

Chapter 3

EXPERIMENTAL TECHNIQUES FOR MATERIAL CHARACTERIZATION

Material characterisation is incredibly useful for researching new materials. Validating filler surface treatment, performing compositional analysis, and evaluating electrical, thermal, and mechanical properties all require a diverse set of characterizations in the study of nanocomposites. This chapter explains the various characterisation and experimental methods employed in this study.

3.1 THERMAL CHARACTERIZATION

3.1.1 Thermo gravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) is a technique that monitors the mass of a substance as a function of temperature or time while the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. The measurements are widely used to assess the thermal and/or oxidative stabilities of a material, as well as its compositional properties. TGA also examines materials that have lost or gained mass as a result of decomposition, oxidation, or volatile loss (such as moisture). It's extremely valuable for polymeric materials research, such as thermoplastics, thermosets, elastomers, and composites.

TGA measurements are utilized in this study to:

- (a) Investigate the thermal degradation behavior of untreated nanoparticles and particles treated with a silane coupling agent.

(b) To determine the thermal and/or oxidative stability of neat epoxy and its nanocomposites (formed with untreated and surface-treated nano-fillers).

The analysis was carried out using a TGA-50 (Shimadzu) apparatus, as illustrated in Figure 3.1. The weight of a sample is measured on an analytical scale outside of the furnace while the temperature of the sample is steadily raised in a furnace [86].



Figure 3.1 TGA-50 (Shimadzu) apparatus at CIF, IIT (BHU)

3.1.2 Differential scanning calorimetry (DSC)

When polymers are heated, they undergo the processes of glass transition (T_g), melting, crystallization, and curing. Differential scanning calorimetry (DSC) has been used extensively in the study of these phenomena. This approach is commonly used to examine the α -transition in polymers and their composites. The Brownian motion of the main chains at the transition from the glassy to the rubbery state, as well as the

relaxation of associated dipoles, is linked to the α -transition. In the case of polymer nanocomposites, the DSC approach can reveal a significant change in T_g caused by the presence of nano-sized filler in the basic polymers.

DSC measurements of the materials were performed in this study using a DSC-60 plus (Shimadzu) instrument (Figure 3.2). The DSC setup consists of a chamber for measurement and a computer. In the measurement chamber, two pans are heated. The sample pan contains the substance being examined. A second pan is used as a reference, which is typically empty. The sample and reference pans' temperatures are increased at the same rate, and the heat flow is monitored. The computer is used to monitor and control the temperature of the pans. A typical heating rate is around 10 °C per minute. The rate of temperature change for a given amount of heat will differ between the two pans. This difference is determined by both the composition of the pan's contents and physical changes such as phase changes. During a phase transition, the rate of temperature rise between the two pans is no longer equal, and the computer controlling the DSC compensates for this by changing the power to the pans to maintain the same temperature. Plotting the heat flow as a function of temperature allows for the detection of phase transitions [86].



Figure 3.2 DSC-60 Plus (Shimadzu) apparatus at CIF, IIT (BHU)

3.1.3 Thermal conductivity measurements

Thermal conductivity measurement is a critical technique for characterizing dielectric materials because the majority of dielectric failures are thermal in nature. In this study, the purpose of this measurement is to determine how nano-filler inclusions affect the thermal conductivity of polymers and to identify the parameters that govern heat transfer in nanocomposites. Thermal conductivity measurements were made using a TPS 500 instrument in accordance with the ISO 22007-2:2008 recommended test procedure. The TPS sensor is fitted between two pieces of sample to perform the measurements, as illustrated in Figure 3.3. Cubic samples with dimensions of 15*15*15mm have been chosen to meet the thermal conductivity measurement setup requirements.

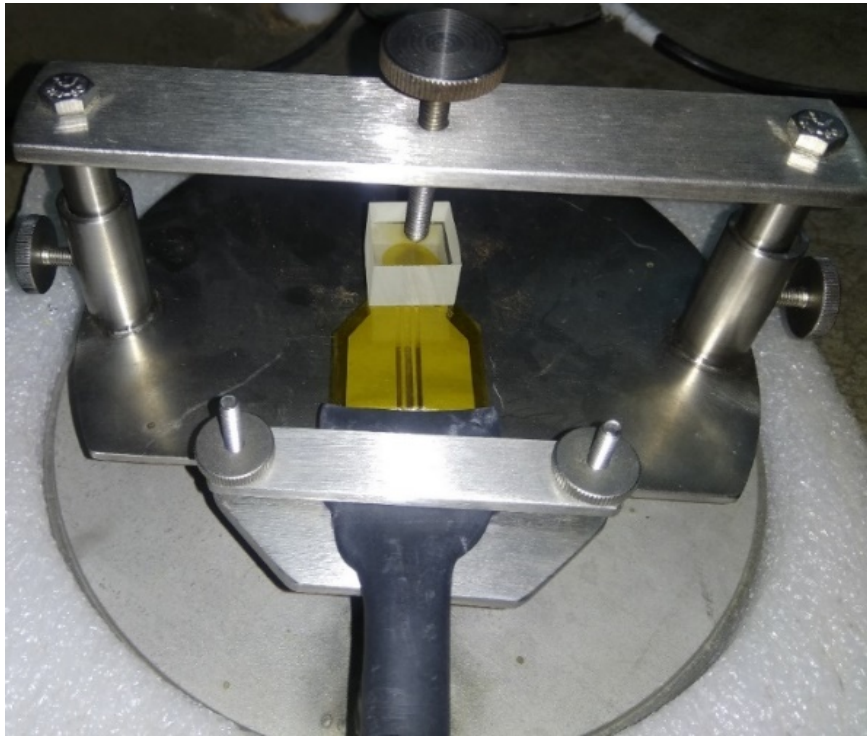


Figure 3.3 TPS sensor sandwiched between samples

3.2 ELECTRICAL CHARACTERIZATION

3.2.1 AC dielectric strength measurement

The dielectric strength of a material is an intrinsic property that indicates the maximum electric field that a material can withstand before losing its insulating properties. The AC dielectric strength of dielectric/insulating material is defined as the highest AC field required for dielectric breakdown.

The schematic diagram and complete experimental setup used in the laboratory to measure ac dielectric strength are illustrated in Figures 3.4 and 3.5, respectively. The dielectric sample is sandwiched between two ASTM standard (D149) circular brass electrodes. Both the electrodes and the sample are immersed in transformer oil to prevent surface flashover. The lower electrode is connected to the ground, while the

upper electrode is connected to a high AC voltage. The ac voltage is increased incrementally across the sample at a rate of 0.5 kV/s until the sample breaks down. Five random samples are tested from each batch.

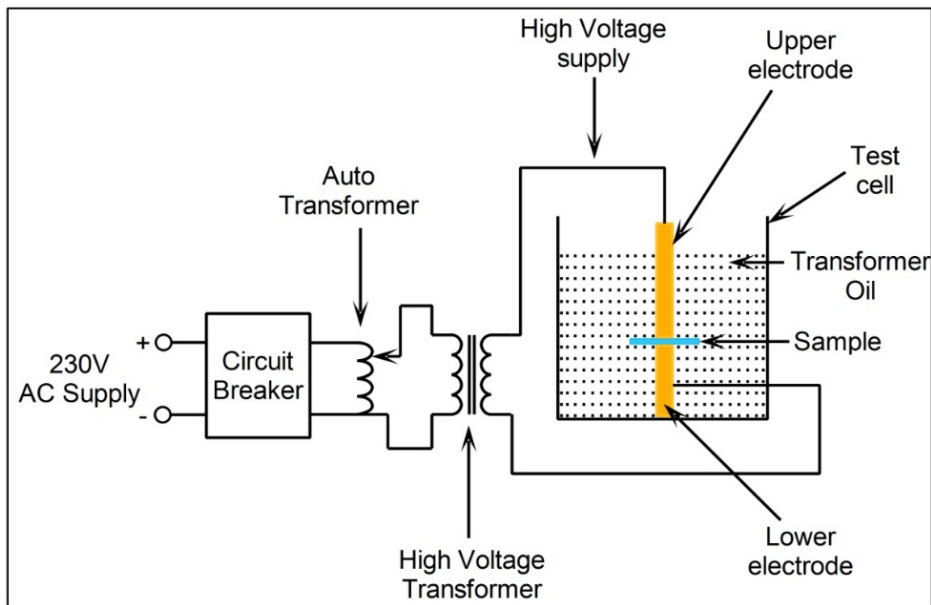


Figure 3.4 Schematic for the measurement of short term AC dielectric strength

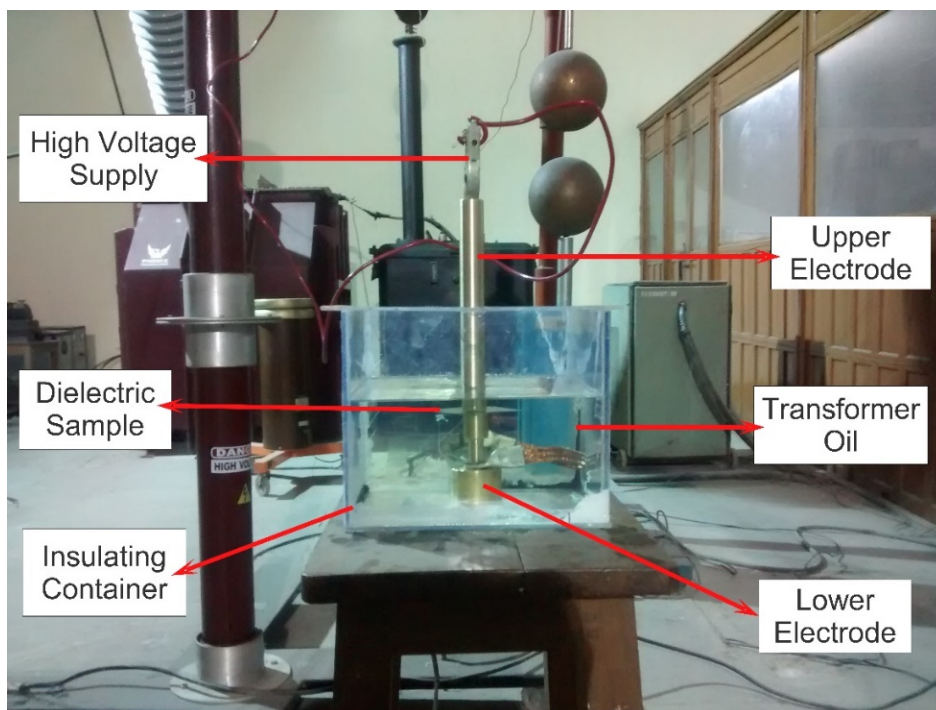


Figure 3.5 Experimental setup for the measurement of AC dielectric strength

Failure data are analyzed using 2 parameter Weibull distribution [87] as described below:

$$f(E) = 1 - e\left(-\frac{E}{\alpha}\right)^\beta \quad (3.1)$$

Where-

f – Cumulative failure probability

E – Applied electric field

α – Scale parameter indicates the electric field strength for which the probability for failure is 63.3%

β – Shape parameter indicates scatter of data.

The greater the values of the scale parameter (α), and the shape parameter (β), the more effective the insulating material will be. A larger scale parameter (α) indicates a greater dielectric strength, while a larger shape parameter (β) indicates that the breakdown data are dispersed over a narrow range [87].

3.2.2 DC conductivity

For electrical insulators operating at high voltages, resistance to current flow at large applied fields is vital. One of the most desirable properties of polymers and polymer-based composites is a high resistivity or low DC conductivity. DC conductivity measurements are made in this work using a standard three-electrode setup, as illustrated in Figure 3.6. The dielectric specimen is sandwiched between two electrodes, one high voltage, and one ground. Apart from the anode and cathode, a guard electrode is used to prevent current from leaking through the dielectric surface. Figures 3.7 and 3.8 illustrate a schematic diagram and an actual experimental setup for DC conductivity measurement, respectively.



Figure 3.6 Three electrodes arrangement for measurement of DC conductivity

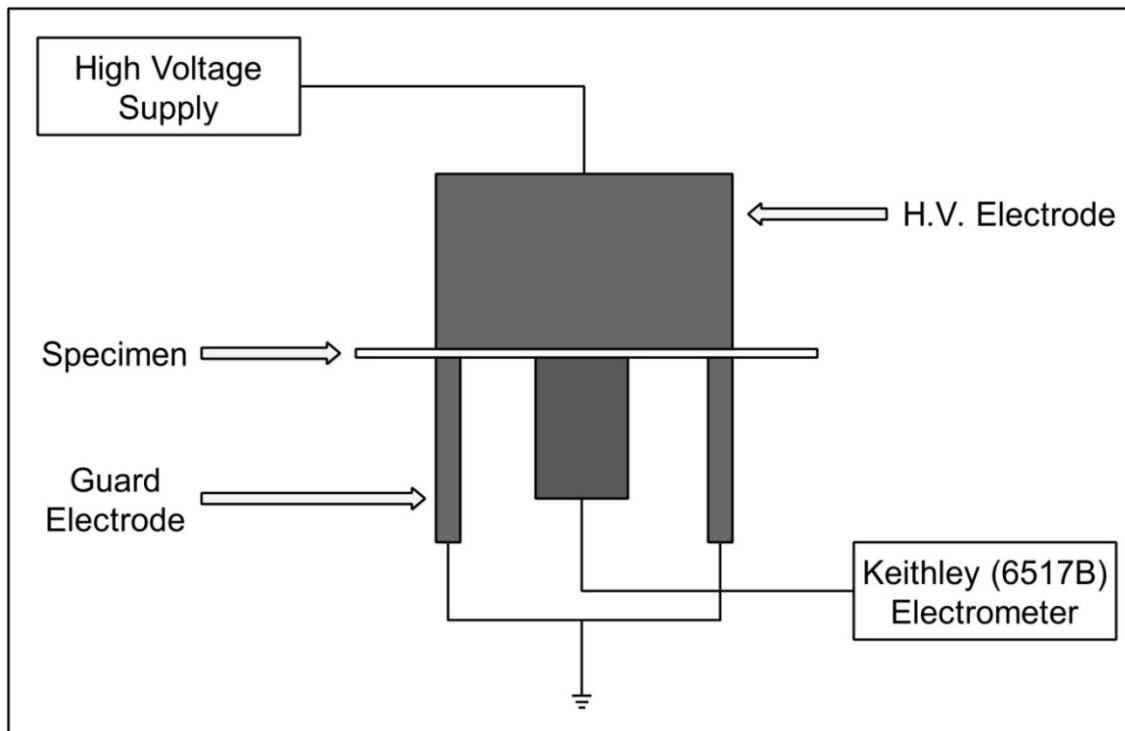


Figure 3.7 Schematics of three-electrode system for measurement of DC conductivity



Figure 3.8 Experimental Setup for the measurement of DC conductivity

The sample being tested is first polarized and then depolarized. Keithley 6517B electrometer is used to measure polarization-depolarization current. The time it takes for both currents to reach stable states determines the length of polarisation and depolarization. The schematic design in Figure 3.9 depicts the polarization-depolarization currents for a particular applied voltage. The following expression can be used to calculate the conduction current:

$$I_c(t) = I_p(t) - I_d(t) \quad (3.2)$$

where, $I_p(t)$ and $I_d(t)$ are the instantaneous but steady value polarization and depolarization current respectively.

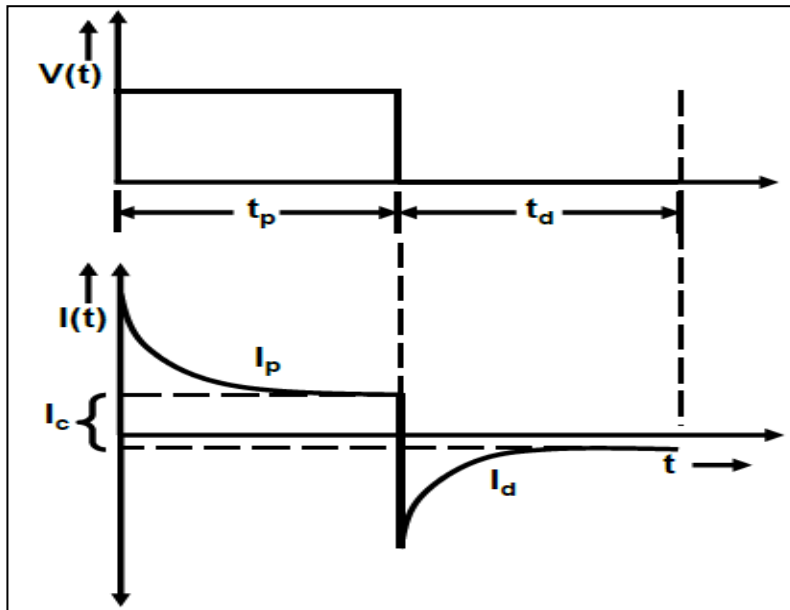


Figure 3.9 Schematics of a typical polarization-depolarization current waveform

The DC conductivity can be calculated from conduction current using the following expression:

$$\sigma_v = \frac{I_c \times t}{V \times A} \quad (3.3)$$

Where –

I_c – Conduction current

t – Thickness of the sample

V - Applied voltage

A – Area of the electrode

3.2.3 Dielectric Spectroscopy

Dielectric spectroscopy is a type of impedance spectroscopy in which the complex permittivity of a medium or sample is measured as a function of frequency. Dielectric spectroscopy is required for a thorough understanding of material physics and for analyzing device performance under a variety of operating conditions. It is based on the interaction between an external field and the material's electric dipole moment. In contrast to metals, which allow charges to move freely within the material, dielectrics bind all charges to specific atoms and molecules. These are referred to as bound charges. However, in the presence of an applied electric field, these charges can be displaced within an atom or molecule. In other words, when an external electric field is applied, a dielectric material becomes polarised. Permittivity is a quantifiable physical property that describes a material's ability to polarise in response to a field. Numerous dielectric polarisation mechanisms may exist in material, all of which contribute to its overall permittivity. Below is a detailed description of various polarisation processes:

Electronic polarization: Electronic polarization occurs when originally symmetrical distributions of the electron clouds are displaced with respect to the inner positive nucleolus under the influence of the applied electric field. It is most frequently observed in materials with no bonding or with pure covalent bonding between atoms. Electronic polarisation occurs across a broad frequency range (up to 10^{15} Hz) and is common in all dielectric materials.

Ionic polarization: Ionic polarisation, also known as vibrational or displacement polarisation, is a type of polarisation that occurs in ionic compounds. It can be found in materials that have an ionic bonding or a covalent bond with an ionic nature. Positive

and negative ions are moved in opposite directions when an electric field is applied across an ionic substance until the ionic bonding forces stop the process, creating a dipole moment. Inorganic crystals, glasses, and ceramics all have this form of polarisation. When an alternating field is applied, the ions continue to oscillate about their equilibrium location, resulting in constant energy consumption in the form of dielectric loss. Because the ions are unable to respond to such a quick reversal of alternating field due to their inertia, there will be no ionic polarisation if the frequency is increased beyond optical frequency (10^{13} Hz).

Oriental/dipolar polarization: Orientation polarization occurs due to the reorientation of the molecules in the material. This polarization occurs in the materials consisting of molecules with a permanent dipole moment. Molecules with a permanent dipole moment are subjected to torque in an electric field, which tends to orient them in the direction of the field. After each half cycle, the dipole's orientation is reversed, resulting in a continuous change in the dipole's orientation. As a result, energy is continuously consumed in the form of dielectric loss. When the frequency is increased beyond radio frequency (10^{10} Hz), the dipoles' inertia prevents them from responding to such a rapid reversal of the alternating field. As a result, orientational polarisation is effective only up to radio frequency.

Interface/space-charge polarization: The electronic, ionic, and dipolar polarization discussed previously are due to bound charges within the atom. However, dielectric polarisation, on the other hand, can be linked to both mobile and trapped charges. This polarization is generally referred as space charge polarization. Long-range charge movement in the material causes space charge polarisation. It can be seen in multiphase materials that include lattice faults. Charge carriers (electrons, holes, and ions) tend to accumulate near interfaces or physical barriers such as defects, voids, impurities, and

grain boundaries. The accumulated charges distort the local electric field, and hence, change the permittivity of dielectric materials. Interface/or space charge polarization is effective only up to audio frequency (20 kHz).

Each polarisation mechanism takes time to complete, and the time constant associated with it is called relaxation time. When the relaxation time is significantly shorter than the frequency of the applied electric field, instantaneous polarisation occurs. Polarization does not occur when the relaxation time is much slower than the frequency of the applied electric field. However, when the relaxation time and the applied electric field frequency are close, a phase lag occurs, and energy is absorbed. The permittivity of dielectric material is governed by the cumulative effect of different polarization mechanisms. The time scale at which the various mechanisms contribute to polarization is depicted in Figure 3.10.

In this research, dielectric spectroscopy measurements were carried out to measure real relative permittivity (ϵ_r'), imaginary relative permittivity (ϵ_r'') as a function of frequency. The purpose of this experiment is to understand how the incorporation of nanofillers and their surface treatment affect the dielectric response of epoxy nanocomposites.

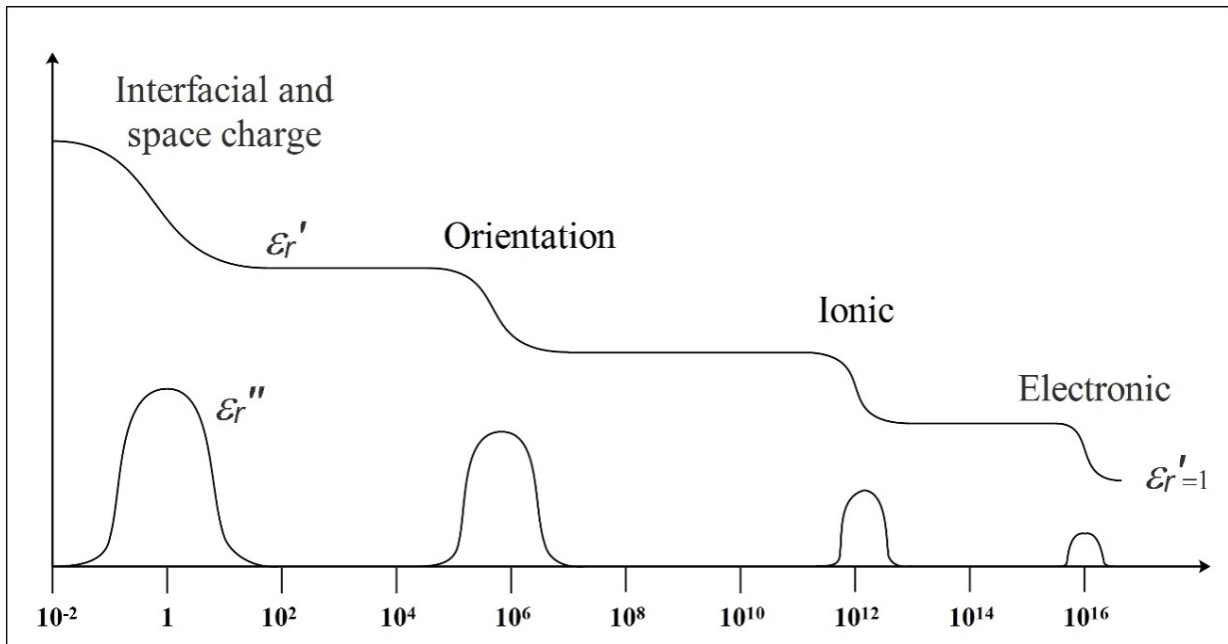


Figure 3.10 Polarization phenomena as a function of frequency

3.2.3.1 Experimental Setup for dielectric spectroscopy

Permittivity and loss factor measurements were performed using a Novocontrol alpha analyzer (type K), as illustrated in Figure 3.11. This instrument operates at a frequency range of 10^{-2} - 10^7 Hz. The sample thickness is approximately 0.3 mm, and the diameter of the instrument's electrode is 12.45 mm. At room temperature, three types of samples were tested: pure epoxy, epoxy nanocomposites (with untreated nanofillers), and epoxy nanocomposites (with surface-treated nanofillers). Circular dielectric samples with a diameter of approximately 15 mm were prepared. Following that, a small amount of silicon oil should be applied to both sides of the samples to prevent an air gap between the electrode and the sample surface. Figure 3.12 illustrates the electrode sample assembly, while Figure 3.13 illustrates the dielectric spectroscopic measurement principle using a schematic.



Figure 3.11 Experimental setup of Dielectric Spectroscopy

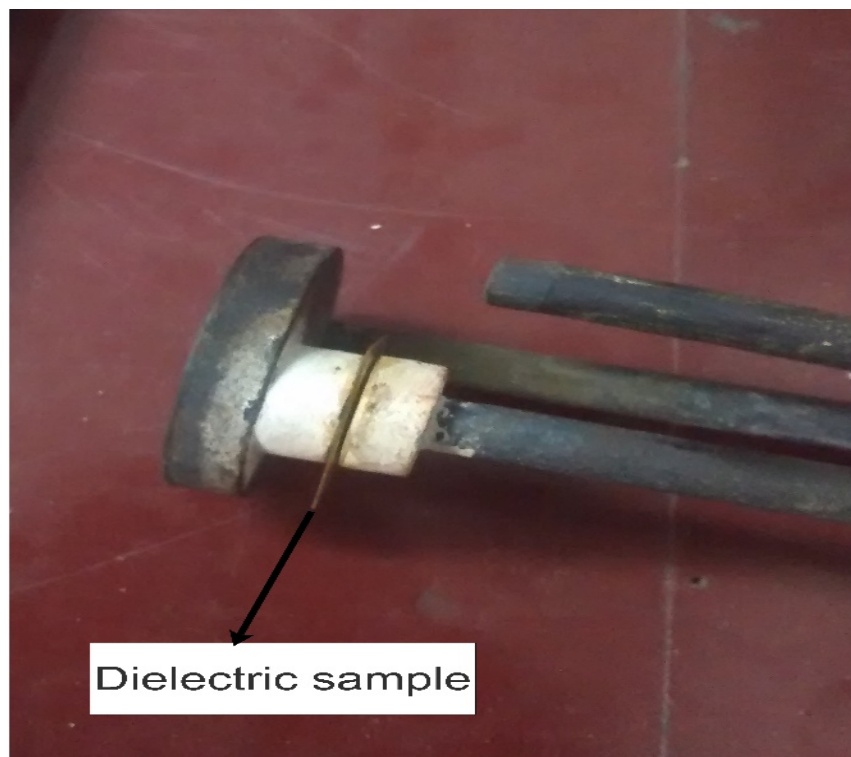


Figure 3.12 Dielectric sample and electrode assembly

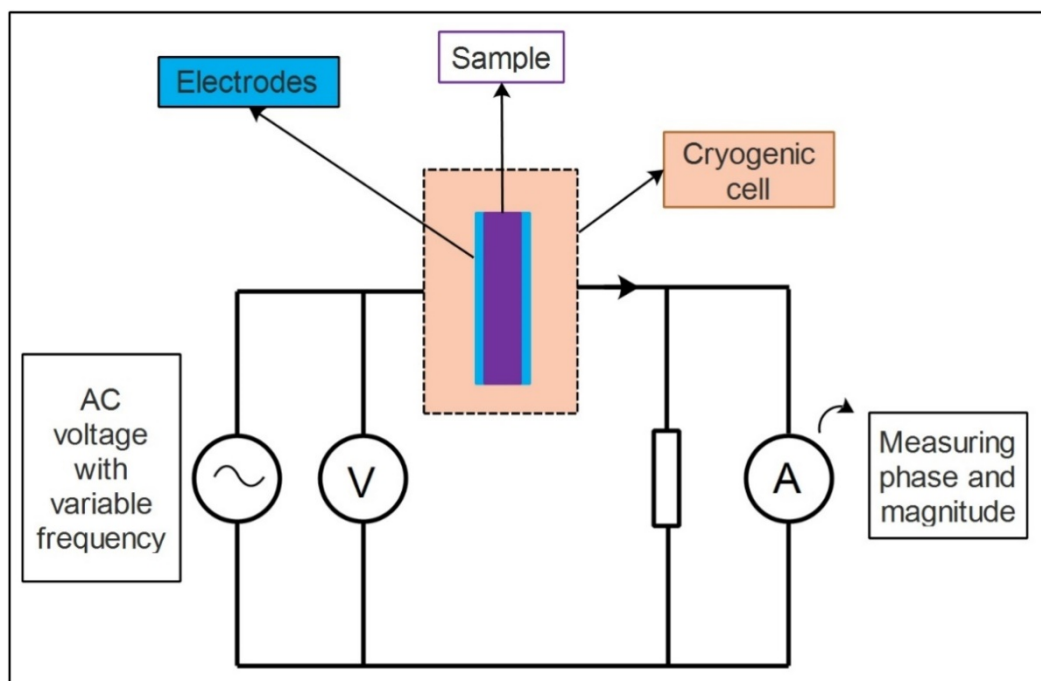


Figure 3.13 Schematics of dielectric spectroscopic measurements

3.3 CHEMICAL CHARACTERIZATION

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy is a highly effective technique for determining the molecular structure of materials as well as the kinetics, mechanism, and pathway of chemical reactions. The FTIR equipment operates on the basis of a Michelson interferometer, which is composed of a beam splitter, a fixed mirror, and a moving mirror. The source's infrared radiation strikes the beam splitter, where 50% of the incident radiation is reflected and 50% is transmitted to the moving mirror. Both mirrors reflect the radiation back to the beam splitter, where each beam is split into 33 distinct beams, one of which returns to the source and the other of which travels to the sample and then to the detector. A difference in optical path length exists between the two beams that recombine at the beam splitter as a result of the moving mirror. At the detector, the optical path difference produces an interference pattern, or interferogram,

as a result of the two beams' constructive or destructive interference. Due to the source's simultaneous emission of a range of frequencies, the resulting interferogram at the detector is the sum of all the interferograms corresponding to the various frequencies. The spectrum is then obtained by computing the interferogram's Fourier transform numerically. Prior to reaching the detector, the infrared signal must pass through the sample. To absorb infrared radiation, the infrared radiation's oscillating electric field component must interact with the bonds in the molecule, causing a change in the dipole moment. The molecules will absorb infrared radiation only at the frequency of their natural vibration. As the detected signal's intensity decreases due to infrared absorption, this will manifest as minima peaks in the transmission spectrum. Due to the fact that different molecules produce distinct spectra, FTIR can be used to identify and differentiate the molecular structure of various materials [88].

In this work, Fourier Transform Infrared Spectroscopy (FTIR) is used in synthesis and characterization of epoxy-based nanocomposites. By detecting and measuring distinct functional groups, FTIR spectroscopy makes it easier to choose the right coupling agent and to validate the surface functionalization of nanoparticles. Additionally, FTIR is used to elucidate surface and interfacial phenomena by analyzing the structural changes that occur in PNC as a result of chemical bonding between the filler and the host polymer. The FTIR scan is carried out on wave numbers between 500 and 4000 cm^{-1} . FTIR measurements are carried out at the Central Instrument Facility (CIF) of the Indian Institute of Technology (BHU) using the Nicolet IS5 model of THERMO Electron Scientific Instruments, as illustrated in Figure 3. 14.



Figure 3.14 FTIR (Nicolet IS5 model) apparatus at CIF, IIT (BHU)

3.4 STRUCTURAL CHARACTERIZATION

3.4.1 X-Ray Diffraction (XRD) Analysis

X-Ray diffraction (XRD) technique is used to analyse the crystal structure of the material synthesized. In the synthesized nanocomposite the polymer matrix is in amorphous phase while the nanoparticles are crystalline. The combined effect of nanoparticle and the polymer matrix provides a range of phase varying in crystallinity. The variation of crystallinity of the synthesized material is analysed using the XRD technique. When there is a perfect ordered crystal structure sharp peaks of the nanoparticles in the XRD graph will appear and a broader peak for an amorphous material. A varying intensity of peaks in XRD graph will confirm the varying crystallinity and hence varying nanoparticle concentration.

X-Ray Diffraction technique depends upon the Bragg's law which states that in a crystal structure X-ray light diffracts from the different layers of the crystal and a peak of constructive interference can be seen at a particular incident angle. This constructive interference peak is observed when incident angle satisfies the criteria

$$2d\sin\theta=n\lambda \quad (3.4)$$

Where d is the distance between layers of the crystal, θ is the incident angle and λ is the wavelength of the X-Ray Irradiation. For a perfect crystal structure when diffraction occurs at every unit cell of the crystal very sharp peaks at defined intervals are obtained for each layer of the crystal. Whereas there is only a broadened peak in the amorphous specimen.

XRD measurements are depicted as a plot of Intensity vs 2θ , which is effectively the angle between transmitted and diffracted wave. Sample platform is rotated to change the incident angle of X-rays on the sample and intensity of diffracted X-rays are recorded using a detector. When Bragg's law is satisfied a constructive interference occurs and a peak at that particular angle is observed which gives phase information of the specimen [88].

As shown in Figure 3.15, XRD measurements are carried out in this work utilizing a Rigaku smart lab 9kW XRD analyzer, which is situated at CIF IIT (BHU). Specifically, the goal of this research is to determine the crystallinity of filler materials and to gain a better understanding of how structural changes caused by the addition of nanofillers to polymers related to change in thermoelectric properties of these materials.



Figure 3.15 XRD (Rigaku smart lab 9kW) apparatus at CIF, IIT (BHU)

3.5 SUMMARY

This chapter provides a detailed description of the thermal, electrical, chemical, and structural characterization techniques used to investigate epoxy alumina nanocomposites. The following chapter discusses the experimental findings and critical analysis based on these characterization techniques' results.