3. EXPERIMENTAL TECHNIQUES

3.1 Synthesis of samples

In research, the Polymers are prepared by the variety of techniques. The chemical oxidative polymerization technique is most widely used, as it is easy has high yield, allows to modify with different chemical groups and is economic [1-3]. Samples of the present thesis have been prepared by chemical method. The chemicals used for the sample preparation were analytical grade Thiophene, Ferric chloride, Methanol and Chloroform. The PTh nanocomposites were prepared by mechanical mixing analytical grade vanadium pentoxide V$_2$O$_5$/CoO PTh.

Synthesis of Polythiophene

Thiophene and chloroform solution was prepared and stirred well. Chloroform and ferric chloride solution were prepared and magnetic stirred for half an hour. To the homogeneous PTh solution, the chloroform, ferric chloride solution was added in drop wise. The whole mixture was magnetic stirred for 24 hours and the black precipitate obtained. It was first washed with chloroform and then with methanol. During this procedure, the precipitate became brown indicating the formation of Polythiophene [4-7].

The collected precipitate was filtered and washed repeatedly with double distilled water and methanol for removing unreacted oxidants and thiophene monomer until the filtrate was colourless. The powder was dried and grinded. The synthesis was
carried out at three different temperatures of 278K, 305K and 323K and the products so obtained were labelled as PTh1, PTh2 and PTh3 respectively.

**Preparation of PTh-V$_2$O$_5$ nano composites**

The PTh-V$_2$O$_5$ composites were prepared by mixing with the prepared Polythiophene and analytical grade V$_2$O$_5$ in different wt% defined as, (PTh)$_{100-X}$ (V$_2$O$_5$)$_X$, where X=5%, 10%, 15%, 20% and 25% labelled as PTh-VO1, PTh-VO2, PTh-VO3, PTh-VO4 and PTh-VO5 respectively. In a hydraulic press, the pellets of suitable size were prepared.

**Preparation of PTh-CoO nano composites**

The PTh-CoO composites were prepared by mixing with the prepared Polythiophene and analytical grade CoO in different wt% defined as, (PTh)$_{100-X}$ (CoO)$_X$, where X=5%, 10%, 15%, 20% and 25% labelled as PTh-CO1, PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 respectively.

**3.2 Characterization techniques**

The samples were investigated using the following mentioned experimental techniques.
X-Ray diffraction (XRD)

X-rays are electromagnetic waves, like visible light. Electromagnetic radiation can be mainly understood in terms of wave interpretation and also in terms of photons. X-ray spectroscopy is one of the most important tool for the study of band structure and chemical bonding in solids [8-10]. The arrangement of atoms and molecules generally lies at a distance of 0.1nm to 0.5nm from one another in a substance. The X-ray diffraction phenomena take place when such a substance is irradiated with X-rays whose wavelength is equivalent to the interatomic or intermolecular distance [11-12].

The methods of observing the X-ray diffraction of crystals are divided into two groups. There are various methods for the recording of patterns produced by single crystals. Such as Laue method, rotation and moving film methods. The process of diffraction of X-rays by crystals was explained by W. H. Bragg and W. L. Bragg. They have pointed out that crystals having a large number of equally spaced identical parallel planes, each contains many equally spaced atoms. These planes are known as Bragg planes.

The beam of X-rays is incident on these planes at a glancing angle \( \theta \). The beam get scattered in all directions by the atoms in different atomic planes condition for X-ray diffraction to occur. As per Bragg the angle can be calculated in terms of the path difference between the ray reflected by one plane and that reflected by the next plane.
in the lattice. Only those \( \theta \) values of are allowed, whose path difference \( 2d\sin\theta \) is an integral multiple of the wavelength.

\[
2d \sin \theta = n\lambda
\]  

(3.1)

where \( n=1, 2, 3 \ldots \) is the order of diffraction. This equation is known as Bragg’s law. This is the condition for reflection of X-rays from a set of parallel atomic planes. For each set of lattice planes (hkl) with its characteristic spacing \( d \). [8, 12, 13].

The materials composed of small crystals, usually randomly oriented are known as polycrystalline materials. For such substances in the form of powders or polycrystalline. The powder crystal method or powder methods are most suitable methods [12].

**Powder XRD method**

X-Ray powder diffraction was pioneered by Debye & Scherrer in 1916. This is a fast, reliable and easy technique for phase identification of various crystalline materials and their quantitative proportions, microstructure evaluation and determining molecular structure [14, 15]. X-ray powder diffractometers consist of cathode ray tube, sample holder and detector. The cathode ray tube produces x-rays by heating a metal filament, such as copper. The voltage is applied to the cathode ray tube causing x-rays to accelerate and bombard the crystalline material at a given angle \( \theta \) [16, 17]. The incident beam is diffracted by multiple layers of atoms of the material creating constructive or destructive interference of the x-ray beams returning to the detector at
an angle of 2θ from the incident beam. For the detector to produce an XRD peak, the diffracted beams must have diffraction rays that are in phase, also known as constructive interference. Constructive interference is only produced when the beams satisfy the Bragg’s Law (Eqn.(3.1, ))

Fig.8. Pictorial representation of incident x-rays diffracting from atoms within different crystalline layers, [15].

A diagram of the diffraction occurring between the different atomic layers of a material can be seen in Fig. 8. The cathode tube and the detector scan the material over a range of 2θ, usually ranging from 5° to 70° for powdered material, but can be extended further to around 140° to ensure that all bands of diffraction are observed. These measurements take into account the random orientations of the different materials that may be present in the powdered mixture. Along with scan range, the increment size and scan time can be varied. The increment size is nothing but the step the detector moves between two points where data is collected. The scan time is the amount of time the detector collects data at a particular point. By decreasing the increment size, more diffraction data can be gathered at various angles. A better resolution and an increased signal to noise ratio is a result from a longer scan time. Also more data can be gathered from each particular angle with a large scan time.
Our powder samples were subjected to X-Ray Powder method of diffraction in a Diffractometer (Model D2 PHASER) in the Department of Physics, Shivaji University. The results are presented in chapter 4.

**UV-VIS Spectrophotometer**

The UV-VIS Spectrophotometer is an important tool used in analytical science [18-21]. It measures intensity, $I$, of light passing through a sample and compares it to the intensity of light before it passed through the sample, $I_0$, expressed in absorbance $A$ or transmittance $T$. The ratio $I_0/I$ is known as the reflectance.

**Principle:**

It obeys the Beer-Lambert law; B-L law states that when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.

The intensity of absorption is derived from Beer-Lambert’s law

$$A = \varepsilon \cdot c \cdot l$$

Where $A$ is the measured absorbance

- $\varepsilon$ is the proportionality constant called absorptivity
- $l$ is the path length of the cell (cm)
- $c$ is the concentration of the analyte
The basic components of UV-Vis Spectrophotometer are source, monochromator, sample holder, detector, amplifier and recorder as shown in Fig.9 [19]

Source: The most widely used sources are Tungsten or Hydrogen-Deuterium lamps. Hydrogen lamp provides wavelength in the range 160nm-380nm and Tungsten filament produces wavelength in the range for 300nm-1000nm region.

Monochromator: It consists of prisms and slits. The most of the spectrophotometer are double beam spectrophotometers. The radiation emitted from source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such that the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further it is divided into two beams with the help of another prism.

Sample holder: One of the two divided beams is made to pass through the solution and second beam is passed through the reference solution. Sample solution and reference solution are contained in the cells. The cells are made of either silica or quartz.

Detector: The combinations of two photocells act like detector. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The reference cell with intensity of the radiation is stronger than the beam
of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

Amplifier: From the photocells, the alternating current of low intensity is generated and that is amplified by the amplifier.

Recorder: The amplifier is coupled to a pen recorder which is connected to the computer. The data generated is stored in the computer and produces the spectrum.
Fig. 9. UV-Visible Spectrophotometer
Scanning Electron Microscopy

The scanning electron microscope (SEM) is used for the examination of the microstructure/morphology of the samples [22, 23]. The principle of SEM is illustrated in Fig.10. The primary electron beam produced is scanned across the surface of a specimen by means of electromagnetic coils. The secondary electrons, and backscattered electrons ejected from the surface are collected in detector, which convert them into a signal that is processed into an image [24].

The basic component of SEM are electron gun, electron lenses, sample stages, detector and output devices. The electron gun produces a stable electron beam with high current and small energy dispersion. The electron emitted from tungsten or Lanthanum hexaboride thermionic emitters are used for the visualisation of surface of the sample. The filament is heated at high temperature 2800K. This results in the emission of thermionic electrons from the tip the electron gun generates electrons and accelerates them to energy in the range of 0.1 to 30 KeV towards the sample. A series of lenses focus electron beam on the sample. Then, many types of signals are generated and any of these can be displayed as an image.

To generate SEM images, two types of signals are often used they are secondary and backscattered electrons. Most of the electrons are scattered at large angles in the range 0° to 180° when they interact with the positively charged nucleus. These are used for SEM imaging. Incident electrons may knock off loosely bound conduction electrons out of the sample. These secondary electrons along with backscattered electrons are used for SEM imaging. Both secondary and backscattered electrons...
signals are collected when a positive voltage is applied to the collector screen in front of detector. When a negative voltage is applied on the collector screen only signals due to backscattered electrons is captured because the low energy secondary electrons are repelled. Electrons captured by the scintillator / photomultiplier are then amplified and used to form an image in the SEM [25-27]

Our polymer and composite powder samples were SEM imaged in a SEM (Model JSM-6360) at Department of Physics, Shivaji University, Kholapur. The results are presented in chapter 4.
Fig. 10. Scanning Electron Microscopy
3.3 DC Electrical conductivity measurement

Electrical conductivity is an excellent experimental tool to probe structural defects and internal purity of materials [28].

There are two methods used for the measurement of electrical resistance; two probe and four probe methods. The two probe measurement is used for higher resistive samples and four probe methods are suitable for low resistive samples and single crystals [29].

We adopted two probe technique for measuring resistivity of our samples. In this method a constant voltage has been applied across the two-side silver painted pellets. The current, I passing through the pellet was measured using a picoammeter. Using ohm’s law, the resistance, R of the sample is determined and using the dimensions of the sample, the conductivity of the sample has been determined.

Resistivity, \( \rho \), has been determined as per,

\[
\rho = \left( \frac{V}{I} \right) \left( \frac{A}{t} \right)
\]  

(3.2)

Where A is surface area and t the thickness of the pellet. Conductivity is given by, \( \sigma = 1/\rho \). The temperature was measured using Chromel-Alumel thermo-couple with an accuracy of \( \pm 1K \).

The experimental setup of two probe method used is shown in Fig.11.
Fig 11. A photograph of experimental setup of two probe method for resistivity measurement.
The present PTh and PTh-composite samples were measured for to electrical conductivity at the Department of Physics, Gulbarga University, Gulbarga. The results are presented in chapter 4.

3.4 Dielectric measurements

Dielectrics are the poor electric conductors and they are considered as are non-ideal insulators. Electrical characteristics of the materials are different to each other as, they dependent on their dielectric properties [37].

As for as dielectric measurements are concerned, no single technique can characterize the all materials over entire frequency band. A measurement of each band and their losses require a different method. There is always uncertainty in dielectric measurements while characterizing the materials. Some significant factors on which they depend are – Frequency, accuracy, temperature, material nature, sample size etc [38].
Fig 12. Experimental setup for conductivity measurement
In this experimental technique, the sample is placed in between two electrodes. The electrodes are connected a computer controlled LCR HiTester. The measurements were carried out for frequencies in the range 200Hz to 5MHz and temperature from 323K to 423K.

The instrument directly gave equivalent parallel circuit capacitance ($C_p$) and dissipation factor ($\tan\delta$) data. The temperature of the sample is controlled by a Dry Temperature Calibrator, with an accuracy of ±2°C. Total conductivity ($\sigma_{ac}$) was determined by using $C_p$ and $\tan\delta$, the dielectric constant ($\varepsilon'$), dielectric loss factor ($\varepsilon''$) by the following expressions [39, 40].

\[
\varepsilon' = \frac{Cd}{\varepsilon_o A} \tag{3.3}
\]

\[
\varepsilon'' = \varepsilon' \tan\delta \tag{3.4}
\]

\[
\sigma_{ac} = \omega\varepsilon_o \varepsilon'' \tag{3.5}
\]

Where $\varepsilon_o$ is the permittivity of free space, $\omega$ the frequency of the input signal, $d$ is the thickness of the sample and $A$ is the cross sectional area of the sample.

These measurements were carried out for frequencies in the range 200Hz to 5MHz and temperature from 323K to 423K on all the series of PTh composites samples. The sample was maintained at a desired elevated temperature and then the LCR meter was
given the commands to perform the measurements at different preset frequencies. The precaution was taken to maintain the temperature constant till the LCR meter performed the measurements as a function of frequency. The measurement data was captured by a computer using a data spreadsheet (Excel data sheet) [41, 42].

The present PTh-composite samples were subjected to study dielectric properties carried out in Department of Physics, Gulbarga University, Kalburagi. The results are presented in chapter 4.
REFERENCES


