CHAPTER 5
EXPERIMENTS AND METHODOLOGY OF INVESTIGATION

5.1 IMPEDANCE SPECTROSCOPY

Impedance spectroscopy is a potent technique for the characterization of electrochemical systems. The elementary approach of the impedance spectroscopy is to apply a small amplitude sinusoidal current excitation to the system under the steady-state and measure the voltage response. The experiment is carried at different frequencies for a wide range.

To measure the ac response samples were prepared by solution cast method. Silver paste is applied on both sides of samples to form the electrodes in contact with the two circular faces.

The AC parameters were measured at room temperature using HIOKI (Japan) LCR meter at the selected frequencies in the range from 50 Hz to 5 MHz. The sample was
then held between two nominally spring loaded copper plates and experiment is carried out.

Using the values of the equivalent parallel capacitance, Cp, dissipation factor, D, and parallel equivalent resistance, Rp, recorded by the LCR meter at a selected frequency, f, dielectric and conductivity parameters have been calculated using the equations given below.

\[
\begin{align*}
\text{Img dielectric} & \quad \varepsilon'' = \varepsilon' / \omega C_p R_p = \varepsilon' D \\
\text{Real conductivity} & \quad \sigma'(\omega) = \omega \varepsilon_0 \varepsilon'' \\
\text{Img conductivity} & \quad \sigma''(\omega) = \omega \varepsilon_0 \varepsilon' \\
\text{Real dielectric} & \quad \varepsilon' = C_p / C_0 \\
\text{Dissipation factor} & \quad D = \varepsilon'' / \varepsilon' \\
\text{Electric modulus} & \quad M = \varepsilon' / (\varepsilon')^2 + (\varepsilon'')^2
\end{align*}
\]

5.2 IONIC TRANSFERENCE NUMBER

Transference number measurements of the Nanocomposite electrolyte systems were made by means of Wagner’s polarization technique. In this method, the dc current is monitored as a function of the time on application of a fixed dc voltage across the cell: polymer Nanocomposite. After polarization of the cell with 9 V dc, the current vs time plot was obtained. Ionic Transference Number is obtained using following equation.

\[
\text{Ionic Transference Number} = (I_i - I_f) / I_i
\]

where,

\[I_i \text{ is initial current and} \]

\[I_f \text{ final residual current}\]
5.3 TENSION TEST

In present work tensile test was carried out using tensometer. The ultimate tensile strength is determined for different composition of nanocomposite. The ASTM standard of D638 - Standard Test Method for Tensile Properties of Plastics was used for the analysis of tensile specimen. D638 type 5 Dimensions is used for the model design of tensile specimen [116]. Figure 5.3 shows the Tensometer and Figure 5.4 shows tensile test specimens [117].
5.4 MICROHARDNESS TEST

Microhardness tests were used to determine the hardness of a material to deformation. The Vickers micro hardness test method uses a diamond indenter. The diamond indenter, in the form of a pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a test force of between 0.1kgf and 1kgf. The full load is normally applied for 10 to 15 seconds and using a microscope the two diagonals of the indentation in the surface of the material after removal of the load are measured and averaged. The area of the sloping surfaces of the indentation is determined. The Vickers hardness was measured by dividing the kgf load by the square mm area of indentation. The Vickers micro Hardness Tester MVH-1 is shown in Figure 5.5

F= Load in kgf \((100 \times 10^{-3} \text{ kgf})\)

\(D = \text{mean } d_1 \text{ and } d_2 \text{ in mm}\)
HV = Vickers hardness

Figure 5.5 Vickers micro hardness tester

The Figure 5.6 below shows the schematic diagram of Vickers micro hardness indentation and the shape of impression.

Figure 5.6 Shape of an impression under Vickers indentation

When the mean diagonal of the indentation has been determined the Vickers hardness may be calculated from the formula. The Vickers micro hardness should be reported like 800 HV/10, which means a Vickers micro hardness of 800, was obtained using a 10 kgf test force. This test gives accurate readings and just one type of indenter can be used for all types of materials under varying load.
5.5 DEGREE OF SWELLING AND SOLUBILITY OF FILM

The degree of swelling and solubility degree are carried as follows
(a) Squares of approximately of 1.5 cm$^2$ were cut and dried at 60ºC until constant weight ($W_1$). Then, they were immersed into 5 ml of distilled water at 26ºC (normal room temperature) for 1 minute.
(b) Afterwards, the samples were taken out from the water and the surface moisture was carefully removed by paper napkin. They were weighted again ($W_2$).
(c) Finally, samples were allowed to dry until constant weight at 60ºC and weighted once more ($W_3$).
(d) The degree of swelling (DS) and the solubility of the film (SF) were calculated according to the equation.
\[
DS(\%) = \frac{W_2 - W_3}{W_3} \times 100 \tag{1}
\]
\[
SF(\%) = \frac{W_1 - W_3}{W_1} \times 100 \tag{2}
\]

5.6 THERMOGRAVIMETRIC ANALYSIS

To study thermal decomposition behavior of samples, Thermogravimetric Analysis (TGA) was carried out for the samples. Thermogravimetric analysis is carried out to study the behavior of the sample with increase in temperature (with constant heating rate) and to evaluate the thermal stability of the sample.
The physical and chemical properties of materials are studied as a function of increasing temperature, or as a function of time. When the temperature increases, various dopants of the sample are decomposed and the weight loss occurs. The graph of temperature versus change in weight are plotted.

5.7 DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature.
Differential scanning calorimetry (DSC) was used to investigate the glass transition temperature (Tg) of the samples. The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions more
or less heat compared the reference sample is required to maintain the same temperature for both reference and sample being studied. The difference in heat flow between the sample and reference are observed, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions and records the glass transition temperature. Figure 5.7 Working principle of DSC and Figure 5.8 shows the Differential scanning calorimetry

Figure 5.7 Working principle of DSC

Figure 5.8 Differential scanning calorimetry
5.8 SCANNING ELECTRON MICROSCOPE (SEM)

In a typical SEM, an electron beam is emitted from an electron gun fitted to tungsten cathode. The primary electron beam interacts with the sample. The electron loses energy by repeated random scattering and absorption by the specimen. Due to energy exchange between the electron beam and the sample results the following

i) The reflection of high energy electrons by elastic scattering,
ii) The emission of secondary electrons by inelastic scattering
iii) The emission of electromagnetic radiation, Each can be detected by specialized detectors.

Figure 5.9 JOEL JSM vl6400 SEM Instrument
Following are steps used for SEM
a) SEM was used to determine size and distribution of particles sample, the sample placed on a SEM sample holder.
b) Carbon tape was placed under the polymer sample and a small roll of carbon tape was placed against the sample to stabilize it on the sample holder.

c) The samples were sputter coated with Platinum using an International Scientific Instruments sputter coater by covering the samples with a thin layer of Platinum atoms to reduce or eliminate charging issues.

d) Images are captured and analysed

5.9 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum. Goal of FTIR is to measure how well a sample absorbs or transmits light at each wavelength. The Figure 5.12 shows FTIR spectrometer and the typical FTIR spectra is shown in the Figure 5.13

![Agilent Technologies Cary 600 series FTIR spectrometer.](image)

Figure 5.12 Agilent Technologies Cary 600 series FTIR spectrometer.
The following steps were carried for FTIR:

a) Agile Technologies FTIR spectrometer 600 series was used to conduct FTIR test.

b) This spectrometer simultaneously collects spectral data in a wide spectral range from 400 to 4000 cm\(^{-1}\) range of wavelength.

c) It was used to determine percentage (%) transmittance of intensity at various spectral ranges of wavelengths.

d) Specimen was placed in the specimen holder and the percentage (%) transmittance was noted at different range of wave length.

e) Plotting of data to obtain FTIR using ORIGIN software.
5.10 X-RAY DIFFRACTION (XRD)

X-ray crystallography is a method used for determining the atomic and molecular structure of a crystal. The crystal atoms diffract X-rays beam into many specific directions. The measurement of the angles and intensities of these diffracted beams one produce a three-dimensional picture of the density of electrons within the crystal.

![BRUKER D8 XRD instrument](image)

Figure 5.14 BRUKER D8 XRD instrument

The X-Ray diffraction studies are carried out to confirm inter-planar spacing, crystallinity, microstructural parameters and lattice parameters from XRD plots. It also provides an important basis in understanding the various physical properties of the materials. The Figure 5.14 shows BRUKER D8 XRD instrument.
Condition for constructive interference is when \( n\lambda = 2d\sin\theta \) i.e. it obey Bragg’s law, where \( n \) is the order of diffraction, \( \lambda \) is the wavelength of X-rays beam Cu k\( \alpha \), \( d \) is inter planar spacing and \( \theta \) is the angle of diffraction.

The structural characterization of the polymer nanocomposite and its constituents are carried out by XRD by mounting the specimen on the specimen holder.

The following procedure were carried for XRD
The structure (crystalline or amorphous) of the phases in the samples was obtained at room temperature by using X-ray powder diffraction. The reflection diffractometer used is CuK\( \alpha \) radiation, and had a graphite mono-chromator in the secondary beam. The specimen was prepared by fill sample powder or the polymer nanocomposite in a glass specimen holder. The output Intensity of the data were measured in the 2\( \theta \) ranges between 2\( ^\circ \)and 110\( ^\circ \)and between 2\( ^\circ \)and 70\( ^\circ \), with a 2\( \theta \) step of 0.02\( ^\circ \)and a measuring time of 1 second per point by step scanning.

5.11 SUMMARY OF CONDUCTED EXPERIMENTS
The nanocomposite systems are experimentally studied using different instrumentation and procedure that were explained in this chapter. The experimental studies to determine conductivity, mechanical, thermal and structural characterisation were performed.