaldehyde and ammonia vapours which may be attributed to decrease in mobility of charge carriers. The decrease in mobility of charge carriers may be due to interaction of lone pairs of oxygen and nitrogen of acetaldehyde and ammonia respectively with positive charged polarons at nitrogens of polyaniline [24, 29].

Thus the mobility of polarons decreases resulting in the decrease in electrical conductivity. The adsorbed vapours of ammonia and acetaldehyde on the surface of polyaniline get loosen from the surface under ambient conditions leads to increase in electrical conductivity.
**Scheme-5.1** Proposed interactions of Pani/SF-4 composite fibers with: (a) ammonia and (b) acetaldehyde.

**CONCLUSIONS**

The Pani/SF composite fibers were successfully prepared by *in-situ* polymerization method and confirmed by FTIR and TGA analysis. SEM analysis confirmed the uniformly deposition of Pani on CSA modified SF fibers. Pani/SF composite fibers showed lower conductivity but greater thermal stability in terms of DC electrical conductivity under isothermal and cyclic ageing conditions than pristine Pani. The results highlighted the excellent reversible acetaldehyde and ammonia sensing indicating that the Pani/SF-4 composite fibers could be utilized as a sensor material.
References


