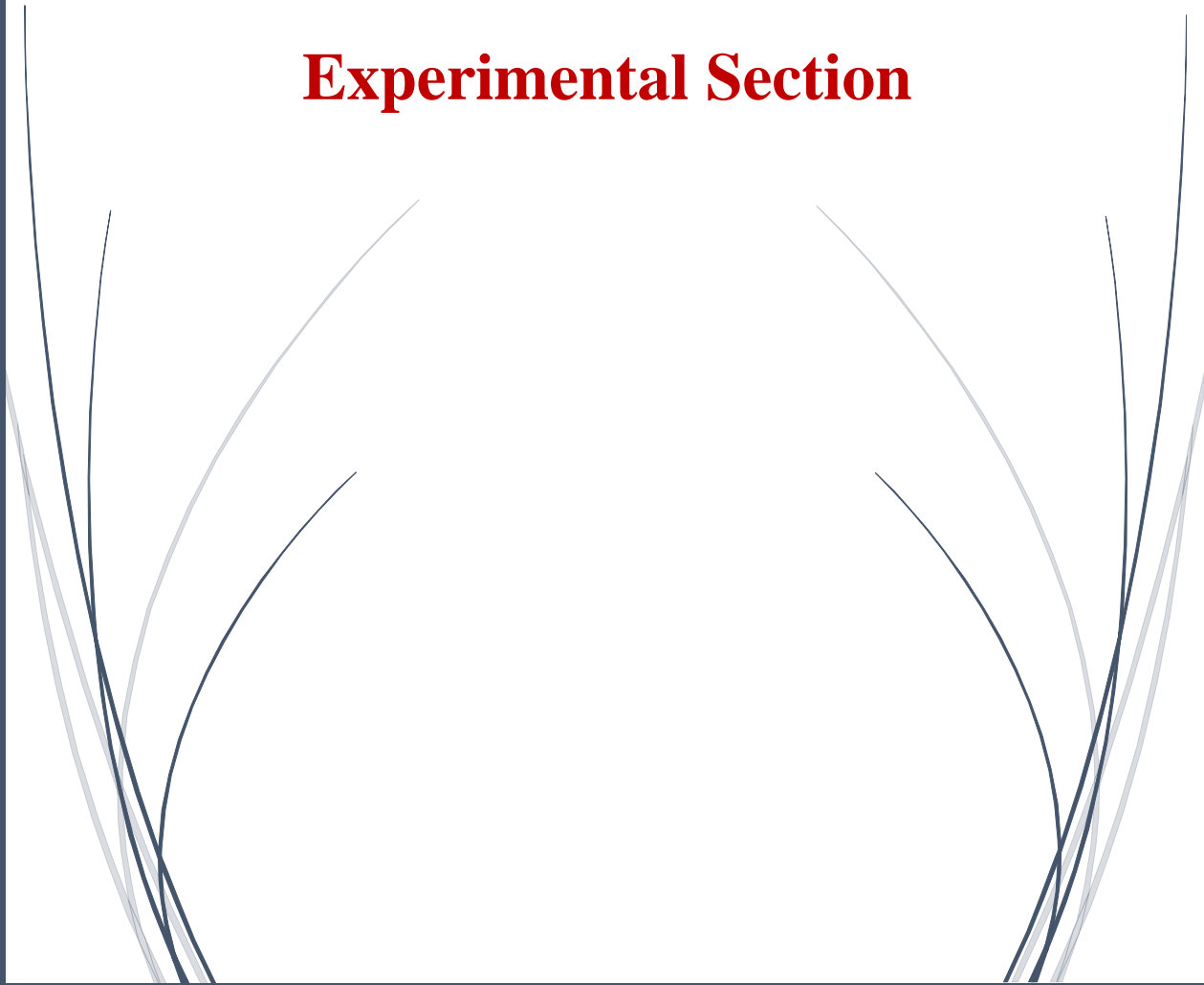# Chapter 2

Experimental Section

2.1 Materials

2.1.1 Materials for nanohybrids

Poly(ethylene terephthalate) (PET) was obtained in granular form from Otto Chemie Pvt. Ltd. India. The density of PET was 1.38 g/cm^3. The fillers used were nanotalc, NK75 and Cloisite 30B nanoclays.

2.1.2 Materials for polymer blends

The poly (acrylonitrile-butadiene-styrene) (ABS) was obtained from the e-waste collected from local sources. The polyethylene used was commercial grade low-density polyethylene (LDPE) which was obtained from Reliance Industries Ltd., India. Maleic anhydride (MA) was purchased from Sigma Aldrich Chemical Pvt. Limited, having density of 98.06 g/mol

2.2 Nanohybrid preparation by solvent casting

The polymer nanohybrids were prepared via solvent casting route (*Figure 2.1*). The DCM was taken as the solvent of PET polymer. PET was taken according to weight ratio required for the composition of nanohybrid. In one beaker, the PET was dissolved in appropriate amount of DCM at room temperature via mechanical stirring. The stirring was continued until the PET granules were dissolved in DCM completely and a homogeneous solution was achieved. In another beaker, DCM was taken and nanoclay was added into it in required weight percentage. To disperse the nanoclay homogeneously in the DCM solvent, sonication was done for about 1 hour.
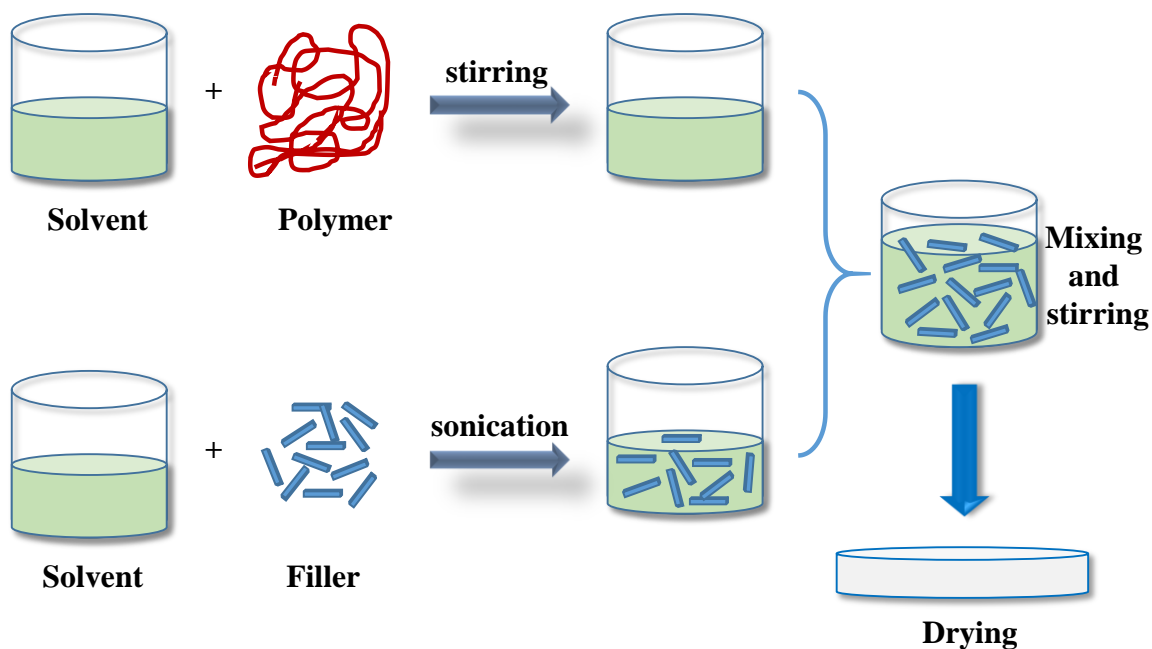
Figure 2.1: Solvent casting route for the nanohybrid preparation.

Dispersion of nanoclay in solvent by sonication also helps to get rid of large agglomerates of nanoclay. This dispersed clay in DCM was then mixed with the dissolved PET. This solution was then mechanically stirred for another one hour for complete mixing of both solutions and through dispersion of nanoclay in the polymer solution. This solution was then taken onto a petri dish. It was dried at room temperature for 24 hours. After that it was put into a vacuum oven for the complete drying of the DCM from the prepared nanohybrid.

2.3 Blend preparation by reactive extrusion

The extrusion technique was used to prepare the polymer blends. It processes the material by mixing them using heat and shear force. The polymers were fed through hopper into the barrel. The barrel is heated and the temperature and rpm of the barrel was optimized to get the desirable properties. A twin screw extruder "*Thermo Scientific Haake Mini Lab 2*" was

used for the blend preparation. The shear force resulting by rotation of two screw caused polymers mixing and heat derived the reactive extrusion to take place.

2.4 Injection molding

Prepared material was molded into the required shape and size for the characterization. Injection molding technique was used to make the dog bone samples. HAAKE micro-injector was used for this purpose. The polymer nanohybrid and blend samples were cut into small pieces and was melted at 250 °C temperature in the heating barrel. The mold was kept at a temperature of 40 °C. The melted polymer was microinjected into the mold with a pressure of 100 bar. Hence prepared dogbone samples had gauge length of 20 mm, width 4 mm and thickness 2.14 mm.

2.5 Compression molding

The films of polymer nanohybrid and polymer blends were prepared by compression molding technique. The compression molding machine used was *S.D. Instruments, India*. The upper and lower plates of the compression molding machine were heated lower than the melting temperature of the materials. The material were put in between the two heated plates and pressed to get the desired thickness.

2.6 Transmission electron microscope (TEM)

To investigate the dispersion of nanoclay platelets in the polymer matrix, TEM was performed. TEM uses the electrons for imaging instead of light. The electrons have much smaller wavelength than light, hence the optimal resolution attained is multitude folds better than the light microscope. With the help of TEM imaging technique, the nanomaterial can

be observed up to sub-nanometer resolution. The common range of acceleration voltage is taken as 80-200kV. To get the internal structure imaging, the electron beam is transmitted through the ultrathin sample. These transmitted electrons are focused by an objective lens on an imaging device (charge couple device (CCD) camera or phosphor screen). The image formed has dark and light areas. The portion of the sample from where the fewer electrons pass, form darker areas, whereas the portion which transmits more number of electrons, forms lighter area. The diffraction patterns can also be attained by the objective lens. These diffraction patterns are useful in studying the crystallographic structures of samples. *FEI Technai 20* was used at an accelerating voltage of 200kV. The ultrathin segments of polymer samples of thickness less than 100nm were cut with the help of *Leica ultracut UCT* equipped with a diamond knife at a temperature of -80 ℃

2.7 Scanning electron microscopy (SEM)

To investigate the morphology of the polymer samples, SEM was used. SEM is an important characterization tool to understand the surface texture, crystalline structure, chemistry, composition, orientation and geometry of the components that are present in the sample. It gives a detailed, high spatial resolution image produced by electron and sample interaction. It uses a focused beam of electron having energy of 1 to 50 keV. This electron beam is generated using filament of lanthanum hexaboride (LaB_6). After the interaction of electron beam and sample, low-energy secondary electrons and high-energy backscattered electrons emit from the sample surface. These electrons contain the information about the sample composition and surface morphology. These electrons are scanned on a detector to produce the image. The surface of the samples is desired to be electrically conductive to achieve a sharp image. For this purpose, samples are coated with evaporating a very thin film of metal

(for example gold) having a thickness ranging 50-100 Å. *SUPRA 40, Zeiss FESEM* was used for the SEM imaging of the samples.

2.8 X-ray diffraction (XRD)

XRD analysis is a technique by which the crystallographic structure of materials is determined. XRD helps in elucidating the information about structures, crystallinity, grain size, crystal structure, phases, preferred orientation of crystals etc. The material is irradiated by the incident X-rays and the useful information is extracted by measuring the scattering angles and intensities of X-rays that reflect from the material. XRD is a nondestructive technique which is very versatile and is most commonly used because of its ease and accessibility. Every material has its unique atomic structure because of which when it is irradiated by X-rays, destructive and constructive interference of scattered X-rays generate. It results in a unique diffraction pattern which contain the information about the material. XRD experiment was performed using *Rigaku Miniflex 600* X-ray diffractometer for obtaining the diffraction patterns of the samples. A graphite monochromator used CuKα radiation (wavelength 0.154nm) at operating voltage of 45kV and current of 20mA. The sample holder used was made of quartz crystal. The experiments were performed at room temperature with a scan rate of 3 deg/min.

2.9 Fourier-transform infrared spectroscopy (FTIR)

FTIR uses infrared light to scan and identify the inorganic, organic and polymeric materials. The resultant signal which has frequency in the range of 4000 to 400 cm^{-1} carry materials' molecular fingerprints. Different functional groups have different absorption frequency. The radiation that is absorbed by a molecule is related to its atoms and the way they are bound

together. The variation in the absorption frequencies signifies the change in composition of material. FTIR spectra of the samples were performed using *Thermo Nicolet 5700* in the range of 3500 to 400 cm^{-1}. The experiments were performed at room temperature with a resolution of 4 cm^{-1}.

2.10 UV-visible spectroscopy

It is a technique in which ultraviolet (UV) –visible light is used. The UV-visible light falls on the material and it is absorbed by the molecule. The absorption takes place when the incoming light frequency is equal to the difference in energy of ground state and excited state. Due to this absorption, the electrons from lower energy states excite to the higher energy states. The energy difference between each ground state and excited state pair associates to an absorption band. These absorption bands contain the information about the molecular structure of the material. Because of varying environmental conditions and different molecular interactions, the wavelength of absorption band shifts. The instrument used was *JASCO V-650* spectrophotometer. The samples were tested in solid state using a quartz sample holder in the wavelength range of 200-800 nm.

2.11 Nuclear magnetic resonance spectroscopy (NMR)

The measurements of solid state 13C NMR were performed at a resonance frequency of 100 MHz on JEOL 400 MHz. The spinning probe used was 4 mm cross-polarization double resonance magic angle probe. For the measurements, weight of 100–200 mg of each sample was taken and tightly packed into a cylindrical zirconium oxide rotor of 4 mm using a kel-F end-cap.

2.12 Atomic force microscopy (AFM)

To study the surface roughness, atomic force microscopy was performed. An NTMDT multimode scanning probe microscope having model NTEGRA Prima was used in semi contact mode. The tip used was of silicon nitride mounted on a long cantilever having frequency of 240–250 kHz and the spring constant was 11.5 N/m.

2.13 Polarized optical microscopy (POM)

To determine the morphology and phase investigations, the thin sheets of samples were investigated by polarized optical microscopy (Leitz Biomed). Thin sheets of samples were tested to identify the different phases, level of mixing etc.

2.14 Thermogravimetric analysis (TGA)

TGA is an analytic technique which determine material's thermal stability by measuring continuous weight change at a constant heating rate in a controlled atmosphere (Ar, N_2, O_2, air). It determines the practical usable temperature range for the specific material. It provides information about phenomenon associated with mass loss or gain upon heating such as decomposition, second order phase transitions, adsorption, absorption, solid gas reactions, loss of volatiles etc. Using TGA, material's characterization can be done by analyzing its characteristic decomposition patterns. It helps in determining inorganic and organic content, reaction kinetics and degradation mechanism. TGA analysis was done using a thermogravimetric analyzer *Mettler-Toledo* which had a differential thermal analyzer. An alumina crucible was used as a sample holder. The temperature range was taken from room

temperature to 600 ºC at a constant heating rate of 20 ºC/min in a controlled atmosphere of nitrogen gas.

2.15 Differential scanning calorimetry (DSC)

DSC is an analytical technique which measures heat required to increase the temperature of the sample compared to the reference material. The temperatures of reference material and sample are kept same and the heat difference is measured as a function of temperature. DSC curves helps in determining different phenomenon such as glass transition temperature, melting temperature, crystallization, chemical reactions such as thermal curing as well as specific heat capacity, material's purity analysis and heat history can also be obtained. A *Mettler 832* differential scanning calorimeter was used for DSC measurements. It was calibrated using indium and zinc before the experiments started. An aluminium crucible was used as the sample holder. The experiments were performed at a temperature range from room temperature to 300 ºC at a constant heating rate of 10 ºC/min. The weight of samples were taken 4-10mg.

2.16 Mechanical properties

To determine the mechanical properties of material, tensile tests were performed. Tensile testing helps in characterizing material's brittleness or ductility as well as its tensile strength, yield strength, elongation, elastic modulus, toughness The injection molded dog bone samples were fixed between two grips and were stretched at a fixed strain rate until the fracture. A universal testing machine (UTM) *Instron 3369* with a load cell capacity of 50 kN was used for tensile testing. The experiments were performed at room temperature with a crosshead speed of 5 mm/min. A stress-strain curve was obtained as output. The Young's

modulus was obtained from slope of the linear part of the stress-strain curve and toughness was calculated from the area under stress-strain curve.

3-point bending tests were performed on the same machine with 3-point bending jaws setup. The span length was taken as 20 mm. The constant strain rate was taken as 3 mm/min. Flexural stress (σ_f), flexural strain (ε_f) and flexural modulus (E), were calculated as:

$$\sigma_f = \frac{3FL}{2bd^2} \tag{2.1}$$

$$\varepsilon_f = \frac{6Dd}{L^2} \tag{2.2}$$

$$E = \frac{L^3 m}{4bd^3} \tag{2.3}$$

where, F is load (N), L is support span length (mm), b and d are the width and thickness of the specimen (mm). D is the maximum deflection at the center of the specimen (mm), m is the slope of the initial straight part of the flexural stress vs. flexural strain curve.

2.17 Vicker Hardness Test

For measuring microhardness of the materials, vicker hardness tests were performed. It is a destructive test which uses a square base diamond pyramidal indenter which has 136° angle between its two opposite faces. The instrument used was a vicker hardness tester, *Tinius Olsen, FH5 series* with indenter number *DK4132*. The diamond indenter was pressed onto the sample with a force of 0.5kgf. The dwell time was 15 seconds. The two diagonals of the

micro indentation resulted on the sample surface were measured using microscope. The hardness is measured in form of VHN (vicker hardness number) which was calculated as:

$$\text{VHN} = \frac{2F\sin(\frac{136^\circ}{2})}{d^2} = 1.854\frac{F}{d^2} \qquad (2.4)$$

Where F is force applied, d is the average of the diagonals of the indentation.

2.18 Dynamic mechanical analysis (DMA)

To investigate about the temperature dependent viscoelastic properties of the samples, DMA tests were performed. The experiments were performed using a dynamic mechanical analyzer *DMA 242 E model, NETZSCH, GmbH* under tensile mode. The temperature range was taken from -10 °C to 200 °C at a constant heating rate of 3 °C/min. The experiments were performed at a constant frequency of 1Hz. The sample dimension was kept 5×5 mm^2 with gauge length of 5mm. The analysis was done at a constant strain amplitude of 20 µm and a dynamic force of 1N.

2.19 Two dimensional small angle X-ray scattering (SAXS)

It is an analytical technique in which intensities of X-rays scattered from sample are measured by a 2 dimensional detector at a very low scattering angle ranging from 0.01 to 5 deg. With the help of SAXS, comparatively larger structures can be identified compared to XRD because as the scattering angle decreases, the observable length scale increases. SAXS is a very useful nondestructive method to examine the materials having components in nanometer range (typically from 1 nm to 100nm). To study the effect of stretching in nanohybrids, SAXS measurements were done. A *XEUSS 2D SAXS* system was used which was equipped with a 6 kW rotating anode generator operating at 0.6mA current and 50 kV

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voltage with Ge monochromator and CuKα radiation. The experiments were performed for 6 hours for each sample. The two dimensional SAXS images were obtained which were then integrated azimuthally for obtaining one dimensional scattering intensity profiles as a function of q, defined as:

$$q = \frac{4\pi \sin \theta}{\lambda}$$

(2.5)

Where q is magnitude of scattering vector, 2θ is scattering angle, λ is the wavelength of radiation. The scattering intensity profiles obtained were corrected for background scattering.

2.20 Gas barrier measurements

The gas barrier measurements were performed to examine oxygen permeability of the samples. An *OX2/231 oxygen permeability tester (ASTM D398)* of *Labthink International, China* was used. The sample films were prepared with a humidifier system at 0% relative humidity and at 25 ± 0.1 °C temperature using temperature controller *TC-01, Labthink*. The sample films were cut in circular shape having area of 50 cm². The experiments were performed at room temperature. High purity oxygen gas (99.99%) was used at a constant flow rate of 20mL min⁻¹ for the gas permeability measurements. High purity Argon gas (99.99%) was used at a constant flow rate of 10mL min⁻¹ for the purging. The experiments were performed for 6 hours for each sample and the tests were done in triplicate for each composition to ensure minimum error estimation. The output permeability values were obtained in cc.cm/m²/day/atm (normalized with film thickness).

2.21 Heat distortion temperature (HDT)

Heat distortion temperature tests were conducted to ensure the applicability of the samples to be able to work under different temperature range for specific weight loading condition. The HDT test was performed on a sample size of $20 \times 4 \times 2$ mm3 with span length of 20 mm. The 3-point bending arrangement was kept in a water bath. The load applied was 0.2 kgf. The temperature of water bath was increased gradually while applying the constant load till the sample deflects by a distance of 0.25 mm. The temperature of this deflection point was noted as heat distortion temperature (HDT).