Introduction and Literature Review

1.1 Introduction:

Energy is the most important parameter required to fulfill every needs at different sectors of the life. The rapidly rising population increases the need to meet every requirement which in turn requires higher consumption of the energy. According to the world energy statistics for the year 2020, the major fulfilling source of energy in the present world is the conventional energy sources like fossil fuels, petroleum, natural gases [1]. The significant rise in the demand and the constantly depletion of the non-renewable sources has pushed the world to the edge where the development of alternative energy sources is the only option for a sustainable future. The use of these conventional fuels has caused some devastating effect on the environment in the form of global warming, melting of glaciers, pollution which is the urgent issue that can only be resolved by limiting the use of these conventional sources and implementing the alternative energy sources [2]. The advancement in the alternative energy has been progressive but the gap is still wide to be filled up easily. Utilization of even the smaller waste or unused sources which possess the potential to be used as productive energy can be of merit. Energy harvesting is one such concept which operates on the waste or unused energies to generate productive output. Maximizing the utilization of these energy sources to produce substantial electric power can be a contribution towards the section of alternate green energy which can be economically and environmentally feasible.

1.2 Energy Scavenging or Harvesting:

Energy scavenging or power harvesting is the most interested topic in terms of the sustainable energy. Here the energy from the different ambient sources like mechanical, vibrations, thermal which are being unused or being wasted is converted to useful electrical energy. The concept utilises the different forms of energy which are not being considered

or ignored to convert them into something beneficial source of output. The power generated from these is relatively of the order of the nanowatt (nW) to miliWatt (mW) which are useful for the small portable electronic devices. The major importance of this energy is that they are self powered without the requirement of any external source which makes it a better alternative to the batteries which is dumped after use and harms the nature [3]. To maximize the content of the energy harvesting, several instances of the daily life are seen where the energy is being wasted or unused. For an instance, the heat and steam generated from the thermal plant or industries can be used to store the energy. There are many ways which if implemented can be of benefit to store energy from the sources which are being ignored. The major motivation behind all these energy sources is the increasing pollution leading towards to the rise in the global warming. The problem being faced today is not going to be reduced unless there is being a significant effort made in minimizing the environmental pollution or depletion of natural resources [4].

Nature is the richest source of alternate and sustainable energy which are being implemented in wider scale. Energy from the solar power, wind power, geothermal is an intense source of energy but there are some limitations which has put it a step back. Solar energy has the drawback of being not achievable after sunset or harnessed indoors, wind is a dependent thing based on the region. Hence energy harvesting from the waste sources provides several advantages such as [5][6]:

- Self-powered i.e. no external source is required.
- With the miniaturization of the electronics, the power consumption is reduced and hence these techniques can be of better use.
- Lower maintenance or replacements once installed effectively.

- A long term solution based on the ambient source without any alterations.

- Environmentally sustainable and feasible as no harmful output or by product is being produced.

Apart from the various merits, there are some challenges which need to be considered:

- Amount of power being low restricts its use for different applications.

- Variation in the source may cause fluctuation in the output response.

- Structuring and designing can be costly.

Though energy harvesting has some limitations but focusing on the positive aspects of it, these techniques can be of greater advantage based on the application it is being implemented. Utilization of these in specific area can reduce the load and consumption of other energy sources and hence the resources can be of productive and effective use for longer period.
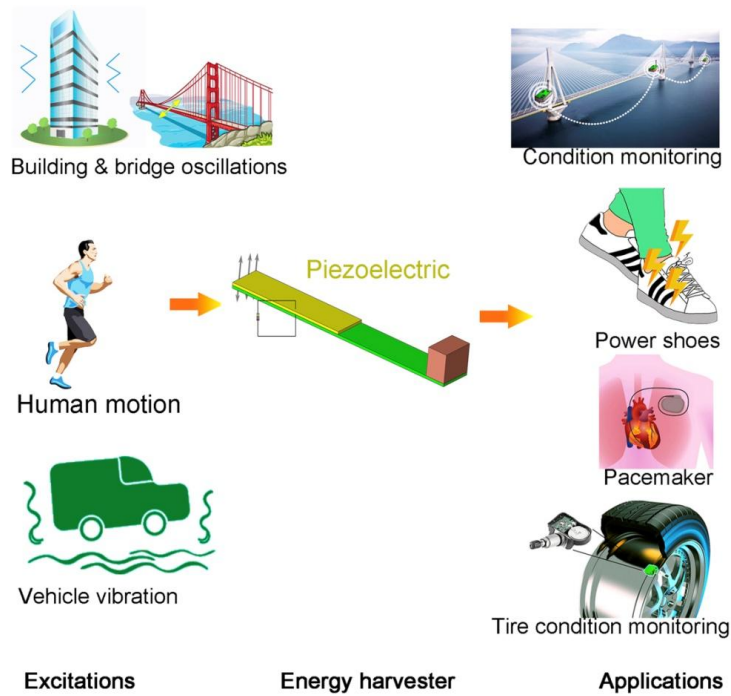

Figure 1.1: Common energy harvesting sources and applications. [7]

1.3 Sources and Mechanisms for Energy Harvesting:

The generation of sustainable energy through energy harvesting incorporates several sources and techniques. The energy source based on the mechanical or vibration energy is the most abundant one. Any object which is in motion or vibration can be a source of the energy. The movements due to flow of air, water or turbines can be a potential source of the energy. Energy can be harnessed from the transportation of vehicles, vibrations of the bridges or tunnels, operation of the industrial machineries like compressors, motors or from the human body [8]. The possible energy harvesting sources is listed in **Table 1.1** [9]**.** Human body is rich source of the energy which is wasted in our day-to-day life. Human body movements exhibit different range of energy which is sustainable, clean and green energy.

Table 1.1 Common sources present in surrounding for energy harvesting. [9]

Natural	Transport	Industrial	Structures	Human body
Solar, wind, ocean tides and waves	Trains, automobiles, aircraft, tyres, tracks peddles	Compressors, motors, turbines, conveyor belts, pumps, fans	Roads, bridges, tunnels, ducts, tracks	Walking, arm movement, limb movement, breathing, heart beat

Human body movement like walking, breathing, finger movement, heartbeat, movement of limbs are rich sources of energy which can be harvested for utilization in small electronics. Some other common sources of energy harvesting are the acoustic waves, radio frequency, temperature gradient, kinetic energy. Among the different available sources, mechanical or

vibration based energy sources are more effective for energy harvesting due to the high power density, greater durability and scalability [10]. The conversion of the mechanical or vibration energy to useful electrical output is generally carried out using three mechanisms: electrostatic [11], electromagnetic [12] and piezoelectric or triboelectric [13][14]. Electrostatic energy harvesting occurs between the parallel plate capacitor where the electrical energy is being stored. The energy is being harvested by fixing one of the plates and allowing to movement the other plates through external motion which changes the parameters of capacitors (separation between plates or the area). The key limitations of these are that they require external source for the movement of the energy harvester. [15] Electromagnetic energy harvesting is achieved with the combination of the magnetism and electric current which results in magnetic field. When an electric current is applied, it leads to the magnetization which generates magnetic energy. The major drawback of this energy harvesting technique is the output energy being relatively lower and it needs amplification for storage of energy [12][16]. Triboelectric energy harvesting is a recent trend in energy harvesting which works on the concept of the generation of the electrical charges on the frictional contact. The energy generated from these mechanisms is of high density and conversion efficiency. But the major limitations of these techniques are the long term durability [17]. Piezoelectric Energy Harvesting (PEH) utilises the concept of the piezoelectricity where the application of stress leads to generation of electrical energy. The energy density generated from these mechanism is higher and posses the ability to be worked on different working modes like longitudinal, transverse and piezotronic [18]. The major advantage of piezoelectric energy harvesting is the no moving parts, uncomplicated

structure, scalability, portability, easy fabrication method, economical and environmentally safe [19].

1.4 Piezoelectric Energy Harvesting

1.4.1 Piezoelectric effect:

Piezoelectric effect is the property which causes alteration in the electric polarization on the application of the exterior stress or pressure. The effect was first introduced by Jacques and Pierre Curie in 1880. One of the first instances of the use of the piezoelectric effect was in the form of ultrasonic submarine detector which was prepared during the First World War. A transducer was prepared from the mosaic of thin quartz crystal which was glued between steel plates and was resonated at the frequency of 50 MHz [20]. Piezoelectric effect is mainly of two types: direct piezoelectric effect and inverse piezoelectric effect. A material, when subjected to the mechanical load, generates strain or polarization is termed as direct effect while the converse phenomenon is the deformation of the material when external electric field is provided. Thus the piezoelectric based energy harvesting implies the principle of the direct piezoelectric effect.

The constitutive equation for the direct and indirect piezoelectric effect is:

$$D_e = d\sigma + \epsilon E \tag{1.1}$$

$$\varepsilon = s\sigma + dE \tag{1.2}$$

the symbols D_e and E implies the electric displacement and electric field respectively; whereas the σ, ε, ϵ represents the stress, strain and permittivity respectively and s and d are the elastic compliance and the piezoelectric coefficients. The equation (1) symbolizes the direct piezoelectric effect whereas the second equation (2) represents the indirect effect.

1.4.2 Mechanism:

The phenomenon of the piezoelectric effect is interrelated to the generation of the net dipole moment in the solids. When external stress is applied over the material, there occurs a change in the polarization which might be due to the alignment of the molecular dipoles or the change in the configuration of the dipoles or its surrounding. Hence the piezoelectric property is a variable parameter depending upon the following [21]:

- crystal geometry or symmetry,

- alignment of the polarization, and

- applied external stress

Crystals usually posses a charge balance, where the positive and negative charges cancel out each other along the rigid plane of the lattice. When an external mechanical stress is applied to the crystals these charge balance gets disturbed leading to generation of the charge carriers developing an electric current in the material. For the inverse piezoelectric effect, application of the external field disrupts the neutral balance of the charge in the crystal resulting in the mechanical stress with some alteration in the lattice structure. The occurrence of the piezoelectric effect is explained better using the crystalline solid and the array of the ions within the unit cell where the positive and negative charges are non-centrosymmetric within the planes of the unit cell under no external stress. The 32 crystallographic classes which are dependent on the symmetry and geometry of the unit cell of which 21 possesses non-centrosymmetric nature and among them all except one shows piezoelectricity. The absence of the symmetry in the arrangements of the ions in these crystalline solids leads to the net dipole moment in the materials which results in the piezoelectric effect. Hence the piezoelectricity is the linear relationship between the

electrical and mechanical properties [3][20]. The schematic representation of the mechanism of the direct and indirect piezoelectric effect is shown in **Figure 1.2** [22].
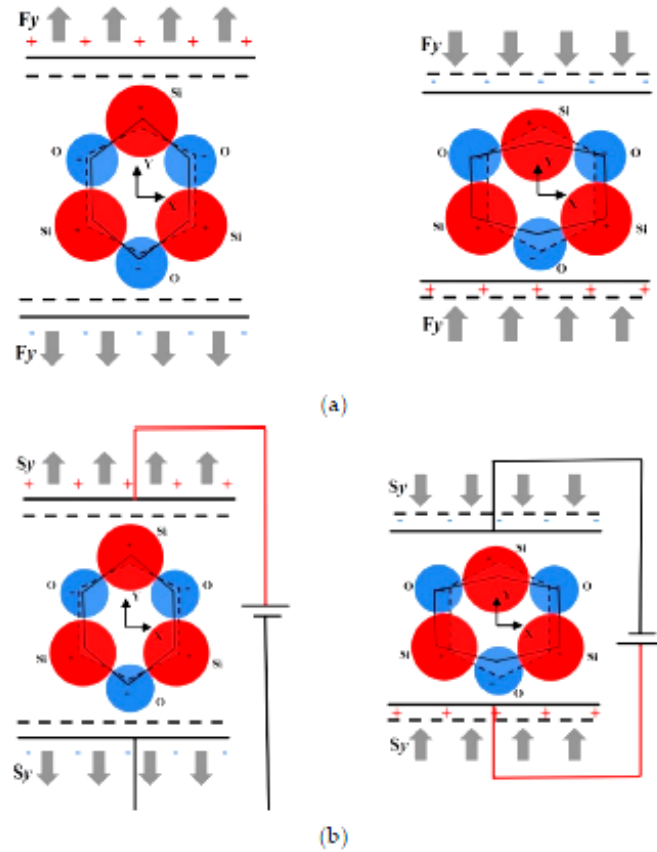

Figure 1.2: Schematic representation of the (a) direct piezoelectric effect and (b) indirect piezoelectric effect. [22]

1.4.3 Piezoelectric Parameters:

To demonstrate the piezoelectric effect quantitatively, certain parameters are being used which is explained as follows [21][23][24].

1.4.3.1 Piezoelectric charge coefficient (d_{ij}): The piezoelectric charge constant or strain constant is the generated electric polarization in a material per unit of the external mechanical stress applied or it may be defined as the strain produced on the

application of the external field. It is usually denoted in coulombs per newton. The first subscript in the notation d_{ij} represents the direction of the produced polarization or the direction of the field strength applied. On the other hand, the second notation signifies the direction of the stress applied or the direction of the strain induced in the material. The common piezoelectric coefficients are:

d_{33}: here the direction of the induced polarization is in 3rd direction (which is parallel to the direction of polarized material) w.r.t per unit of the applied stress in direction 3.

d_{31}: here the induced polarization in direction 3 (which is parallel to the direction of polarized material) w.r.t. per unit of the applied stress in direction 1 (perpendicular to the direction of polarized material).

d_{15}: induced polarization is in direction 1 per unit shear stress applied in 2nd direction.

1.4.3.2 Piezoelectric voltage constant (g_{ij}): It is defined as the generated electric field per unit of the applied mechanical stress or the experienced mechanical strain per unit of the applied electric displacement. It is generally denoted in volts per newton. The initial subscript in the notation g_{ij} represents the direction of the generated electric field or the direction of the electric displacement while the second subscript is the direction of applied stress or the direction of the induced strain in the material. The common terms for the g_{ij} are:

g$_{33}$: here the direction of the induced electric field is in 3rd direction (which is parallel to the direction of polarized material) w.r.t the per unit applied stress in direction 3.
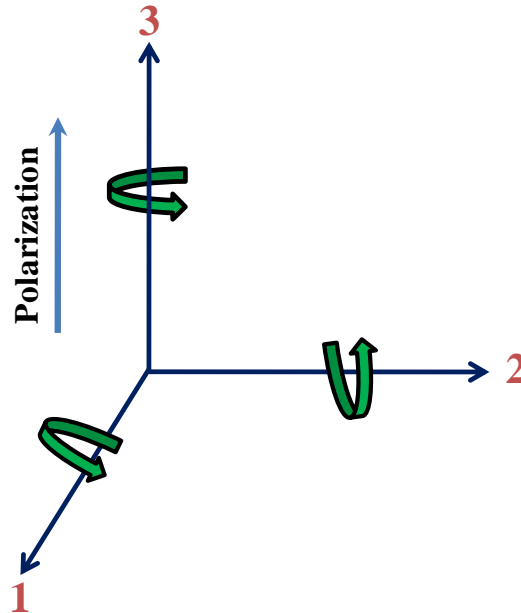

Figure 1.3: Direction of forces for piezoelectric material.

g$_{31}$: here the induced electric field is in direction 3 (which is parallel to the direction of polarized material) w.r.t per unit of the applied stress in direction 1 (perpendicular to the direction of polarized material).

g$_{15}$: induced electric field is in direction 1 per unit shear stress applied in 2nd direction.

1.4.3.3 Electromechanical coupling coefficients (k$_{ij}$): It is the ratio between stored mechanical energy and the applied electrical field or vice-versa. The units of these are dimensionless as the ratio is being of the energies. Electromechanical coupling in terms of piezoelectric coefficients can be equated as:

$$k_{ij}^2 = (d_{ij}^2)/\sqrt{\varepsilon_0 \varepsilon_r s_{ij}} \tag{3}$$

1.5 Piezoelectric Materials:

The performance and the applicability of the energy harvester primarily depend on the choice of the materials. The ability to transform the input mechanical or vibrational energy to the useful electrical energy output effectively is the prime requirement of the piezoelectric material. Piezoelectric materials are the class of smart materials which on application of external pressure generates electrical current. The class of piezoelectric materials with some examples is being stated in the **Table 1.2**. There are various piezoelectric materials which can be classified broadly into single crystals, piezo-ceramics, piezo-polymers and piezo-composites.

Table 1.2 Common classes of piezoelectric materials [20]

Classes	Examples
Natural crystals	Quartz, Rochelle salt, topaz, sucrose, berlinite
Synthetic crystals	Langasite, lithium niobate, gallium orthophosphate.
Bio-based	Cellulose, collagen, bone, DNA, tendon, silk
Ceramics (lead based)	Lead zirconate titanate, PMN-PT, lead titanate, PZN-PT.
Ceramics (Lead-free)	$BaTiO_3$, ZnO, $(K,Na)NbO_3$, $ZnSO_3$, $BiFeO_3$
Polymers	PVDF and its copolymers, polyamide.

The single crystals comprise of the organised arrangement of the negative and positive ions over their configuration which leads to the alignment of the dipoles resulting in the net dipole moment. Common single crystals for piezoelectric applications are quartz, lithium niobate, and lithium tantalite. The major disadvantages of these materials are its brittle nature, high cost, intricate preparation process which inhibits its usage in different

applications. Also the single crystals tend to lose their piezoelectric properties when exposed to higher electric field [25][26]. Piezoelectric ceramics are the promising materials for piezoelectric-based energy harvesting applications. Piezo-ceramics are inorganic polycrystalline materials with high piezoelectric coefficients and dielectric constants. Common piezoelectric ceramic materials are zinc oxide (ZnO) and aluminium nitride (AlN), Barium Titanate (BaTiO$_3$), Lead zirconate titanate (PZT), PMN-PT, PZN-PT. Lead based piezo-ceramics are the most efficient piezoelectric material as they possesses higher value of dielectric constant, d$_{33}$ value and electromechanical coupling factor. But the presence of the lead restricts its usage in biomedical and other related applications. The lead-free ceramics are being used as replacements but the efficiency is not so comparable as compared to their counter parts. The piezo-ceramics despite having high piezoelectric properties are being avoided due to their brittleness, rigidity, high density, and lack of flexibility [27][28]. Piezoelectric polymers are one of the most enriched materials for piezoelectric energy harvesting applications. The polymer are having the benefits of better flexibility, durability, biocompatibility, low density, higher dielectric breakdown, low fabrication cost and easy processable as compared to other materials. Common piezoelectric polymers are PVDF and its copolymers, nylon, cellulose. Of the available polymers, PVDF has extremely high piezoelectric properties due to its unique molecular configuration and crystalline forms [25]. Polymer-based composites with the different electroactive fillers are being highlighted these days because it provides better mechanical, electrical, optical and thermal properties. The main advantage of these are that the individual properties are being collaborated delivering the synergistic properties resulting

in enhanced applications. The piezoelectric coefficients for some of the piezoelectric materials are shown in **Table 1.3**.

Table 1.3: Piezoelectric parameters and their values for some common piezoelectric materials [29][3]

Piezoelectric Material	d_{33} (pC N^{-1})	ε_r	Electromechical coupling factor (k_{33})
Quartz	-2.3 (d_{31})	4.6	0.1
LiNbO$_3$	6	28.7	0.23
PZT	593	3400	0.75
PMN-PT	2820	8200	0.94
BaTiO$_3$	149	1200	0.49
ZnO	12.4	11	0.48
GaN	3.7	-	-
AlN	5	12	0.23
CdS	10.3	10.3	0.26
Polyamide 11	4	5	-
PVDF	-33	7.6	0.19
P(VDF-HFP)	-24	11	0.36
P(VDF-TrFE)	-25 to 40	18	0.29
P(VDF-HFP)	-140	13	0.36

1.6 Poly (vinylidene fluoride):

Poly (vinylidene fluoride) or commonly abbreviated as PVDF is semi-crystalline fluoropolymer with the chemical formula of $-(CH_2-CF_2)-$ obtained from the free radical polymerization of the vinylidene fluoride monomer. PVDF possess excellent features like greater flexibility, chemically inert, non-reactive, biocompatibility. PVDF comprise of exceptional physical properties of piezoelectricity, ferroelectricity and pyroelectricity

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which makes it a remarkable polymer in the field of energy harvesting. The characteristic properties of the PVDF are being listed in the **Table 1.4.** PVDF and its copolymers possess special properties which lists them as an outstanding polymer in the field of piezoelectric energy harvesting.

Basically PVDF exists in five different conformations namely α, β, γ, δ and ε. Of the five different phases, primary phases of importance are α, β, γ phases as shown in **figure 1.4**. The α – phase is a kinetically favoured phase with monoclinic crystal structure possessing trans-gauche (TGT$\bar{G}$) type conformation which makes it non-polar in nature with no piezoelectric property. The crystalline β-phase is the most important phase of the PVDF in terms of its application point of view. The orthorhombic crystal structure of the β-phase is the thermodynamically stable phase with all trans (TTTT) conformation. The semi-polar γ phase possesses $T_3GT_3\bar{G}$ conformation having some dipole moment but lower than the polar β-phase. The predominant α-phase which is piezoelctrically inactive has the ability to get transformed to the electroactive phases with some processing techniques which makes the PVDF highly efficient polymer for sensors, actuators and energy storage applications [29][30][31].
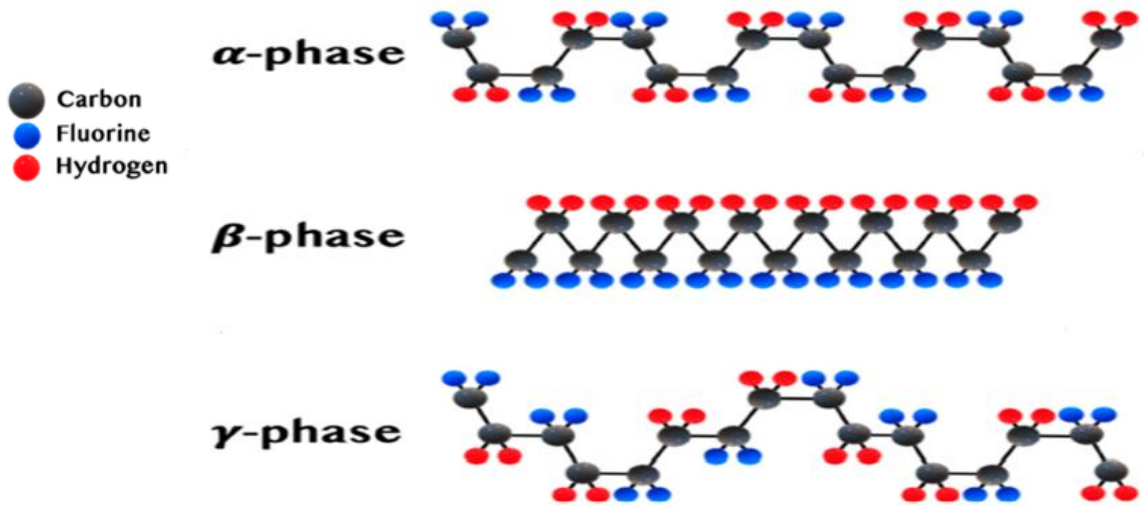
Figure 1.4: Structure of primary phases of PVDF [32]

Table 1.4 Physical properties of PVDF [30][33]

Density ~1.78 g/cm^3	Glass Transition Temperature: -40 to -30 ^{o}C
Tensile strength: 20-50 MPa	Melting Point: 155-192°C
Young's Modulus: 2-4 GPa	Temperature stability: 80-100°C
Elongation at break: 20-50%	Coefficient of thermal expansion: 120-145 ppm/k
Curie Temp.: 195-197 ^{o}C	Thermal conductivity: 0.2 Wm/k
Dielectric constant 8.15-10.46 (at 25 °C; 1 kHz)	Coefficient of friction, static 0.2-0.4
Loss tangent: 0.02 at 1 kHz	Strain coefficient d_{33} -15-30 pC/N
DC breakdown field 80 V/μm at 25°C	Strain coefficient d_{31} 6-23 pC/N
Dissipation Factor: 0.005-0.026	Voltage coefficient g_{33} 0.14-0.33 Vm/N
Refractive Index: 1.41-1.42	Voltage coefficient g_{31} 0.06-0.22 Vm/N
Crystallinity: 50-70 %	Pyroelectric coefficient: 19-30 μC/m^{2}K

1.7 Processing methods to impart piezoelectricity in PVDF:

The structure of the PVDF consists of carbon, hydrogen and fluorine with the alternating $-CH_2$ and $-CF_2$ groups linked together. The predominant α – phase has the molecules arranged in antiparallel form which leads to almost no net dipole moment in the PVDF. The PVDF consists of nearly 59 wt. % fluorine and around 3 wt. % of hydrogen. The presence of fluorine atoms with higher van der Waals radius (1.35$\mathring{A}$) as compared to the hydrogen atom (1.2$\mathring{A}$) and higher electronegativity develops a tendency to achieve a net dipole moment in the polymer chain. The difference in the electronegativites of the hydrogen and fluorine generates the polarity in the polymer which leads to piezoelectricity [29]. Piezoelectricity in PVDF was first reported by Kawai in 1969 [34]. When an external pressure is applied to the poled part of the polymer, the PVDF stretches along the length and when it's applied over the opposite direction of the poled part, it leads to contraction in the polymer chain. These features make the polymer a piezoelectric active polymer applicable for energy harvesting applications. Since the pristine PVDF is non-polar and piezo inactive, several approaches has been implemented which leads to development of polar part in the polymer with the transformation of the non-polar part to electroactive part. The most used approaches to enhance the electroactive phase in PVDF are: [29][35][36][37][38][39]

1.7.1 Stretching: Stretching of the polymer leads to the alignment of the polymeric chain and disrupts the antiparallel arrangement. The alignment of the chains in the planar direction leads to the rotation of the crystals on the application of the external electric field. This alignment allows the dipoles of the polymeric chain

to get aligned normal to the applied stress direction. Hence the stretching of the PVDF generates polar phase which can be configured in presence of temperature also.

1.7.2   Poling: The induction of the polar phase in the PVDF can also be achieved through poling. It is a method in which the alignments of the dipoles are being achieved through external electric field generally at elevated temperatures. When an electric field is provided to the polymer, spontaneous polarization occurs as it passes through the Curie temperature which leads to the alignment in single direction. These alignment results in the orientation of the dipoles which on the removal of the external electric field gets locked in its near alignment and develops a remanent polarization in the polymer (**figure 1.5**).
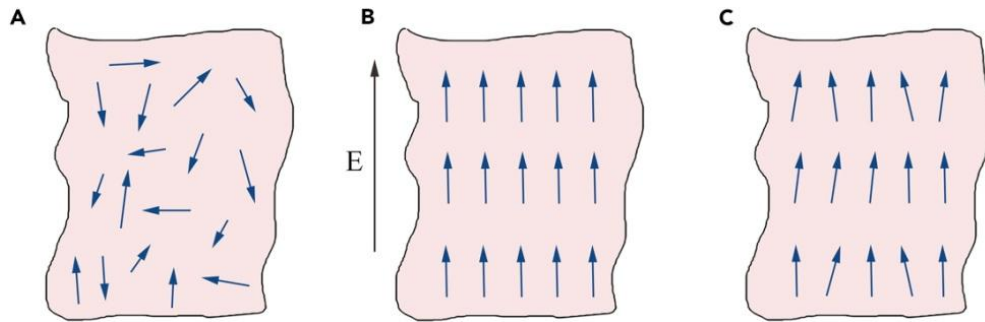

Figure 1.5: Effect of poling on piezoelectric ceramic [7]

A: Random orientation of dipoles before poling
B: Poling under the influence of electric field
C: Remanent Polarization after exclusion of electric field

1.7.3   Electrospinning: Electrospinning process to induce the electroactive phase in the PVDF is highly favoured technique. In this method, flexible, thin scaffold of the polymer is achieved through the combined in-situ process of mechanical stretching and poling. The basic setup consists of the polymer solution,

collector, and potential source as shown in **figure 1.6**. When a high DC voltage is applied to the polymer solution, the potential difference leads to the ejection of the charged jet of polymer solution. These electrically charges jet of the polymer solution gets sprayed over the collector (rotating or fixed) after the evaporation of the low boiling point solvents.
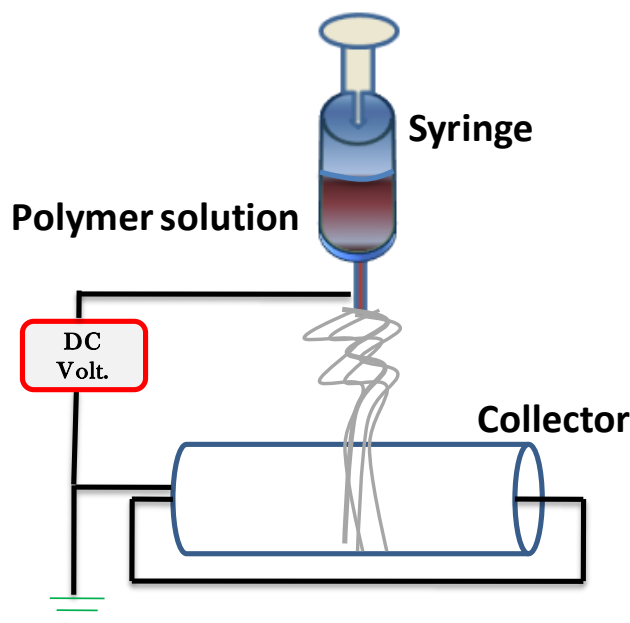

Figure 1.6: Electrospinning set up.

The strong electric field applied over the polymer solution and the collector leads to the formation of the Taylor cone at the tip of the spinneret. Due to the electrostatic forces acting over the polymer solution, the viscous force and the surface tension are overcome generating a fine spray jet of the polymer solution which results in a good quality, mechanically strong polymeric fibres. The fibre quality of the polymers depends mainly on the solution concentration, voltage applied, spinneret to collector distance, flow rate and the environment. During the process of electrospinning, the electrostatic forces leads to conformational changes in the

PVDF chain due to the parallel arrangement and disentanglement of the fibres. When the polymer is exposed to higher field strength with a rotating collector, the phenomenon of poling and stretching results in the polar phase generation which induces piezoelectricity in the polymer.

1.7.4 Copolymerization: The simple molecular structure of the PVDF provides ample opportunities to tailor the interaction between the different monomer resulting in a copolymer which shows better piezoelectric properties. The common copolymers of PVDF are P(VDF-TrFE), P (VDF-HFP), and P (VDF-CTFE) which shows better properties than PVDF as shown in the **Table 1.3**. P (VDF-TrFE) is prepared through the free radical polymerization of the two monomers, VDF and TrFE. The addition of the TrFE comonomer leads to crystallization of the β phase which enhances the electroactive property. Also this copolymer shows higher remanent polarization due to the better orientation and crystallinity of the crystallites. When hexafluoropropylene (HFP) is introduced into the PVDF, the crystallinity of the copolymer P (VDF-HFP) gets reduced while the piezoelectric coefficient gets enhanced. Depending on the processing techniques, the properties can be tuned accordingly. In P (VDF-CTFE), addition of the CTFE monomer shifts the T_g with increase in the dielectric constant and piezoelectric coefficient value.
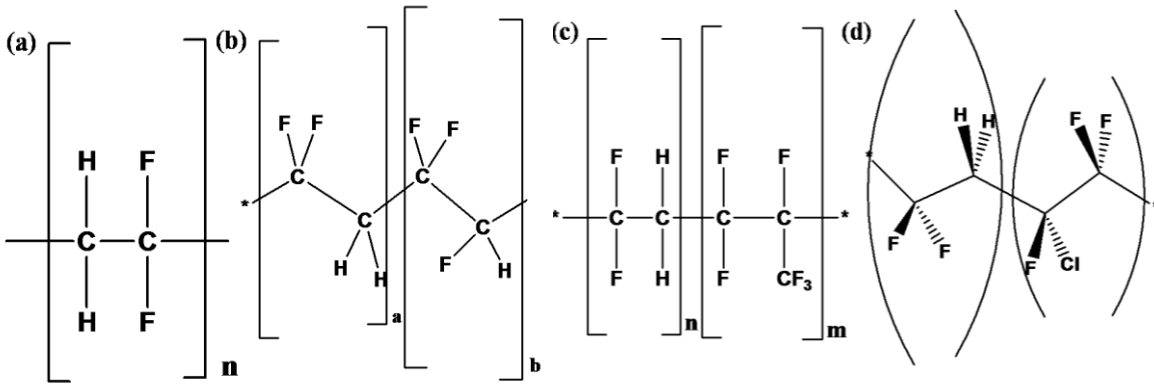
Figure 1.7: Chemical structure of a) PVDF; b) P(VDF-TrFE); c) P(VDF-HFP) and d) P(VDF-CTFE).

1.7.5 Incorporation of electroactive filler: The formation of composite or hybrids with the reinforcing fillers with polymers has been an effective way to enhance the piezoelectric property. Addition of the electroactive fillers leads to induction of the piezoelectric phase through the nucleation of the crystalline β phase over the polymer. Several electroactive fillers like carbon-based, bio-based, inorganic materials has been added to the PVDF to enhance the polar phase content which leads to rise in the piezoelectric property.

1.8 Literature Review: PVDF has emerged as one of the remarkable polymer in the field of energy harvesting due to its ability to get transformed to electroactive phase when subjected to different processing methods. To enhance the piezoelectric properties of the system, addition of electroactive fillers is also a widely used process. Polymer based nanohybrids have gained large attention in the field of energy harvesting. Different area of application is also considered based on the efficiency of the system developed.

1.8.1 Effect of processing techniques: The transformation to the piezoelectric phase can be achieved using different processing methods as illustrated below:

Different processing techniques are been implemented to enhance the electroactive properties of the polymer. Sencadas et.al. [40] showed the transformation of α to β phase due to the effect of stretching and poling on the PVDF films. The samples were stretched and poled at different temperatures and field respectively. Maximum polar phase was obtained at the stretch ratio of 5 at 80 °C. The degree of crystallinity also got influenced with the stretching. Jin et. al [41] analysed the effect of the poling and stretching of the PVDF-HFP films at different temperatures and elongation ratios. Maximum output voltage of 3.67 V was obtained at poling temperature of 40 °C and when the same film was stretched at elongation ratio of 5 and generated maximum output. Pariy and coworkers [42] demonstrated the effect of annealing and poling on the PVDF micropillars which led to higher crystallinity (22.7%) and β phase (42%) that resulted in 2.9 fold rise in the piezoelectric response. During the stretching the molecules get aligned due to the stress applied which results in rise in the polar phase. Electrospinning is one technique most widely used due to its ability to generate piezoelectric properties during the process itself. In this technique the stretching and poling occurs simultaneously leading to better quality fibres with enhanced electroactive phases. The details about the electrospinning process are elaborated in the introduction section. Matabola et al. [43] observed the effect of polymer concentration, voltage and spinning distance on the fibre morphology prepared through electrospinning. Increasing the voltage to 16 kV for a 22 % PVDF polymer solution, the fibre diameter was increased. While when the voltage was at 18 kV, thinner fibers were obtained. At lower voltage beaded fibres were seen which on raising the potential improved

the fibre quality. The work also showed that the effect of addition of metal salts like NaCl helped in achieving better quality fibres. Increase in the applied voltage from 14 to 20 kV also led to rise in the crystallinity (X_c) 48% to 56.3% which resulted in increase in the β-phase from 70% to 76% as shown by Jiyong and co-workers [44].

1.8.2 Polymer based composites / nanohybrids: Polymer based nanohybrids are being widely considered for different applications due to their enhanced properties which makes them better choice as compared to the pristine material. Addition of specific filler leads to achievement of the required properties applicable to required application study. Addition of certain additive also leads to enhancement of the piezoelectric properties. Different fillers like ceramics, 2D fillers, organic fillers has been added to the polymer matrix which lead to effective piezoelectric properties. Ceramics have been one of the better materials in the field of the piezoelectric energy harvesting due to their higher d_{33} value, dielectric constants and electromechanical coupling factor. Tiwari et al. [45] prepared composite films of PVDF/PZT at different ratios using solution casting process. Addition of the PZT leads to rise in the β-phase as compared to the pristine PVDF. The maximum piezoelectric coupling coefficient (d_{33}) of 84 pC / N was achieved for the PVDF/PZT composite as compared to -32 pC / N for neat PVDF. Jain et al. [46] obtained similar conclusion for PVDF-PZT composite films. The average and maximum piezoelectric charge coefficient obtained for the composite was 40 and 100 pC / N respectively while the value for the pristine polymer was 22 pC / N.

Mokhtari et al. [47] prepared fibre of PVDF – LiCl in DMF/Acetone solution. Addition of the LiCl leads to rise in the solution conductivity which reduces the bead formation and better fibre morphology is seen. Xing et.al [48] prepared nanofibers of PVDF and 1-butyl-

3-methylimidazolium hexafluorophosphate ([BMIM] [PF$_6$]) at varying concentration of the ionic liquid (IL) and studied the effect of IL on the morphology, structure, thermal and electrical properties. Addition of the IL leads to the better quality fibres leading to enhancement in the polar β phase (almost 100 %) as shown in **Figure 1.8**. Due to the better interaction of the PVDF with the IL, the resultant electrical conductivity get increased which justifies the prepared fibre as better antielectrostatic fibrous material. Carbon based fillers are one of the most used reinforcer with polymers in the field of energy harvesting. Their higher electrical, mechanical, thermal properties make them a remarkable candidate as filler for polymer based composites for energy harvesting applications.
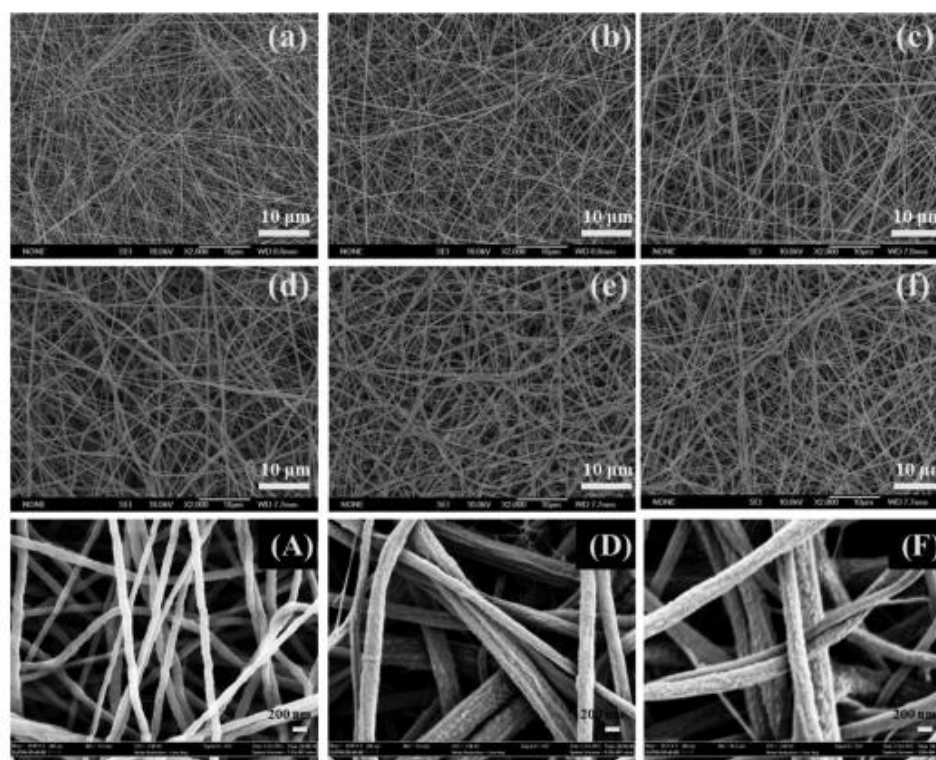

Figure 1.8: FESEM micrographs of electrospun PVDF and PVDF/RTIL nanofibers with different RTIL contents: (a) 0 wt % (neat PVDF); (b) 5 wt %; (c) 10 wt %; (d) 20 wt %; (e) 30 wt %; (f) 40 wt %, respectively. [48]

Wu and coworkers [49] prepared fibres of PVDF-CNT through electrospinning process. Addition of CNT nanoparticles to the aligned PVDF fibres lead to significant rise in the polar β phase to 89 ± 2 % from 79 ± 3 %. The piezoelectric coefficient (d_{33}) for the random fibres of neat PVDF was 16.8 ± 1.4 pC/N which gets enhanced to 31.3 ± 2.1 pC/N for aligned PVDF-CNT fibres. Addition of the electroactive fillers leads to phase transformation from non-polar to polar or semi-polar phases. The transformation of the α- to γ-phase on addition of Fe-doped RGO to the PVDF was reported by Karan and co-workers [50]. The characteristic peaks at 1232 and 832 cm^{-1} in FTIR analysis reveals that the addition of Fe-doped RGO leads to phase transformation. Neppalli et al. [51] studied the effect of clay and electrospinning process on the structure, morphology and polymorphism of the PVDF – clay nanofibers. Different concentration of Cloisite 20A was taken with PVDF matrix and the change in phase was determined using different techniques. Electrospinning and clay synergistically facilitated the generation of the better fibres which lead to better piezo-phase development. Hence addition of the electroactive fillers results in change in the structure and morphology which enables generation of better piezoelectric phases that can be applied for further applications. The prepared scaffolds are further designed or fabricated to a nanogenerator or a device form that enables the conversion of the external stress to electrical output. Highly aligned nanofibers of PVDF/ $BaTiO_3$ were prepared through electrospinning process by Lee and co-workers. The diameter of the prepared nanofibers was around 200 nm. The highest output voltage obtained was around 0.48 V for the composite PVDF-16wt. % $BaTiO_3$ which was 1.7 times higher than the neat PVDF fibers [52]. Si et.al [53] prepared nanocomposites of

PVDF/zinc titanate using the solution casting method. Addition of ZTO provided high surface area for the adsorption of the polymer which facilitated the γ-phase nucleation. The piezoelectric nanogenerator (PNG) developed using the copper electrodes were able to harvest energy from different mechanical sources. The PNG of PVDF / 2 wt% ZTO generated voltage, current and power density of ~25.7 V, 1.2 µA and 8.22 µW cm^{-2} respectively. Jana et al. [54] prepared composite films of PVDF and ZnO nanoparticles through solution process. Incorporation of the ZnO leads to development of the γ-phase without the effect of poling. The maximum piezoelectric coefficient (d_{33}) obtained without poling was around -6.4 pC/N. The fabricated device was able to generate maximum output voltage of 28 V and current of 450 nA. Also the device was able to light 48 LEDs instantly through finger imparting mode. A flexible nanogenerator developed by Bairagi et al. [55] prepared from the PVDF/ 4 wt% KNN generated highest piezoelectric β-phase of 26 % and the maximum output voltage and current of ~3.7 V and 0.326 µA respectively through finger tapping mode. Rahman et al. [56] prepared a durable and flexible nanocomposite of PVDF / laponite nanoclay through simple solvent evaporation technique. The incorporation of the nanoclay leads to significant rise in γ-phase (98%) and also enhanced the mechanical properties of the composite. The fabricated nanogenerator generated maximum output voltage and current of 6 V and 70 nA respectively under the compressive load of 300 N through hand punching. Yu et al. [57] developed nanofibers of PVDF/MWCNT through electrospinning process. The addition of CNT leads to rise in the surface conductivity which was clearly seen by the rise in the output voltage and average capacitor charging power. The maximum piezo-voltage generated was around 6 V for PVDF/ 5 wt% MWCNT while further addition of MWCNT led to decrease in the voltage output. Maity et al. [58]

synthesized 2D-MoS$_2$/PVDF nanofibers from electrospinning process. The developed nanogenerator showed better charging ability and charged a capacitor to 9V within 44s. Also the PENG demonstrated seventy times improvement in the acoustic sensitivity as compared to the pure PVDF nanofibers. Huang et.al [59] developed a flexible piezoelectric sensor based on PVDF/graphene composite coated on commercial available fabrics. The developed material was analysed to study the piezoelectric effect. The piezoelectric sensor developed generated a voltage less than 10 V while PVDF@P and PVDF/graphene@P generated maximum voltage of around 15 V and 20 V respectively as shown in **Figure 1.9**. The durability of the device is also demonstrated for 125 cycles. Karan et al. [60] prepared a nanocomposite of AlO doped rGO and PVDF. Addition of 1 wt% of the filler (AlO-rGO) enhanced the β-phase to nearly 90% and the measured d$_{33}$ value for the same was around 45 pC/N. The developed device was able to generate the V$_{oc}$ of 36 V and I$_{sc}$ of 0.8 µA which may be attributed to the rise in the electroactive phase. The prepared device was able to harvest energy from different sources and also was able to charge capacitors of different ratings demonstrating the applicability of the material.
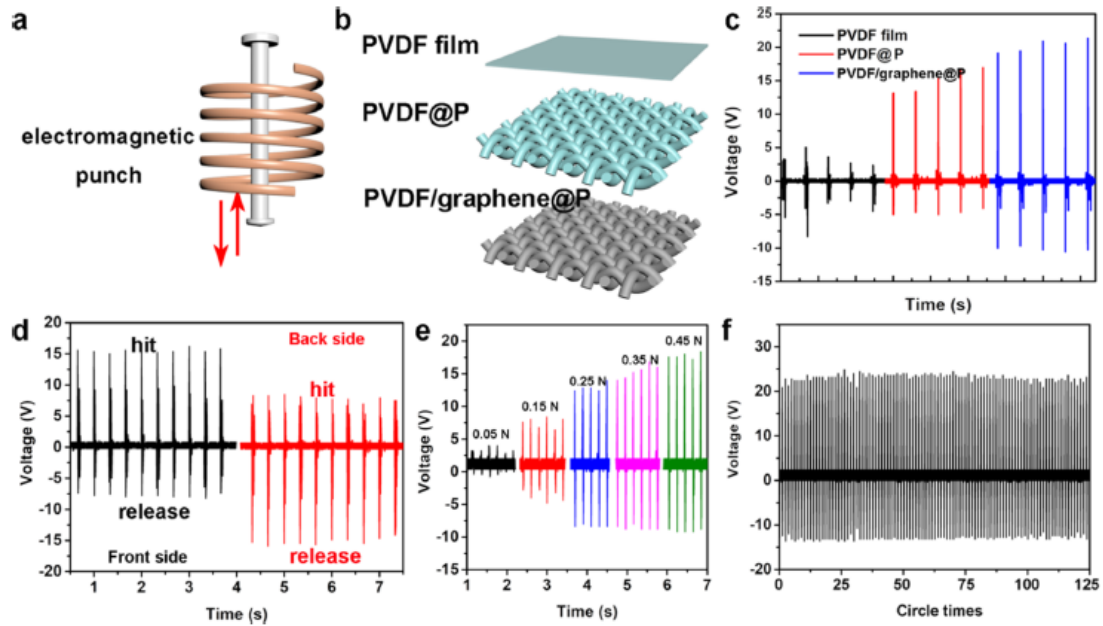
Figure 1.9: Three-dimensional (3D) models representing (a) electromagnetic punch and (b) PVDF film, PVDF@P, and PVDF/graphene@P; (c) Output voltage of prepared PVDF film, PVDF@P, and PVDF/graphene@P; (d) The output voltage signals of hitting the front (black signals) and back (red signals) side of PVDF/graphene@P; (e) The relationship between voltage output and different strength input (from 0.05 to 0.45 N); (f) durability of prepared device for more than 125 cycles of voltage output of PVDF/graphene@P. [59]

Bio-waste materials have also been proven as an efficient energy harvester in their raw form or as filler. Maiti et al. [61] fabricated a bio-waste onion skin as an efficient piezoelectric energy harvester which had the energy conversion efficiency of around 61.7 %. The prepared bio-piezoelectric nanogenerator was able to generate output voltage, power density and current of 18V, 1.7 μW cm^{-2} and 166 nA respectively. The single device was able to glow up around 30 LEDs on application of compressive stress while 73 LEDs were lit when six devices were connected in series. Tomato peel based piezo and tribo-electric properties were explored by Saqib and co-workers [62]. The device designed from

the tomato peel was able to generate piezoelectric output of 2.5 µA current, 24.5 V of voltage and 19.5 µW of instantaneous power. The device was also used for the triboelectric response and the combined effect of the piezo and tribo-electric was analysed. Tamang et al. [63] developed a flexible nanogenerator from PVDF and DNA where the incorporation of DNA led to β-phase nucleation and alignment of the molecular dipoles which enhanced the piezoelectric properties. When a stress of 13 kPa was applied the output voltage and short circuit current obtained was 6 V and 0.088 µA respectively while on increasing the applied stress to 63 kPa, the voltage and current value increased to 20 V and 0.184 µA respectively. A high performance biomimetic wearable piezoelectric energy harvester is prepared using PVDF / tetraphenylphosphonium chloride (TPPC) / barium titanate through combination of shear milling and fused filament fabrication 3D-printing technology. The energy harvester with 30 wt. % of barium titanate generated highest output voltage and current of 11.5 V and 220 nA respectively. The energy harvester was able to light up nine LEDs (green). To demonstrate the practical applicability of the material, a 3D-printed biomimetic wearable energy harvester was fabricated which was able to harvest energy from the movement of bicycle tyre as shown in **Figure.1.10** [64].
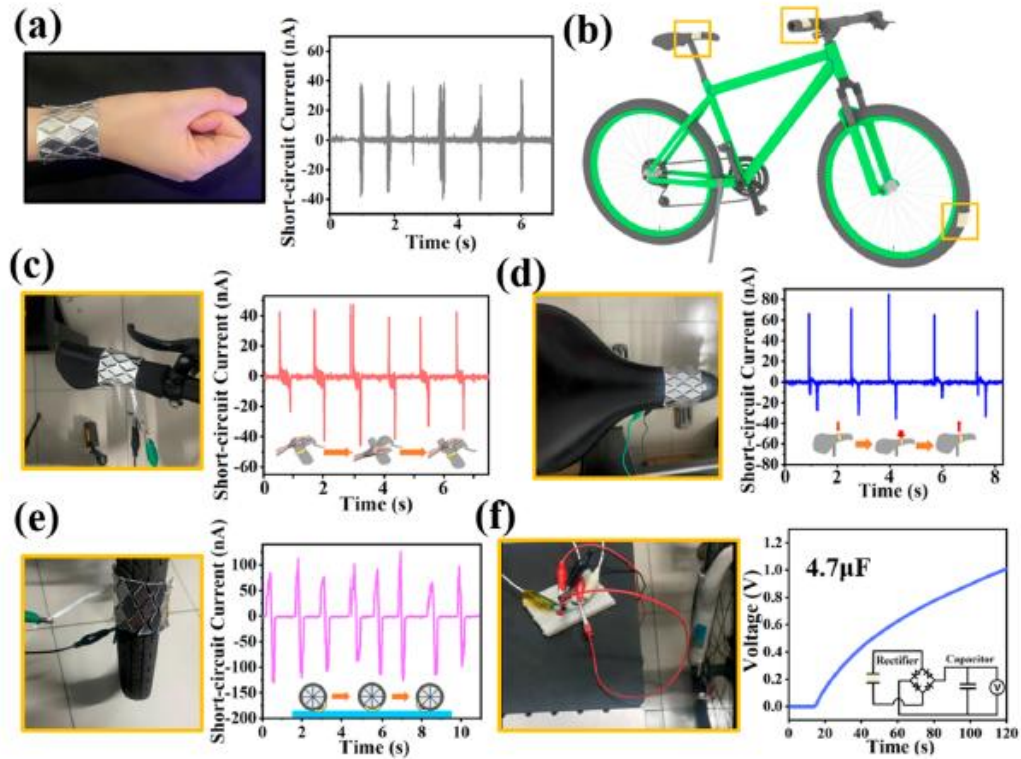
Figure 1.10: (a) Pictorial view of the wearable fish-scale-like energy harvester and its corresponding output signal (b) Schematic representation of the prepared energy harvester attached to bicycle and the corresponding digital picture and output voltage generation through (c) pressure on handgrip, (d) pressure on seat (e) movement of tyre; and (f) capacitor charging due to rolling of the tyre. [64]

Table 1.5: Processing methods, properties, and electromechanical response of PVDF-based hybrids.

Material	Processing Technique	Property Enhancement	Electromechanical Response	Ref.
Ce^{3+}-Doped Electrospun PVDF/Graphene nanofibers	Electrospinning @ 12 kV, 0.8 ml/h.	Better quality fibres due to the incorporation of fillers.	Output voltage of 11V and maximum power 6.8 µW @ 6.6 kPa. 3V @ 88dB of sound energy.	[65]

PVDF-nanoclay Nanofibers (5 wt%)	Electrospinning @ 20 kV, 1000 rpm.	Enhancement in piezoelectric phase.	2.76 V in free vibration damping test and 0.83V on finger tapping	[66]
PVDF/graphene Nanoplatelets (0.1,1,3 5 wt%)	Electrospinning @ 20 kV, 17 cm and 1 ml/h.	Better fibre quality with enhancement in electroactive phase (β = 83%)	V=7.9V, I= 4.5μA @0.2MPa Capacitor charged to 6.5V	[67]
PVDF+BT	Solvent evaporation process on glass substrate; Poling at 2 kV for 8 hours; ITO on PET as electrodes	Enhancement in polar phase, poling leads to rise in output values.	150 V, 1500 nA @10 MPa stress; 3 LED were lit up	[68]
PVDF-TrFE+BT (0-35 wt %)	Electrospinning @ 18 kV, 1.5 ml/h	Enhancement in output voltage and current to 200 % as compared to Pristine material.	25V, ~8μA; 4.7μF capacitor charged in 72 steps	[69]
PVDF-TrFE + MgO nanoparticles (2 -8%)	Solution Casting process; Curing at 140 °C and then ice-water quenching	Increase in crystallinity Saturation and remanent polarization values upto 2 wt% MgO loading.	d_{33}~65 pm/V; 2V max(4.5V pp) on bending on impact 0.4 V	[70]
PVDF-cellulose nanocrystal nanofibers	Electrospinning @ 10 kV, 2 ml/hr, 2000 rpm.	High content of electroactive phase and crystallinity on CNC additionβ-phase-89.96%	Maximum voltage output = 60 V for 2 wt % CNC	[71]
Egg shell membrane		% crystallinity ~35%	26.4 V, 1.45 μA 23.7 pC/N ~11.90 μW/cm2 (~238.17 μW/cm3)@15MΩ	[72]
Spider silk		%crystallinity~43%; 82.2 kPa, strain rate ($\dot{\epsilon}$) of 0.226% s−1	21.3 V, 0.68 μA energy conver. eff.= 66% 0.36 pm/V; 4.56 μW/cm^2	[73]

1.8.3 Applications: PVDF based nanogenerator has gained much attention in the field of piezoelectric energy harvesting. The applicability of the PVDF based composites is diversified to different fields where the device is used to harness energy from different type of mechanical sources. Deng et al. [74] projected a piezoelectric sensor of cow-pea structured PVDF / ZnO nanofibers for tactile based applications. The piezoelectric sensor demonstrated good sensitivity with bending mode with a 4.4 mV / deg with a response time of 76 ms and for pressing 0.33 V / kPa with a response time of 16 ms. The material showed a potential applicability to be used for interactive Human-machine Interface (iHMI). PVDF based nanocomposites also finds its use as force sensor due to its better flexibility. Wang et al. [75] developed a PVDF based force sensor with better breathability and sensitivity. The PVDF fabric was prepared using electrospinning process. The device was designed using a plastic film coated Indium tin oxide (ITO) and an ITO coated glass as electrodes; polymer fabric was embedded between these electrodes. The fabric prepared at 12 kV potential, 12 wt. % concentrations and at flow rate of 0.02 ml / min had generated maximum β-phase content and showed highest sensitivity of 42 mV/N as compared to the other films. The device was also able to generate substantial signal at different frequencies. Yang et al [76] developed a flexible sensor based on the PVDF–CNT nanofibers prepared through electrospinning. The nanofibers prepared with 0.05 wt. % CNT and PVDF demonstrated better properties and sensitivity. The flexible capacitive sensor was able to provide sensitivity of 0.99 / kPa and a dynamic response time of ~ 29 ms. The prepared device was also used for real application as an electronic skin which showed good stability and flexibility. PVDF based materials are also used as a humidity sensor. Corres et al. [77] proposed a PVDF nanofiber based optical fiber humidity sensor which showed better

sensitivity and response time. Different application of PVDF-based piezoelectric material is shown in **Figure 1.11** [32].

Figure 1.11: Some applications of piezoelectric PVDF films [32]

1.9 Objective of the Thesis work:

The rise in population with increase in demand of the energy sources has led to reduction of the conventional energy sources and has created an alarming situation for the future. The need for an alternative, sustainable and green energy sources is on high demand. Utilization of the natural, renewable resources as an alternate energy sources is being expedited but the efficiency is still an area which needs to be enhanced. Apart from the natural resources, there are different ambient waste energies which can be harnessed for efficient energy harvesting applications. The concept of energy harvesting utilises the process of harnessing the waste energy sources to useful electrical energy.

The objective of the entitled thesis is to prepare a flexible, light weight PVDF hybrid for energy harvesting applications. The polymeric hybrids are being developed using solution casting, drop casting and electrospinning process after optimization of the parameters. Different electroactive fillers are being incorporated with the PVDF at different concentrations to enhance the piezoelectric phase content. The role of processing and electroactive fillers is being studied in the induction of the piezoelectric phases in the materials. The prepared hybrids are being designed and fabricated to a device form to measure the elelctromechanical response through different external modes. The major outline of the entitled thesis is:

- ✓ Preparation and synthesis of the PVDF and its hybrid through different optimized routes.

- ✓ Demonstrate the role of electroactive fillers and processing techniques in enhancement of polar phase content.

- ✓ Analysis of the prepared hybrids through different characterization techniques to study the changes in morphology and structure.

- ✓ The prepared hybrid is being fabricated to a device form to measure the electromechanical responses for energy harvesting application.

- ✓ Utilise the device for different practical daily life applications.