# Chapter 2

Experimental

2.1. Materials:

2.1.1. Polymer: Commercial poly(vinylidene fluoride) (PVDF) SOLEF 6008 with molecular weight 2.7×10^5 and its copolymer poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) SOLEF 11008 were kindly supplied by Ausimont, Italy for the study. The copolymer is termed as HFP hereafter.

2.1.2. Fillers:

1. *Cloisite 30-B:* An organically modified clay, Cloisite 30B [bis(hydoxyethyl) methyl tallow ammonium ion exachangemontmorillonite], density 1.98 g/cc southern clay, U.S. Tallow is a mixture of C16 and C18 long chain alkenes.

$$CH_3 - \overset{\overset{\displaystyle CH_2CH_2OH}{|}}{\underset{\underset{\displaystyle CH_2CH_2OH}{|}}{N^+}} - T$$
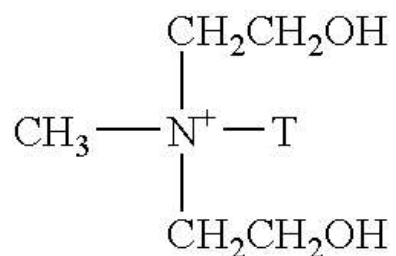
Where T is tallow (~65% C18; ~30% C16; ~5% C14)

Figure 2.1: Organic modifier used for modification of nanoclay.

Tallow is a mixture of C18 and C16 long-chain alkene. The interplanar distance of the clay increases to 1.8 nm from the 1.1 nm after organic modification. The lateral dimension of nanoclay is ~250 nm.

2. *Egg shell membrane:* Raw egg purchased from local market. Egg is broken and the inner flexible layer of eggshell is carefully peeled, dried and crushed to fine powder to use as filler.

3. *Orange Peel*: Fresh oranges were peeled and its peel is dried and crushed to fine powder to use as filler.

4. *Pomegranate peel*: Fresh Pomegranates were peeled and its peel is dried and crushed to fine powder to use as filler.

Dimethyl formamide (DMF) form Hi-Media is used as common solvent, PDMS (Polydimethylsiloxane) purchased from Ellsworth Adhesives, India is used for encapsulation of the prepared device.

2.2. Hybrid preparation:

Hybrids of polymer and filler are prepared by solution route (**Figure 2.2**). The polymer is dissolved in Dimethyl formamide (DMF) at 60ºC on magnetic stirrer and the filler is dispersed in the DMF separately through sonication. After the polymer is completely dissolved in the solvent and the filler properly dispersed in the DMF, both the solutions are mixed together and kept on stirring for proper mixing. After the mixing, the mixture is poured in the petri-dish and kept for drying. To completely remove the solvent, it is kept in vacuum oven overnight. The prepared hybrid is then collected.
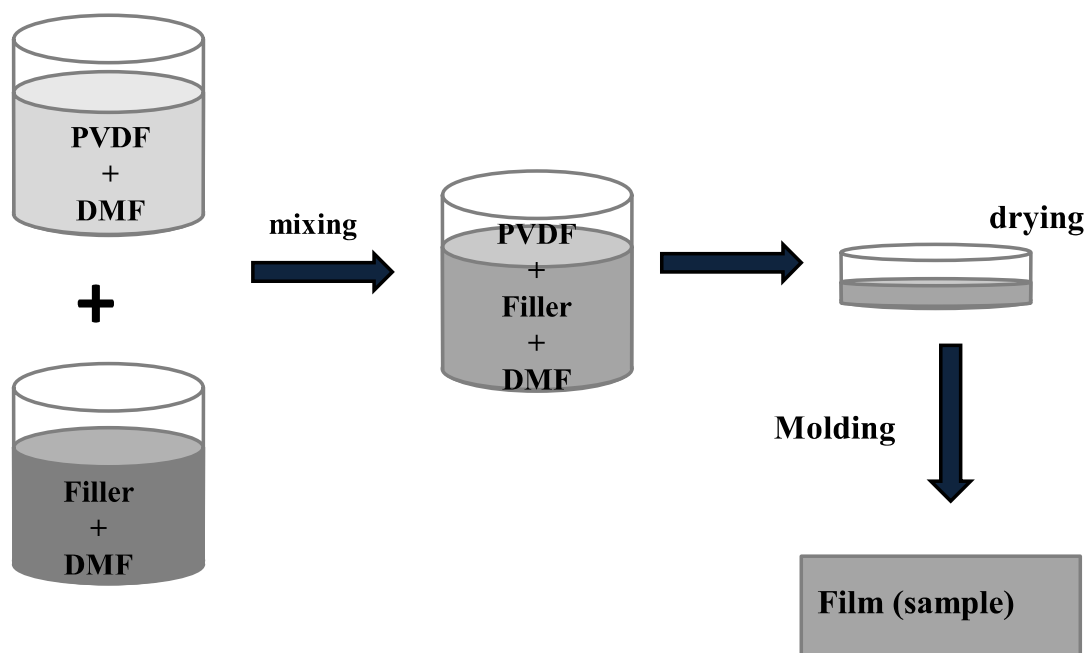
Figure 2.2: Hybrid preparation through solution route.

2.3. Film preparation: The Compression molding machine (S. D. Instruments, India) is used for preparation of films. The polymer and hybrid is compressed above their melting temperature in polyamide films and films of desirable thickness are prepared. The films of 300 μm thickness were prepared.

2.4. Unimorph fabrication: The unimorphs from pure polymer and nanohybrids are prepared to demonstrate their use in energy harvesting. A unimorph, also known as monomorph is a cantilever type structure that consists of one non-active or structural layer and one active or piezoelectric layer, the thickness of structural layer is taken in such a manner that the neutral axis of the unimorph lies in the non-active layer. The non-active layer used is a polyester sheet of 170 mm. The thickness of piezoelectric layer is ~ 100 μm. The

piezoelectric film is bonded to polyester film using thin double sided pressure bonded tape (3M VHB make). The electric contacts were made on the piezoelectric layer for the measurements, before bonding.

2.5. Device fabrication: The film samples were taken and a layer of conducting silver paste is coated on both sides of the sample. Then two copper electrodes are attached on both sides for measurement. The assembly then encapsulated with PDMS, in which the epoxy and hardener is taken in 10:1 ratio.

2.6. Characterization Techniques:

Different characterization techniques were used to characterize the polymer and the prepared hybrids.

2.6.1. Transmission electron microscope (TEM):

TEM is a microscopy technique for imaging nanomaterials with sub-nanometer resolution. In this technique a beam of electron is transmitted through a specimen for image. The typical acceleration voltage is 80-200 kV. The electrons are emitted from a field emission or thermionic electron guns. The specimen is an ultrathin section of thickness less than 100 nm or a suspension on grid. As the beam is transmitted through the samples, an image is formed, which is magnified and focused onto an imaging device. The objective lens also helps in formation of diffraction pattern. These diffraction patterns are used to recognize the crystallographic structure of sample. The samples were subjected to *Technai 20 TEM* with an operating voltage of 200 kV. A thin layer around 70 nm of sample was cut at -85°C using *Leica ultramicrotome* with diamond knife. Sample for TEM were prepared by placing droplet of composite solution on a carbon coated copper grid followed by drying.

2.6.2. Ultra-violet visible (UV-vis) spectroscopy:

The UV-visible region for visible-spectrum covers 1.5 to 6.2 eV, which corresponds to wavelength of 200-800 nm range. When a material absorbs light, it promotes to the higher energy state, and the spectrophotometer produce spectra corresponding to the level of absorption. The UV-visible spectra were performed using JASCO V-650 spectrophotometer in solid state, in the range of 200-800 nm wavelength.

2.6.3. Tensile Testing:

The mechanical properties of the samples, modulus and toughness were measured using Universal testing machine, *Instron 3369* at strain rate of 5 mm/min. The modulus was calculated by fitting the linear region of the curve and toughness is calculated by the area under the stress-strain curve.

2.6.4. Scanning electron microscopy (SEM):

SEM is a type of electron microscope which produces the sample image by scanning the surface with a focused beam of electrons, with energy between 1 and 50 keV. The electron beam is generated from lanthanum hexaboride (LaB_6) filament. These electrons interact with the atoms in the sample and produces signals that contains information about sample surface morphology and composition. The electron beam is scanned on the sample surface and the position of the beam is combined with the detected signal and an image is produced. The samples can be observed in high vacuum, low vacuum, wet condition, in variable pressure range and at cryogenic or elevated temperatures. A *Supra 40, Zeiss FESEM* was used to obtain the surface morphology of the samples.

2.6.5. Atomic Force Microscopy (AFM):

To scan the bulk morphology of the samples, NT-MDT multimode (Russia) is used. The semicontact mode was used with a resonance frequency of 240 to 255 kHz. To measure the changes in magnitude and phase of the piezoelectric phase PFM (piezo force microscopy) mode is used in which the sample is grounded and a DC bias voltage of 10V is applied by the scanning tip in the contact mode.

2.6.6. Polarized optical microscopy (POM):

The change in bulk morphology in the optical range was examined by polarizing optical microscope, *Leica*. The samples were crystallized on a Mettler hot stage.

2.6.7. X-ray diffraction (XRD):

X-rays are electromagnetic waves, have wavelength in the range of 0.01 to 10 nm. When an X-ray beam hits a crystalline material, Diffraction occurs due to change in the direction of the wave. There are constructive and destructive interference between the diffracted beams. Constructive interference is when the incident wave of wavelength (λ) and angle (θ) between incident ray and crystal plane conform to Bragg's Law $n\lambda=2d\sin\theta$, where d is crystal plane spacing. The X-ray diffraction was performed using *RigakuMiniflex 600* X-ray diffractometer with Cu-Kα radiation (λ=1.54 Å) at 40 kV voltage and 20 mA current. The film samples were placed on the sample holder and scanned with the rate of 3º/min, at room temperature.

2.6.8. Fourier-transform infrared (FTIR) spectroscopy:

FTIR is commonly used technique to obtain the information about the material based on the functional groups present. The infrared range in the electromagnetic radiation is from 700 nm to 1 mm. FTIR collects data over a wide spectral range. The radiation wavelength that a molecule absorbs depends on its atoms and how they are bound together. The fourier-transform infrared spectroscopic experiments were performed with Thermo-Nicolet 5700 FTIR in the range of 400 to 3500 cm^{-1} with resolution of 4 cm^{-1}.

2.6.9. Differential Scanning Calorimetry (DSC):

To examine the melting behavior of the sample, *Mettler 832* differential scanning calorimetry is used. The measurement was done from room temperature to 200°C at scan rate of 10°C/min. The melting temperature and enthalpy of fusion were calculated from the plots obtained using area under the curve.

2.6.10. Thermo-gravimetric analysis (TGA):

TGA is a method of thermal analysis by which changes in samples weight is measured as a function of temperature, in a specific atmosphere (Ar, O_2, air). The change in properties is due to different types of functional groups or the volatile part present in the material. This analysis tells about the temperature range in which we can use the material. In this, a thermal degradation curve is obtained, in which the mass change of weight fraction corresponding to each degradation can be measured. TGA analysis was performed thermo gravimetric analyzer *Mettler-Toledo*. The samples were heated from room temperature to 600°C at a rate of 20°C/min in nitrogen atmosphere.

2.6.11. Piezoelectric coefficient: Poled samples were used to measure the piezoelectric coefficient. Poling of both pure PVDF and nanohybrid samples before and after stretching is done by applying a high electric field across the film samples at optimized high temperature (90 ºC) for 30 mins. The piezoelectric coefficients of the poled samples were measured using a wide range d_{33} meter (Piezo Meter System PM 200). The electroding of the sample was done using silver paste.

2.6.12. Power measurement: Output voltage was measured to calculate the power generation from the devices. The finger tapping method is used to apply the stress on the devices and voltage was measured using Tektronix TBS-1072B digital storage oscilloscope. Power density was calculated by measuring the open circuit voltage at different external resistances by:

$$P = \frac{V^2}{R \times A}$$

Where, P is power density, V is open circuit voltage (peak to peak), R is external resistance and A is the area of the device.