Chapter 2

Experimental

2.1 Materials:

2.1.1 Polymer: A commercial grade poly (vinylidene difluoride) (PVDF) (SOLEF 6008) was kindly supplied by Ausimont, Italy. The molecular weight of the polymer is around 2.7 × 10^5 $gmole^{-1}$ and PDI is around 2.1.

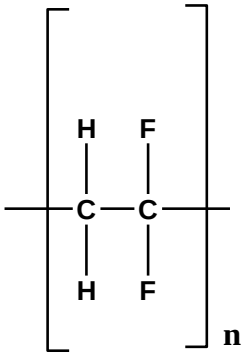

Figure 2.1: Chemical structure of PVDF

2.1.2 Fillers: Electroactive fillers were used with the PVDF to generate better properties and response. Different fillers were used to understand the effect of nanoparticles in the energy harvesting applications.

2.1.2.1 Nanoclay: Cloisite 30B [bis (hydroxyethyl) methyl tallow ammonium ion exchanged montmorillonite], an organically modified nanoclay having density of 1.98 g / cc is supplied by Southern Clay, U.S.A. Tallow used is a mixture of the long chain alkenes (C_{18} and C_{16}). The lateral dimension of the nanoclay is around 250 nm. Addition of organic modifier leads to rise in the interplanar distance to 1.8 nm from 1.1 nm.

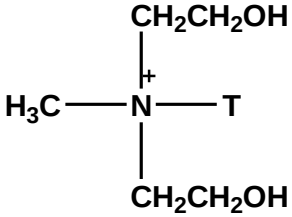

Figure 2.2: Organic modifier for Nanoclay 30B

[T is Tallow (~30% C16; ~65% C18; ~5% C14)]

2.1.2.2 Ionic Liquid: 1-Butyl-3-methylimidazolium chloride (≥98.0%) purchased from Sigma-Aldrich, India is used as filler.

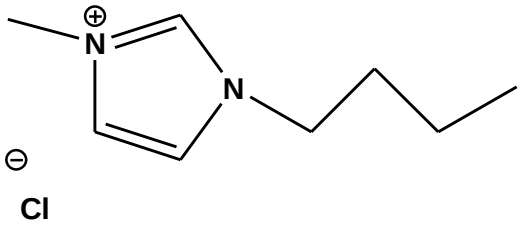

Figure 2.3: Chemical Structure of Ionic liquid

2.1.2.3 Carbon nanofibers: Carbon nanofibers (CNF) having dimensions D × L 100 nm × 20-200 μm with more than 98% carbon basis (>98% carbon basis) was procured from Sigma-Aldrich, India.

Dimethyl formamide (DMF) and Acetone were used as solvents and were supplied by Merck, India. Poly (dimethyl siloxane) (PDMS; 184 silicone elastomer) used as an encapsulation was provided by Ellsworth Adhesives, India.

2.2 Preparation of Polymer-filler solution: The polymer-filler solution used for the preparation of nanofibers through electrospinning was prepared by solution route. Initially the required amount of polymer is dissolved in measured quantity of DMF solvent and is stirred at 60 °C until the complete dissolution of polymer is seen. The filler in required proportion is firstly dispersed into acetone through sonnication. Now the filler and polymer solution is mixed together and kept stirring at 60 °C till an almost homogeneous solution is obtained.

2.2.1 Procedure for Electrospinning:

The final homogeneous solution for polymer and polymer-filler is transferred to a syringe with a needle diameter of 0.8 mm and is used for the electrospinning process. The polymer

– filler solution is electrospun at optimized parameters like flow rate, voltage, distance between the spinneret and rotating drum, solvent ratio and concentration of the solution. After the solution is electrospinned, the scaffold is vacuum dried at 50 °C and then used for further characterizations and fabrication of the device.

2.3 Device Designing: The electrospun polymer-filler nanofibers are designed into the device form which is used to analyse the efficacy of the material for energy harvesting applications. The prepared scaffold is cut into a size and then sandwiched between aluninium foils and then electroded with copper wires. Now the complete part is wrapped in commercial tape to avoid any damage to the material. Further, the complete set is encapsulated with PDMS to provide rigidity and stability to the device for better durability and different applications. The PDMS and its crosslinker are taken in the ratio of 10:1 and hand mixed. Then it is degassed to remove any traces of air to form a uniform and stable device. The fabricated device is then used for the analysis of electromechanical response.

2.4 Characterization Techniques:

The prepared material is studied and analysed using the different characterization techniques to understand the properties and its applicability.

2.4.1 Morphological Study: The prepared electrospun nanofiber was confirmed through the morphological techniques like Polarized Optical Microscopy (POM) and Scanning Electron Microscopy (SEM).

2.4.1.1 Polarized Optical Microscopy (POM): The bulk morphology of the electrospun fibers was observed using the polarizing optical microscopy, Leica. The specimens were placed over the transparent glass slides and the quality of fibers was analysed.

2.4.1.2 Scanning Electron Microscopy (SEM): The surface morphology of the neat polymer and its nanohybrids is studied using the SEM technique. The electron microscopy process with the focused beam of electrons having energy between 1-50 keV scans the surface of the sample generating images of the nanofibers. The source for the electron beam used is lanthanum hexaboride filament. Prior to scanning, the samples are gold coated to impart conductivity to the samples which under the influence of the electron beam produces the respective image. The fiber produced from the electrospinning process is visualised using SUPRA 40, Zeiss scanning electron microscope.

The fiber diameter is calculated using the SEM images with the help of ImageJ software. The change in fiber dimension is further analysed as discussed in later part of the thesis.

2.4.2 Structural Analysis: The addition of the nanoparticles / filler to the polymer matrix results in the change or some modification of the structure which is studied through some characterization techniques as discussed below.

2.4.2.1 X-ray diffraction (XRD): When a sample is subjected to X-rays, the direction of the beam gets differed or changed which leads to diffraction pattern which helps in determining the change or modification in the structure. The electrospun nanofibers were analysed using the Rigaku Miniflex 600 X-ray diffractometer. The characterization was performed at 20 mA current and 40 kV voltage with Cu-K_α radiation (λ=1.54 Å). The scaffolds were analysed at the scan rate of 3° / min placed on the sample holder at room temperature.

2.4.2.2 Fourier-transform infrared spectroscopy (FTIR): The transformation of structure or identification of the functional groups can be studied using the FTIR through

the change in the dipole moment of the molecule or compound when subjected to the electromagnetic infrared rays. The polymer and its nanohybrid were analysed in the attenuated total reflection (ATR) mode with the diamond crystal while the powdered samples were studied in the standard potassium bromide (KBr) pallet mode. The characterization was performed using Thermo-Nicolet iS5 FTIR in the range 600 – 4000 cm^{-1} with resolution of 4 cm^{-1}.

2.4.2.3 Ultra-violet visible (UV-vis) spectroscopy: When a material is exposed to the UV-vis light source, electronic transition occur which leads to the change in absorbance. The samples were analysed using the JASCO 650 spectrophotometer in the wavelength range of 200-800 nm.

2.4.3 **Thermal behavior study*:*** The thermal stability and change in nature with temperature of the pristine polymer and its nanohybrids were studied using the differential scanning calorimetry and thermogravimetric analyser.

2.4.3.1 Differential scanning calorimetry (DSC): The change in the melting behavior of the samples with temperature was analysed by Mettler 832 DSC with Star-e evaluation software. The samples instrument was calibrated with Indium / Zinc prior to experiment and the samples were placed into the crucible and measured in the temperature range of 25-200 °C at the heating rate of 10 °C / min under inert conditions.

2.4.3.2 Thermogravimetric analyser (TGA): TGA is a characterization technique where the degradation of the material is observed as change in mass with respect to temperature. The thermal behavior of the samples were studied by Mettler Toledo TGA where the samples are placed into the alumina crucibles and subjected to temperature in the range of 40-600 °C at the heating rate of 20 °C / min under the inert atmosphere.

2.4.4 **Mechanical properties study*:*** The mechanical stability and flexibility of the samples were studied using the tensile test experiment.

2.4.4.1 Tensile testing: The tensile test of the polymer scaffolds placed between the two jaws of the sample holder were measured using the Instron 3369 universal testing machine at room temperature at the rate of 5 mm / min. The modulus was calculated using the linear fit while the toughness of the sample was measured as area under the curve.

2.4.5 Electromechanical response measurement: The electrospun scaffolds and the fabricated device were subjected to different characterization methods to analyse the response against external stress or pressure.

2.4.5.1 Piezoelectric coefficient (d_{33}): Scaffolds were electroded using the aluminium foils and the piezoelectric coefficients were measured using the Piezo Meter system, Piezotest (PM-200) at room temperature.

2.4.5.2 Output voltage and Power measurement: The designed and fabricated samples from the electrospun scaffolds were subjected to different external pressure and the

generation of the voltage output and power density is measured using the Tektronix TBS-1072B digital storage oscilloscope at room temperature. Power density obtained from the impact of different modes of external stress application is calculated using the variable resistance box as shown in the following equation:

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

Where P is the power density, Vis the generated output voltage, R is the resistance load and A is the area of the active material.

2.4.5.3 Output current measurement: The prepared device generates output current when subjected to external stress and the current measurement produced is measured using the Keysight 34470A digital multimeter.

2.4.5.4 Dielectric Study: The dielectric study was carried out using the Keysight E4990A in the frequency range 20 Hz to 6 MHz. The polymer scaffolds sandwiched between the aluminium foils is placed under the sample chamber and the change in the parameters were studied against frequency.