Chapter 2
Experimental: Materials and Methods
Chapter 2

Experimental: Materials and Methods

This chapter discusses materials used, synthesis techniques, characterization methods, measurement and device fabrication adopted in this work. Dispersion polymerization and interfacial polymerization are the two methods used for polymerizing the monomers. We prepared PANI- PVA blend as in-situ whereas PPY- PVA as ex-situ. The films obtained from the above solutions are characterized by conventional techniques viz., FTIR, FESEM and X-ray diffraction. Whereas the electrical property study is done through conductivity measurement, I-V characteristics and temperature dependent conductivity.

2.1 Starting materials

Starting materials required in the present work are aniline, pyrrole and PVA. Their chemical structures are shown in figure 2.1. Along with these, we used some oxidants; ammonium persulphate (\( (NH_4)_2S_2O_8 \)), ferric chloride (\( FeCl_3 \)); some solvents (toluene and water) and some acids (HCl). PVA (1700-1800 repeat units) of high purity (99.9%) has been acquired from Sigma Chemical Co. Aniline, pyrrole and toluene are obtained from Emerck, Germany and are purified by repeated distillation under vacuum prior to every use. Hydrochloric acid (HCl), ammonium persulphate (\( (NH_4)_2S_2O_8 \)) and ferric chloride (\( FeCl_3 \)) have been obtained from same source with the same purity (99.9%). These reagents and PVA are used without any further purification.
2.2. POLYMERIZATION AND BLEND FORMATION TECHNIQUES

We have adopted chemical polymerization technique [GA97, CCC92]. For PANI- PVA blend preparation we adopted in-situ method for obtaining PANI by dispersion polymerization in PVA matrix. Aniline is polymerized in PVA water solution. The blend mixture so obtained is used directly to obtain free standing films by spin casting. By this process, more intimate mixing of the two components is possible than is obtained by mechanical blending because of the incompatibility of most polymers by this method.

Dispersion polymerization is a very attractive method owing to the inherent simplicity and scalability of the single-step process [QY03]. Typically, a precursor solution is dispersed in a immiscible continuous phase by mechanical shearing forces with the help of surface modifiers. The dispersed droplets are then further processed in order to form particles by cross-linking or polymerization (hardening process) of the precursor liquid. The slow as well as fast hardening processes can lead to good particle quality. However, specific user-needs and specifications often require the complete individual de novo design of a dispersion polymerization process in order to achieve appropriate product properties.

We adopted this method in our work for PANI- PVA blend preparation. The PVA solution is obtained by soaking in water, constant stirring and heating it to $60^\circ C$ in magnetic stirrer. To this solution freshly distilled aniline (1 $M$) in 1 $M$ $HCl$, is added. A 1 $M$ of ammonium persulfate oxidant in 1 $M$ $HCl$ solution is prepared separately. Under constant stirring at low temperature ($-5$ to $0^\circ C$), oxidant solution is added dropwise to the aniline- PVA mixture. Resultant mixture

Figure 2.1: The chemical structure of aniline, pyrrole and polyvinyl alcohol.
is stirred for another one hour or more. The solution mixture gradually shows change in colour
to bluish green. Complete change of colour indicates the complete polymerization. The process
is repeated for different molar ratios of aniline to vinyl alcohol repeat units in PVA in order to
obtain various types of PANI- PVA blends.
For PPY- PVA blend we adopted ex-situ process by mixing the PPY obtained by interfacial
polymerization to PVA solution. Interfacial polymerization reaction occurs at the interfacial
boundary of two immiscible liquids [HSKJ07, JL07]. Under right condition, thin flexible walls
of polymer form rapidly at the interface. In particular, freshly distilled pyrrole (1 M) is dis-
solved in double distilled 10 ml toluene. Separately, 1 M of FeCl$_3$ (oxidant) and 1 M of HCl
is dissolved in water. These two immiscible solution are mixed in a container to form toluene-
water interface. Polymerization takes place at the interface. The PPY formed at the interface
are taken out by using wired mesh. It is then washed, dried thoroughly to remove unreacted
oxidant from the surface and mixed with PVA water solution. The polymerization process is
repeated for two different temperatures.

2.3 Film preparation

Both PANI- PVA and PPY- PVA blends obtained by above mentioned methods are used directly
to prepare films by spin casting method. Here, with the help of a spin coater films are prepared
at room temperature at a speed of 30 rotation per minute (rpm) on different substrates (ITO
coated glass, PVA sheet, transparent sheet and Si wafer, which are cleaned properly before
film deposition) for specific uses. The obtained cast films are dried thoroughly, washed with
deionized water and methanol, dried again, then stored in vacuum, to be available for needed
investigation to be performed later.

2.4 Characterization techniques

The spin cast films obtained are characterized by conventional techniques viz., FTIR, FESEM
and XRD.
2.4. CHARACTERIZATION TECHNIQUES

2.4.1 FTIR spectroscopy

FTIR stands for Fourier transform infra red. Infrared spectroscopy is the subset of spectroscopy that uses with the infrared part of the electromagnetic spectrum [GH] as exciting wavelength. It can be used to identify functional groups present in a compound. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some pass through (transmitted). The resulting spectrum represents both the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. FTIR spectrometers unlike dispersive spectrometers, use broad energy IR sources. They are based on the principle of interferometer originally designed by Michelson and a mathematical procedure developed by Fourier that converts response from ‘time’ to ‘frequency’ domain. A FTIR Spectrometer is schematically shown in figure 2.2. It consists of two parts: (a) an optical system, which uses an interferometer and (b) a dedicated computer which stores data, performs computations and plots the spectra. In the interferometer, the originally generated IR beam is split into two beams and an interference pattern is created by sending one of the two beams in and out-of-phase, using a movable mirror at all times. The energy versus mirror displacement data is thereby converted into energy versus absorbance relationship. Measurement of a single spectrum is faster for the FTIR technique because the information at all frequencies is collected simultaneously i.e. the incorporation of the interferometric technique in the studies allows multiple vibrational frequencies to be monitored simultaneously across a wide spectral window [CG00]. This results in a substantial increase in the sensitivity of the instrument by enhancing signal to noise ration [BC].

2.4.2 FESEM

FESEM is the abbreviation of field emission scanning electron microscope. The block diagram of a FESEM is shown in figure 2.3 [SP]. FESEM is a microscope that uses electrons as probing beam instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern. It is used to visualize minute topographic details on the surface of entire or fractioned objects. Researchers in biology, chemistry and
physics apply this technique to observe structures that may be as small as 1 \text{nm}. Emitted electrons are accelerated in a high electrical field gradient. Within the high vacuum column these so called primary electrons are focussed and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result, the secondary electrons are emitted from each spot on the object. The angle and velocity of these secondary electrons relate to the surface structure of the object. A detector catches the secondary electrons and converts to an electronic signal. This signal is amplified and transformed to a video scanned image that can be seen on a monitor or can be converted to a digital image that can be saved and processed further.

2.4.3 X-ray diffraction studies

X-ray diffraction (XRD) analysis is the primary tool for investigating the structure of crystalline materials, from atomic arrangement to crystallite size and the imperfections [CS, PZ]. XRD is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. By varying the angle of incidence $\theta$ (figure 2.4), the Bragg’s-law [Bra13]

$$2d \sin \theta = n \lambda$$

(2.4.1)
conditions are satisfied by different d-spacings in polycrystalline materials, $\lambda$ being the wavelength of X-rays and $n$ is the order of diffraction. Plot of angular positions and intensities of the resultant diffracted peaks of radiation, is the XRD spectra and is material specific. This pattern contains a mixture of different phases. The resultant diffractogram is formed by addition of the individual patterns. Based on the principle of XRD, a wealth of structural, physical and chemical information about the material can be obtained.

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector as shown in figure 2.5. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons towards a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being $K_\alpha$ and $K_\beta$. $K_\alpha$ consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material ($Cu, Fe, Mo, Cr$). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays. $K_\alpha$ and $K_\beta$ are sufficiently close in wavelength, so in all practical purposes a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with $Cu$
2.5 Measurement of properties

Film properties have been measured through electrical conductivity, I-V characteristics and temperature dependent electrical conductivity measurement. But before that, thickness of the films are measured which will be required for calculation of electrical conductivity. Following subsections detail these measurement techniques.
2.5. MEASUREMENT OF PROPERTIES

2.5.1 Thickness measurements

The thickness of the film is measured by taking the SEM picture of the spin coated film along the thickness side.

2.5.2 Electrical conductivity measurements

We adopted four-probe method to measure electrical conductivity of these films. This is one of the standard and most widely used methods for the measurement of resistivity of semiconductors [ML65]. In this method, four collinear probes are on the surface of the film. A constant current (~ few mA) is passed across the two outer terminals (a and 4 of figure 2.6) where as the terminals 2 and 3 are used to measure the voltage drop. This method is basically useful to eliminate the contact resistance that arises in two probe measurement. This seriously hampers the electrical conductivity measurement in semiconductors. Experimental arrangement of the measurement is shown in figure 2.6. Because of pressure contacts, the arrangement is also specially useful for quick measurement on different samples or sampling different parts of the same sample. A Keithley constant current source (model220) is used as the current source and an HP multimeter (E-2373A) used to record the voltage.

The conductivity, $\sigma_{dc}$, of the sample can be calculated using the following relation.

Figure 2.5: Schematic diagram of X-ray diffraction.
Where $S$ is the spacing between the probes (usually $\sim 0.1$ cm), $I$ is the current supplied and $V$ is the measured voltage drop across the terminals 2 and 3. This equation is however to be corrected by the thickness parameter for very thin films.

![Figure 2.6: Schematic of Four-Point Probe](image)

**Figure 2.6: Circuit diagram of four-probe conductivity measurement.**

### 2.5.3 I-V characteristics

A current-voltage (I-V) characteristic is a relationship, typically represented as a chart or graph between an electric current corresponding to applied voltage or potential difference [vdB19]. In electronics, the relationship between the DC current through an electronic device and the DC voltage across its terminals is called the I-V characteristic of the device. A more general form of I-V characteristics is one that described the dependence of a terminal current on more than one terminal voltage difference; electronic devices such as vacuum tubes and transistors are described by such characteristics. We have recorded the I-V characteristics of the films of CP blends using a constant DC power supply and Keithley CV meter (model595) which has an in built voltage source along with current measuring facility. The current is recorded as a function
of the change in applied potential across the two terminals. The obtained I- V characteristics may be ohmic \( I \propto V \) or non-ohmic (power law) obeying the expression (2.5.2).

\[
I \propto V^n,
\]  

where,

\[
n = \begin{cases} 
1 & \text{for ohmic} \\
\text{else nonohmic} & \end{cases}
\]  

(2.5.3)

2.5.4 Temperature dependence of conductivity

Experimental study of the temperature dependence of conductivity is very valuable in building and testing theoretical models [SK94, Phi91]. The temperature dependence of conductivity is determined by placing the polymer film in a suitably designed apparatus schematically in figure 2.7. The film is fixed in a holder with four probes for electrical conductivity measurement. A pair of copper-constantan thermocouple is placed near the sample to measure the inside temperature. The whole system is placed inside an brass chamber lined with teflon, which is sealed and connected to a rotary vacuum pump and liquid nitrogen source. A small heater is mounted close to the sample and has arrangement for liquid nitrogen flow. Using a suitable control device its temperature is controlled. A digital temperature indicator is connected to a thermocouple to record temperature of the sample. Temperature is varied from room temperature 93 to 300 K. The change in the conductivity with temperature is noted using four probe method described in subsection 2.5.2.

2.5.5 Fabrication of field effect transistor (FET)

Technologically, the most important polymer device fabricated and studied is FET, as it forms the basic building blocks in logic circuits and switches for display. In our present research work, we fabricated p-channel FET using PANI- PVA blend and PPY- PVA blend and studied their I-V characteristics for different gate voltages. The blend solution is spin cast on gate dielectrics (Si wafer, transparent sheet, glass slide and PVA sheet) of 5\( \mu \)m thick. An ohmic contact to the gate is made by depositing silver. Source and drain electrodes are also of same material and are
Figure 2.7: Schematic diagram for the study of temperature dependence conductivity.

Separated by 200μm gap. Schematic of FET fabrication and the circuit diagram for FET I-V measurement are shown in figure 2.8 (a) and (b) respectively.
Figure 2.8: (a) Schematic of FET construction. (b) Circuit diagram for FET I-V measurement.