Chapter 1

Introduction and literature review

1.1. Introduction:

Energy plays a very important role in our present and future as it is the one of the most important input for the achievements related to our life and different industrial process. The demand of energy is constantly and rapidly growing with increasing population and industrial development. According to world energy statistics, world's energy consumption for year 2015 is shown in **Figure 1.1** [1]. We can see that most of the energy demand is still fulfilled by fossil fuels such as petroleum fuel, coal and natural gases. However, using these energy sources have side effects, which are affecting us directly or indirectly like a rapid decrease in forests, continuous fluctuation of fuel price, the concern of national energy security, increasing atmospheric pollution level etc. [2]. Only 7% of electricity generation is by other sources like renewable energy and waste energy. On the other hand there is lots of "waste" energy that can be useful, if captured. If we could recover even a fraction of this waste energy; that would make a positive environmental and economic impact and this is where "Energy Harvesting" comes in.

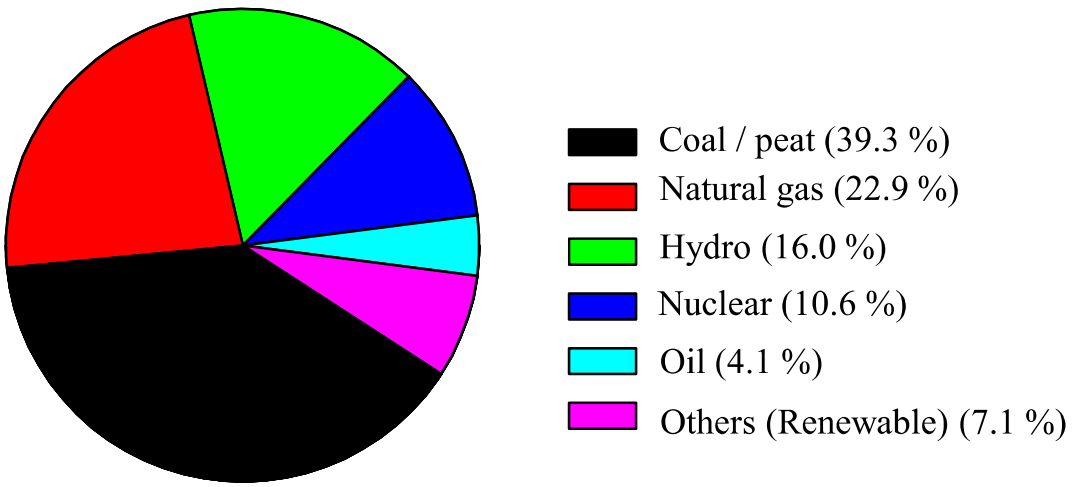


Figure 1.1: 2015 World electricity generation by different types of fuels [1].

1.2. Energy Harvesting:

Energy harvesting is a process by which unused or waste energy from the ambient sources (e.g. thermal, vibration, solar, wind) is captured and harvested into electrical energy and used to power the miniature devices [3, 4].This harvested energy is normally very less (of the order of mili joules) compared to energy from renewable energy sources like wind and solar farms (of the order of mega joules). These energy sources are small in size so these are portable and readily available for the use, unlike the large power stations. There are abundant sources of unused or waste ambient energy, so we don't need to purposely extend our efforts to create the energy harvesting sources. For example the burning of fuels creates the steam which can be used to rotate the turbine to create electrical energy. The history related to energy harvesting starts from the use of waterwheel and windmill. From many decades, people have searched the ways to store and utilize the energy from heat and vibrations. The most important reason behind the motivation of energy harvesting is the issue of climate change and global warming due to increasing pollution. Generally energy can be stored in capacitor, supercapacitor or battery. In recent years energy harvesting from environment has been in major focus of research [5]. These ambient energy sources are prospective contestants to replace current power sources like batteries, which have a limited lifetime and energy storage capacity [6].

Most of the environmental energy sources are sustainable and renewable. Various studies have done, to know the amount of energy that can be harvested from the unused ambient energy. The solar energy source provides the highest power but there is limitation as it doesn't work indoor. The energy harvesting sources like solar, wind and vibrations can provide high output which depend on the availability of energy sources at the application

areas like a sunny day, a coastal area, traveling vehicles and strong vibrations for a bridge structure and so on. The energy harvesting technology gives various advantages to the user, some of these are elaborated the following [7, 8]:

1. With the new advancement of small scale electronics, the consumption of power is decreasing, so the harvested energy may be sufficient to operate them and can eliminate the use of batteries completely.

2. As the self-powered energy harvesting sources do not require any power cable or wiring hence these are easy to install thus eliminates the high installation cost.

3. Once the system is installed, it can function unattended which eliminates the need of service visit to replace the batteries and hence reduce the maintenance cost.

4. In hard to access and risky environments, it provides the sensing and actuation capabilities.

5. Provide the long-term solution as the self-powered system remains functional as long the ambient energy is available. These are suitable for the long term applications which need to be monitored at decades.

6. Reduce the environmental impact as energy harvesting eliminates the use of millions of batteries, which are dumped after use and have negative environmental impact.

In spite of having many advantages the energy harvesting technology is not perfect but also have many challenges:

1. Low power generation is not sufficient to operate some systems.

2. In some cases, power supply is totally dependent on the weather like no sun light at night.

3. Fluctuation in energy sources may affect the operation and lifetime of system.

4. From fabrication to the application, they are expensive as compared to fossil fuels most of the time.

It can be clearly deducted from the list of advantages that the energy harvesting is a feasible technique to power the small scale, wireless portable electronics for long term with the supplement of energy storage devices; even if not completely eliminating but reducing the use of the batteries.

1.2.1. Energy harvesting from mechanical energy:

Mechanical energy is the most abundant energies in our surroundings that can be reused. The mechanical energy sources might be a moving object, a vibrating source or a vibration induced by flow of air or water. The movements or induced vibrations by air or water flow in form of wind and hydroelectric energy, which can be used for the large scale power generation. The mechanical energy used for small scale power generation is low-level vibrations or movements. The possible low level vibrations, which can be used for energy harvesting, are summarized in the **Table 1.1** [9]. The vibration to electrical conversion can be apprehended by three basic mechanisms, electromagnetic [10, 11], electrostatic [12] and piezoelectric [13] transductions.

Table 1.1: Potential mechanical energy sources [9].

Human body/ motion	**Transportation**	**Infrastructure**	**Industry**	**Environment**
Blood pressure/flow, breathing, talking, exhalation, finger motion, arm motion, walking, jogging	Aircraft, train, automobile, tires, turbines, tracks, peddles, brakes, engine vibration, noises	Bridges, tunnels, roads, farm, house structure, water/gas pipes, control-switch, AC system	Motors, compressor, pumps, chillers, fans vibrations, cutting and dicing noise	Wind, ocean current/ waves, acoustic wave

Among these three mechanisms of energy harvesting, the piezoelectric transduction have gained the greatest attention. This may be due to the fact that the piezoelectric materials have higher feasibility for practical application and higher power density than the materials which are used in other two techniques [5]. The voltage output in the electromagnetic energy is very low and requires amplification to charge the storage devices. While the output voltage from piezoelectric energy harvesters can be used directly. In case of electrostatic energy harvesting, we need to apply an external electric voltage to trigger the vibratory motion, which outputs the alternating electrical current [12]. No such external applied voltage is needed in the piezoelectric energy harvesters. One more advantage of piezoelectric energy harvester is that it can be fabricated at both large and small scale [14].

1.2.2. Applications of Mechanical Energy Harvesting:

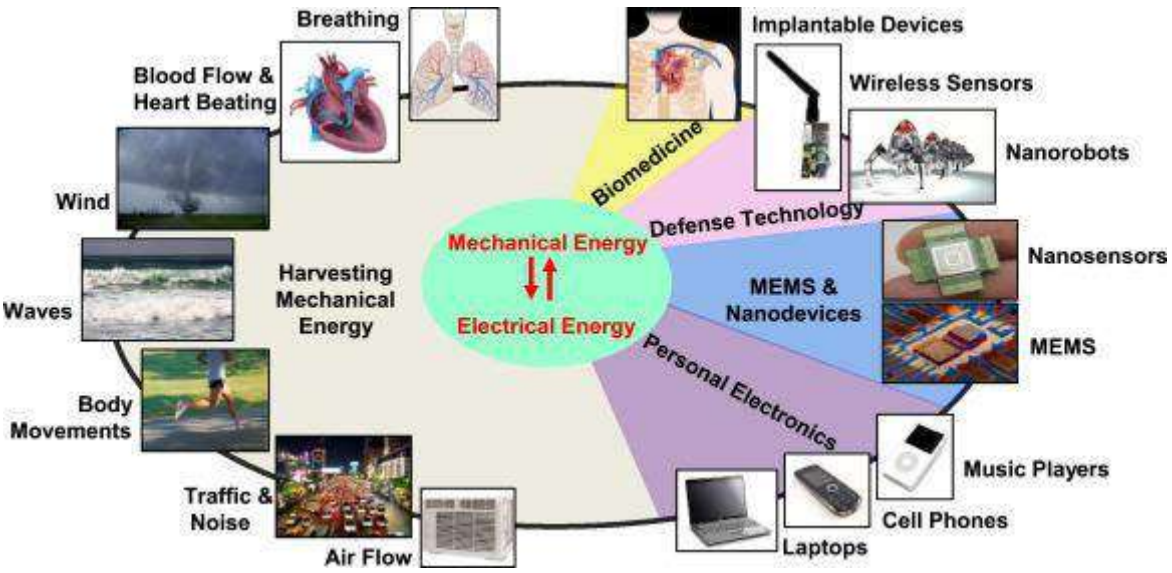


Figure 1.2: Possible sources of mechanical energy harvesting (left) and possible applications in sensing and actuation (right) for piezoelectric devices [15].

Different modes of operation in piezoelectric devices offers the basis for the application in diverse fields like defense technology, biomedicine, nano-devices, micro-electromechanical systems, portable electronic devices and various mechanical energy harvesters [15, 16]. **Figure 1.2** summarizes the applications of such piezoelectric devices and the possible sources of the input energies.

1.2.3. Approach for mechanical energy harvesting

Nanogenerators are the devices, which are able to produce low cost, efficient and sustainable energy by harvesting ambient energy [17]. Basically these are the structures those convert mechanical or thermal energy into electrical energy [18]. Because of their nano/macro dimensions, we can integrate them into functional devices so, it is convenient to build a system that generates their own energy [19]. Nanogenerators uses three kinds of approaches that includes triboelectric, piezoelectric and pyroelectric. The thermal energy is converted into electrical energy using the pyroelectric effect. In converting mechanical energy into electrical energy, the nanogenerators have added a new dimension using triboelectric and piezoelectric effects. Also, it is reported that the piezoelectric nanogenerators perform better than the triboelectrics [20]. The triboelectric nanogenerator works on the triboelectric effect and electrostatic induction, while the piezoelectric nanogenerator works on the piezoelectric effect.

The nature of waste energy is usually multi axial e.g. finger movement, joint, knee, centrifugal force, different tensile and compressive movements and different human motions. So, to capture these multi-axial movements, the nanogenerator should be flexible. As polymers are flexible and mechanically stable, these are preferred to prepare nanogenerators.

Polymers can be used as matrix with fillers in the nanocomposites or the piezoelectric polymers can be used directly [21].

1.3. Piezoelectric Nanogenerators:

Piezoelectric nanogenerators (PENG) are the very first type of nanogenerators invented and they have been developed with novel integration [22], advanced materials [23, 24] and different applications. When a piezoelectric material is subjected to mechanical stress, a net positive and negative charge results on the surface that creates the potential difference. Similarly, when a piezoelectric material is subjected to voltage difference, it deforms mechanically [25]. The piezoelectric effect is usually defect in the crystal structure. It is evident that in polymers, the piezoelectric effect is observed by means of opposite poled deposited in amorphous regions [26], also the electronic difference of atoms in polymer chains causes piezoelectric effect. For example Fukada observed the piezoelectric effect in the biopolymers due to electrical gradient [27].

The present thesis is on mechanical energy harvesting using piezoelectric nanogenerators.

1.4. Piezoelectricity and charge separation mechanism

The piezoelectricity is the electric charge generated on the exertion of force on certain materials such as crystals, certain ceramics, bone, DNA and various proteins. This is the intermingling of electric charge and elasticity (**Figure 1.3**). This effect results from the electromechanical interaction between the mechanical and electrical states in the material. It is a reversible process i.e. in a piezoelectric material the generation of electric charge on application of mechanical stress (direct piezoelectric effect) also exhibit the generation of mechanical strain on application of electric field (inverse piezoelectric effect).

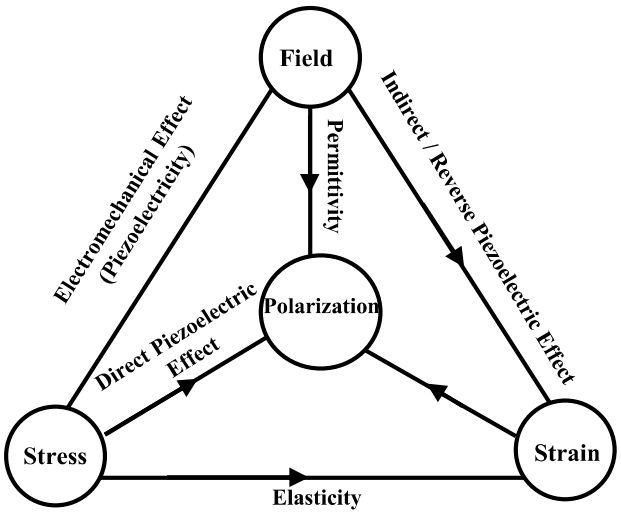


Figure 1.3: The relation between electric charge and elastic phenomena [28].

The following molecular model (**Figure 1.4**) explains the piezoelectric effect. This shows the charge generation on the application of external force on the material. Before the application of force on the material the centers of positive and negative charges in the molecule coincides, which results in the electrically neutral molecule (**Figure 1.4a**). On the application of external force the centers of positive and negative charges rearrange and generate small dipoles (**Figure 1.4b**). As a result of which inside the material, opposite facing poles cancels each other and the charge only appears on the surface (**Figure 1.4c**). In that way the material get polarized and this effect is known as direct piezoelectric effect. The induced polarization creates an electric field, this principle is used to convert mechanical energy into electrical energy.

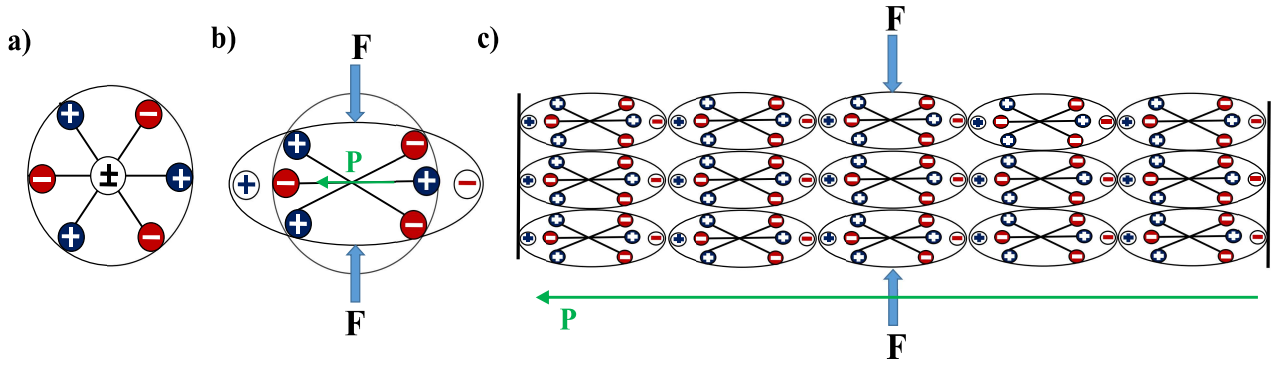


Figure 1.4: A molecular model to explain the piezoelectric effect (a) An undisturbed molecule with no dipoles or polarization (b) on the application of an external force (F) it induces polarization (P) (c) the overall effect of polarization on the surface after application of external force [28].

Some materials also shows the reverse piezoelectric effect i.e. when a voltage is applied on the material, the mechanical deformation or strain is produced in the material. This property of the material can be utilized in sensor applications and in nano-positioning devices.

1.4.1. Piezoelectric coefficient and constitutive equation

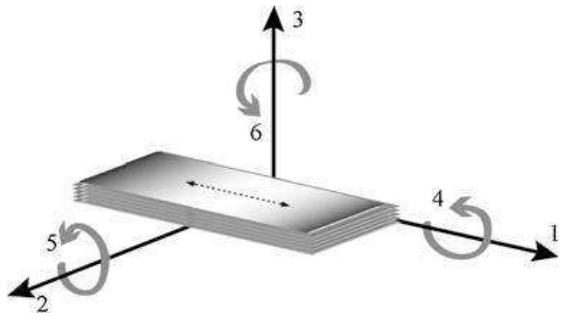
The piezoelectric constant (dij) is the polarization generated per unit mechanical stress applied or it's the mechanical strain in a piezoelectric material per unit of electric field applied. The first subscript denotes the direction of generated polarization or the direction of applied field strength and the second subscript denotes the direction of applied stress or the induced strain, respectively [29]. For a thin film sample shear stress can be neglected, so we measure d_{33} piezoelectric coefficient.

The direct and inverse piezoelectric effect is a relationship between the elastic variables i.e. stress σ and strain s, and the electric displacement D and electric field E. As per the linear theory of piezoelectricity [29], the relation can be given as a tensor notation as:

$$s_{pq} = S^{E}_{pqrs}\sigma_{rs} + d_{rpq}E_r \qquad \text{(i)}$$

$$D_p = d_{prs}\sigma_{rs} + \varepsilon^{\sigma}_{pr}E_r \qquad \text{(ii)}$$

Where, s_{pq} is the mechanical strain, S^{E}_{pqrs} is elastic compliance at constant electric field, σ_{rs} is mechanical stress, d_{rpq} is piezoelectric constant, E_r is the electric field, D_p is the electric displacement and $\varepsilon^{\sigma}_{pr}$ is dielectric constant under constant stress.



#	Axis
1	X
2	Y
3	Z
4	Shear around x
5	Shear around y
6	Shear around z

Figure 1.5: Axis nomenclature.

Equation (i) express the converse piezoelectric effect, while equation (ii) express the direct piezoelectric effect. In matrix form these equations can be written as:

$$\begin{bmatrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{21} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{31} & S_{32} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{41} & S_{42} & S_{43} & S_{44} & S_{45} & S_{46} \\ S_{51} & S_{52} & S_{53} & S_{54} & S_{55} & S_{56} \\ S_{61} & S_{62} & S_{63} & S_{64} & S_{65} & S_{66}) \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{bmatrix} + \begin{bmatrix} d_{11} & d_{21} & d_{31} \\ d_{12} & d_{22} & d_{32} \\ d_{13} & d_{23} & d_{33} \\ d_{14} & d_{24} & d_{34} \\ d_{15} & d_{25} & d_{35} \\ d_{16} & d_{26} & d_{36} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \qquad \text{(iii)}$$

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{31} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} + \begin{bmatrix} \varepsilon^{\sigma}_{11} & \varepsilon^{\sigma}_{12} & \varepsilon^{\sigma}_{13} \\ \varepsilon^{\sigma}_{21} & \varepsilon^{\sigma}_{22} & \varepsilon^{\sigma}_{23} \\ \varepsilon^{\sigma}_{31} & \varepsilon^{\sigma}_{32} & \varepsilon^{\sigma}_{33} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \qquad \text{(iv)}$$

For shear stress these notations can also be used

$\tau_{23} = \sigma_4,\ \tau_{31} = \sigma_5,\ \ \tau_{12} = \sigma_6$

Assuming the poling direction along axis 3, and the piezoelectric material as a transversely isotropic material, some of the parameters in the matrix will be zero and some can be expressed in terms of other parameters. Particularly, the non-zero compliance coefficients are:

$S_{11} = S_{22}, S_{13} = S_{31} = S_{23} = S_{32}, S_{12} = S_{21}, S_{44} = S_{55}, S_{66} = 2\,(S_{11} - S_{12})$

The non-zero piezoelectric strain coefficients are

$d_{31} = d_{32}$, and $d_{15} = d_{24}$

Finally, the non-zero dielectric coefficients are $\varepsilon_{11}^{\sigma} = \varepsilon_{22}^{\sigma} = \varepsilon_{33}^{\sigma}$. So, the equation (iii) and (iv) can be simplified as:

$$\begin{bmatrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{13} & 0 & 0 & 0 \\ S_{13} & S_{13} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{bmatrix} + \begin{bmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{31} \\ 0 & 0 & d_{33} \\ 0 & d_{15} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}$$

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} + \begin{bmatrix} \varepsilon_{11}^{\sigma} & 0 & 0 \\ 0 & \varepsilon_{11}^{\sigma} & 0 \\ 0 & 0 & \varepsilon_{33}^{\sigma} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}$$

The piezoelectric constant (d_{ij}) is the polarization generated per unit mechanical stress applied or it's the mechanical strain in a piezoelectric material per unit of electric field applied. The first subscript denotes the direction of generated polarization or the direction of applied field strength and the second subscript denotes the direction of applied stress or the

induced strain, respectively [30]. For a thin film sample shear stress can be neglected, so we measure d_{33} piezoelectric coefficient. The equation (iii) applies to PZT materials, for PVDF, this matrix should be modified to

$$\begin{bmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{32} \\ 0 & 0 & d_{33} \\ 0 & d_{25} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

This reflects the fact that in PVDF films the induced strain is nonisotropic on the surface of the film. Hence, an electric field applied in the direction of the polarization vector will result in different strains in 1 and 2 directions.

One another important parameter used in piezoelectric applications is the Electro mechanical coupling factor. This is used to compare different piezoelectric materials, which is a measure of interchange of electrical and mechanical energy and is expressed as:

$$k^2 = \frac{Converted\ Electrical\ energy}{Input\ Mechanical\ Energy}$$

Or

$$k^2 = \frac{Converted\ Mechanical\ energy}{Input\ Electrical\ Energy}$$

1.5. Piezoelectric materials

There is a vast range of piezoelectric materials that are used in different applications [5, 31-33]: single crystals, ceramics, polymers, composites etc. Single crystals like quartz, lithium tantalite ($LiTaO_3$) and lithium niobate ($LiNbO_3$) are important for high-frequency filter applications and surface acoustic wave devices [32] but there have been very less studies on

their use as energy harvesters. These materials have high electromechanical coupling coefficient and less dielectric coefficient compared to PZT [34].

The polycrystalline ceramics are the most widely explored energy harvesting materials [5, 31]. Piezoelectric ceramic materials include both ferroelectric materials such as barium titanate ($BaTiO_3$), lead zirconate titanate ($PbZr_xTi_{1-x}O_3$), lead titanate ($PbTiO_3$) and materials such as ZnO and AlN, which are non-ferroelectric. Among these ceramics PZT has high dielectric, piezoelectric properties, and high piezoelectric coupling coefficient; its properties are also affected by dopant materials such as Ta, Nb and Mn. Bulk PZT is used in sensors, actuators and transducer applications while thin film PZT is used in MEMS (Micro electromechanical systems) applications due to their higher piezoelectric coefficient than bulk PZT [33, 35].

The non-ferroelectric piezoelectric semiconductor materials like ZnO and AlN has also been of interest because they can be used for integrated circuit designing using conventional processing techniques, which offer the advantage to be used for MEMS and PVEHs. Although the piezoelectric properties of these materials are poor than ferroelectric ceramics their semiconducting characteristics and application in bio-chemical sensors with high sensitivity and selectivity (e.g. ZnO nanorods) makes them a potential candidate [32].

Nowadays ceramics, metals, and alloys are being replaced by polymers for different applications like automotive and aerospace industry, sensors and actuators and biomedical applications. Polymers with modified properties including mechanical, chemical, thermal, surface and other properties for specific applications are being developed using different processing techniques [36, 37]. Polymers have many advantages over the inorganic or ceramic materials as they are light weight, mechanically stable, inexpensive, have excellent

compatibility with other materials for developing multi-functional materials and some of the polymers are also bio-compatible and bio-degradable [38, 39]. With the advancement in materials science and engineering, there have been significant improvements in the area of smart materials and particularly smart polymers for various application areas [40, 41]. Smart materials are those which have one or more properties that can be changed in a controlled manner when subjected to external stimuli. The smart materials can be categorized according to their output; as piezoelectric materials, shape-memory materials, temperature-responsive materials, magnetostrictive materials, self-healing materials, pH-sensitive materials and thermoelectric materials, etc. [42, 43].

1.6. Piezoelectric polymers

There are various synthetic and natural polymers, which show the piezoelectric effect. These are listed in below **Table 1.2 and 1.3**.

Table 1.2: Natural and synthetic piezoelectric polymers [44-47].

Polymer	**Piezoelectric coefficient (pC/N)**
PLA (Polylactic acid)	9.82
Polyhydroxybutyrate (PHB)	1.6-2.0
PVDF	24-34
Poly(vinyl fluoride-trifluoroethylene) (PVDF-TrFE)	38
Polyamide-11	4

Table 1.3: Bio polymers used as piezoelectric materials [48].

Natural Polymers			**Piezoelectric coefficient (pC/N)**
Polysaccharides	Cellulose	Wood	0.10
		Ramie	0.20
	Chitin	Crab shell	0.20
		Lobster apodeme	1.50
	Amylose	Starch	2.00
Proteins	Collagen	Bone	0.20
		Tendon	2.00
		Skin	0.20
	Keratin	Wool	0.10
		Horn	1.80
	Fibrin	Elongated films of fibrinogen-therombin clot	0.20
		deoxyribonucleic acids salmon DNA (at -100oC)	0.07

1.7. PVDF and its Copolymers:

PVDF is a highly non-reactive, semi-crystalline, thermoplastic fluoropolymer. It is produced by polymerization of Vinylidenedifluoride (**Figure 1.5**).

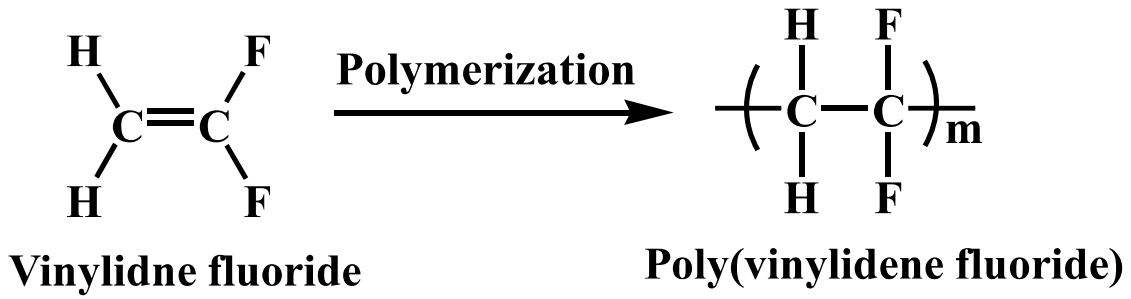


Figure 1.6: Polymerization of vinylidene fluoride to form PVDF.

Copolymers of PVDF are Poly(vinylidene fluoride-co-Hexafluoropropylene) P(VDF-HFP), Poly(vinylidene fluoride-co-chlorotrifluoroethylene) P(VDF-CTFE) and

Poly(vinylidenefluoride-co-trifluoroethylene) P(VDF-TrFE), the chemical structures are shown in **Figure 1.6**. Most commonly used copolymer of PVDF is P(VDF-TrFE) because of its good piezoelectric and ferroelectric properties.

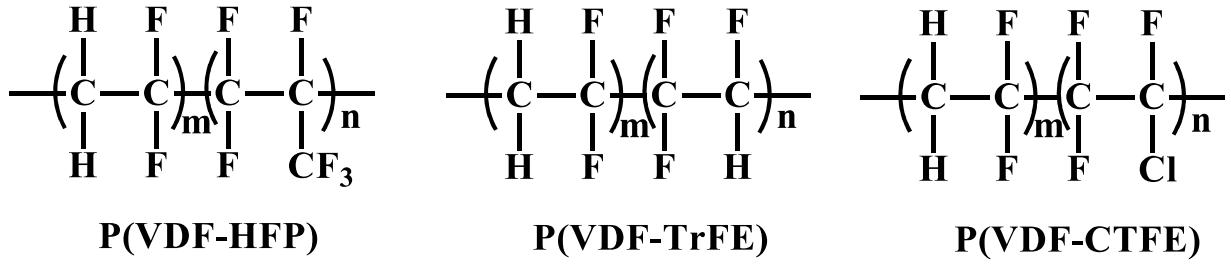


Figure 1.7: Chemical structures of copolymers of PVDF.

1.7.1. Properties and configuration

PVDF is a special polymer used in applications where high purity is required. It is resistant to various solvents, oils, acids, and bases and also shows the permeability to gases and liquids. It has low density of 1.78 g/cm^3 comparative to other fluoropolymers. PVDF is 50-60 % crystalline and has a glass transition temperature (T_g) and melting temperature (T_m) in the range of -40 to -30 ^oC and 155-192 ^oC respectively, which depends on its molecular weight and the number of defects in the chain [49]. The curie temperature is 195-197 ^oC and dielectric coefficient and dissipation factor at 25^oC, 1 kHz is 8.15-10.46 and 0.005-0.026, respectively [50]. Unlike other piezoelectric materials like lead zirconate titanate (PZT), PVDF has a negative piezoelectric coefficient (d_{33}), which means that it compresses on the application of the electric field.

Table 1.4: Thermal, Mechanical, Electrical and Piezoelectric properties of PVDF [51, 52].

Mechanical	**Thermal**
Density ~1.78 g/cm^3	Glass Transition Temperatire >-35^{o}C
Tensile strength 20-50 MPa	Melting Point ~175^{o}C
Young's Modulus 2000-4000 MPa	Temperature stability 80-100^{o}C
Elongation at break 20-50%	Coefficient of thermal expansion 120-145 ppm/k
Coefficient of friction, static 0.2-0.4	Thermal conductivity 0.2 Wm/k
Electrical	**Piezoelectric**
Dielectric constant 6-13 (at 1 kHz-1 MHz)	Strain coefficient d_{33} -15-30 pC/N
Loss tangent 0.02 at 1 kHz	Strain coefficient d_{31} 6-23 pC/N
DC breakdown field 80 V/μm at 25^{o}C	Voltage coefficient g_{33} 0.14-0.33 Vm/N
Other Properties	Voltage coefficient g_{31} 0.06-0.22 Vm/N
Refractive Index 1.41-1.42	Pyroelectric coefficient ρ_Q 19-30 μC/m^{2}K
Water absorption (230^{o}C, 10 kg) <0.04 gm/10min	Coupling coefficient k_t 10-15%
Specific gravity 1.78	

Depending on different processing methods the PVDF shows α, β, γ, δ and ε phases **[50, 53]**. The monoclinic α-phase is most common while the orthorhombic β-phase shows the piezo-, pyro- and ferroelectric properties. The β-phase is kinetically favorable while the α-phase is most thermodynamically stable. The α and ε-phases are non-polar due to antiparallel packing of the dipoles [54] and the other three phases are polar and mostly studied because of their properties and widespread applications [55]. The α-phase is of most of the interest as it can be crystallized in β and γ-phase, which are electrically active [56, 57]. The β and γ-phase PVDF can be utilized in sensors and energy storage devices because of their piezoelectric properties. **Figure 1.7** shows the arrangement of atoms in PVDF in its α, β and γ-phase.

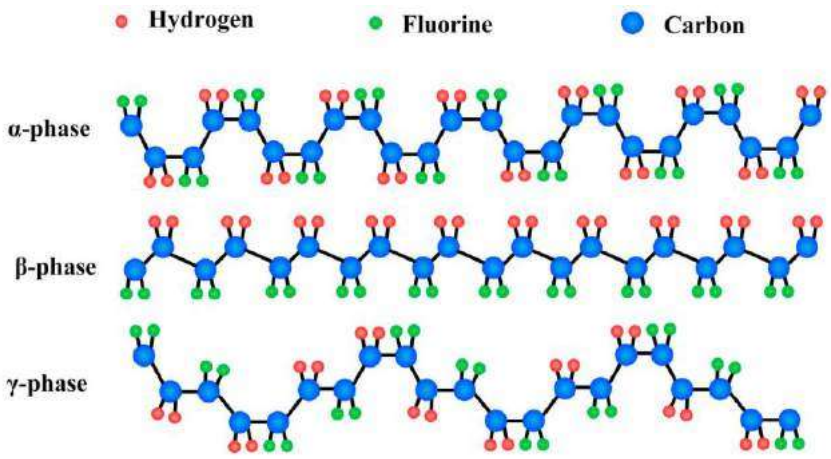


Figure 1.8: α, β and γ-conformations of PVDF.

1.7.2. Piezoelectricity and PVDF:

Piezoelectric and ferroelectric effect in PVDF is due to the presence of non-centrosymmetric unit and a net polarization. A large dipole moment in the unit cell, possibility of crystallization in a non- centrosymmetric unit cell and the orientation of the dipoles are the characteristics of a common piezoelectric polymeric material. Normally the PVDF is not piezoelectric because of its non-polar α-phase but we can transform it into piezoelectric β and γ-phase by mechanical processing or incorporating the nanofiller in it. The poling process also aligns the dipoles of PVDF. The Piezoelectric effect of the PVDF depends on the electroective phase and crystallinity. In pizo-ceramics also, the dipoles are randomly aligned initially. On application of external applied electric field, the response of the dipoles cancels each other and they produces no gross change in the piezo-ceramic dimension. The dipoles must be permanently aligned to each other in order to have useful piezoelectric response, for this Poling process is used. When the piezoelectric material is heated above its curie temperature the piezoelectric material change the orientation of its dipoles in the solid phase. In poling process, the electric field is applied on the material, while it is heated. The

polarization direction is the same as the applied electric field and the dipoles align with it. Applying the electric field material is cooled, which results in the permanent alignment of the dipoles and the material is said to be poled [58].

1.8. Nanohybrids

Nanohybrids are multiphase materials in which at least one phase with nano dimensions (<100 nm) is embedded in a metal, ceramic or polymer matrix [59]. The general idea behind adding the nano phase is to create a synergistic effect between the constituents, such that the enhanced properties can be achieved. The properties of these nanohybrids depend on the matrix materials, nanosize dimension, degree of dispersion, size, shape, and orientation of nano phase in the matrix and the interaction between the phases. Different types of ceramics [31, 32], metal oxides [60] layered silicates [61], graphene [62], layered hydroxides [63] and organic fillers like cellulose [64], etc. are used to prepare the nanohybrids depending upon the properties required. Nanohybrids show superior mechanical, structural, thermal and electrical properties than the pure polymer.

Different methods for nanohybrids synthesis are used. *Intercalation method* for layered silicates, a *sol-gel* process that uses hydrolysis and condensation reaction, *In-situ* polymerization of monomers in the presence of nanofillers and *direct mixing* of the polymer and fillers with or without solvent [65]. Here we use solvent casting methods to prepare hybrids where the polymer and fillers are mixed in the presence of an appropriate solvent.

1.9. Literature Review:

Piezoelectric nanogenerators have been used for energy harvesting for a very long time. Earlier the semiconductor and the ceramic materials were used for this purpose. In 2000, Wang and Song [18] revealed the piezoelectric nanogenerator, based on zinc oxide nanowires, which can harvest nanoscale mechanical energy to electrical energy with an efficiency of 17-30%. Later, the same group developed a hybrid solar cell using semiconducting properties of ZnO, which can harvest solar and mechanical energy at the same time [66]. Imec created a wireless energy harvesting sensor using AlN [67] that can power a temperature sensor which requires 10 μW-105 mW power. Zhu et al [68] prepared an effective mechanical energy harvester using ZnO nanowires on a substrate, which with the use of multilayer integration gives output power of 0.44 mW/cm^2.

Ceramics have higher voltage, power output and efficiency as compared to polymers, but most of the ceramics are brittle, toxic and non-scalable. On the other hand, polymers are light weight, flexible and most of the polymers are bio-compatible. The use of polymeric materials has been increased to overcome the disadvantages of ceramic materials. Different polymers have been used for energy harvesting with or without the incorporation of fillers. Jung et al [69] used Poly dimethylsiloxane (PDMS) and $KNbO_3$ (potassium niobate) composite, which is sandwich by Au/Cr-coated polymer substrate at 0.38% strain produces voltage of 3.2 V. Lin et al [70] prepared composite of PDMS and Barium Titanate nanotubes, which after poling at 80 kV/cm for 12 hours and on 1 MPa stress gives output of 5.5 V and 350 nA. More than one fillers also have been used like Jeong et al [71] used a hyper stretchable elastic generator made of carbon nanotube and PMN-Pt($(1-x)\{Pb(Mg_{1/3}Nb_{2/3})O_3\}-x\{PbTiO_3\}$ (lead magnesio niobate–lead titanate)) nanoparticles in silicon rubber matrix, gives an output of

~4V and ~500 nA on a stretchability of 200%. Other polymers with various fillers and outputs from energy harvesting are shown in **Table 1.5**.

Table 1.5: Output voltage and power of the devices prepared by different polymers with fillers.

Material	**Processing**	**others**	**Power**	**Reference**
PDMS+ $KNbO_3$ nws (3gm PDMS+ 0.1-0.8gm KN)	PI-Au/$KNbO_3$+PDMS composite/Au-PI layers on PET substrate	Poling 5kV/mm @RT for 1hr	10.5 V, 1.3 µA @0.7gm	[72]
BZT-BCT nanorods +PDMS	Ratio: 0.4:10:1	Poling 3.5 kV/mm 20mins	0.8V, 7nA @finger pressing	[73]
PDMS+BZT-BCT nps	ITO/PET film and Cu as electrodes		0.6V, 7.6nA	[74]
BCZT nws by electrospinning+PDMS	Nws : PDMS= 0.4:10 Poled @4kV/mm for 20 mins		Vpp=2.2+1.2V Ipp= 180nA	[75]
BT nps in 3D network of calcium alginate biopolymer	Single worm of 1.5 to 3.5cm, by hand force diameter ~550 µm, length ~2.5 cm)	Maximum for L=2.5 cm, D=550 µm	5.92 V, ~74.189 mW/m^2	[76]
BZT–BCT NW and PDMS cantilever @40wt%	Corona poling 15 kV 2hrs d_{33}= 90 ± 5 pm V^{-1}	6.25 V Max 6.8Vpp 19nA @ max displacement	88nW 2.25 µWcm^{-3} @10MΩ	[77]
PDMS-cellulose nanofibrils	PDMS spin coated (100µm)on both sides then Al electrodes attached	Capacitor upto 3.7 V 19 blue LED	60.2 V,10.1 µA 6.3 mW/cm^3	[78]
FaPbBr3+ PDMS (5, 20, 35, 50%)	Spin coated on ITO coated PET substrate Max at 35%	d_{33}~25pm/V	8.5 V and 3.8 µA/cm^{-2}	[79]
$K_{0.485}Na_{0.485}Li_{0.03}NbO_3$ (KNLN) with PDMS	Nps aligned with application of an AC field	g_{33}=220 mV m N^{-1} d_{33}~17pC/N	16Vpp at 5N sinusoidal force	[80]
Cellulose microfiber+PDMS+MWCNT		~500nA ~30V @ hand punch	~9.0 $\mu W/cm^3$	[81]
$ZnSnO_3$+PDMS+ MWCNT	Finger impact	40V, ~0.4µA	~10.8 µWcm^{-3}	[82]

Various polymers as discussed in **Table 1.2 and 1.3**, shows the piezoelectricity but the PVDF has been a good candidate for this as its piezoelectric voltage constant is ~261 Vm/ N, which is about 20 times higher than PZT (~6.6 Vm/N) and 40 times higher than BT (~10 Vm/N) [83, 84]. Different techniques have been developed to induce the piezoelectric β-phase in the PVDF matrix, either by incorporation of filler or by mechanical stretching. Jiang et al [85] used a laminated PVDF cantilever with a magnetic mass attached for low-frequency energy harvesting. At one end of cantilever, the magnet is attached and below it a coil is attached for electromagnetic energy harvesting, which gives 32 V and 16 μW power at a frequency of 14Hz. PVDF stalks have been used for ambient wind energy harvesting, which shows from a single leaf peak power of 600 μW and power density of 2 mW/cm^3 has been obtained [86]. Electrospinning technique is also used to prepare the nanofibers of PVDF, in which there is simultaneous stretching and poling occurs, which enhances the piezoelectric property of the PVDF. Chang et al [87] prepared nanofibers of PVDF, which on mechanical stretching and releasing at 4 Hz gives an output of 10 mV and 1.8 nA.

PVDF with various fillers has used for energy harvesting. On adding the filler in the PVDF matrix, there are structural and morphological changes, which leads to better piezoelectricity, which enhances the energy harvesting capability of the material. Karan et al [88] prepared a composite of PVDF and Al_2O_3 particle containing reduced graphene oxide (AlO-rGO) with different weight %, we can see in **Figure 1.9a** that with increasing the filler content piezoelectric β-phase is increasing in the PVDF. By XRD deconvolution the phase fractions can be calculated. Similarly, Mahanty et al [89] prepared ZnO nanoparticle etched porous sponge-like P(VDF-HFP) film, whose FTIR spectra is shown in **Figure 1.9b** which shows

that the piezoelectric properties in the film induces after treatment. As we can see the piezoelectric β and γ-phases are inducing and the α-phase is reducing.

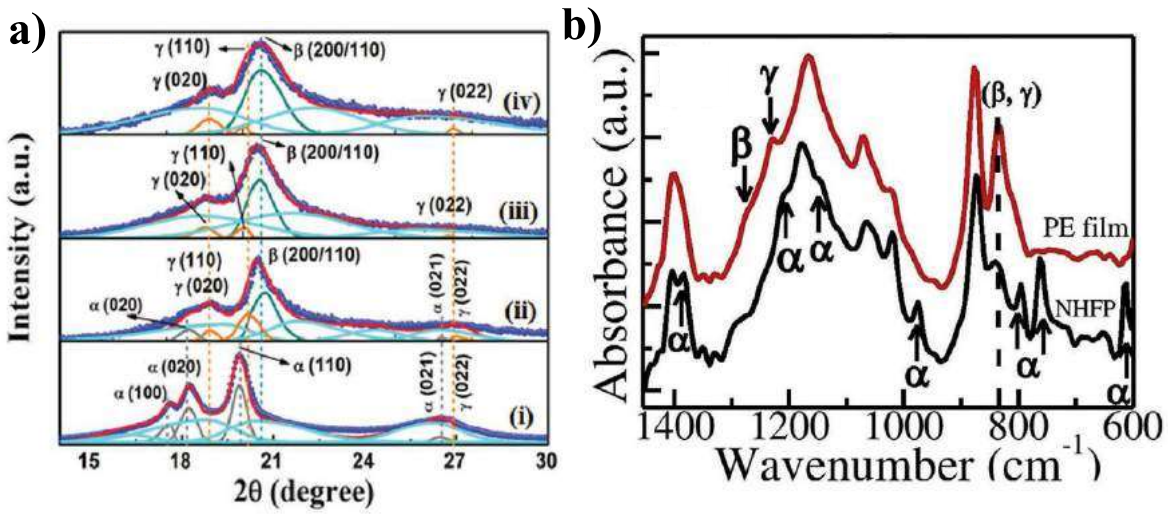


Figure 1.9: (a) XRD pattern of (i) Pure PVDF, nanocomposite with (ii) 0.1 wt%, (iii) 0.5 wt% and (iv) 1.0 wt% AlO-rGO content [88] (b) FTIR spectra of neat P(VDF-HFP) film and ZnO nanoparticle etched porous film [89].

The changes in surface morphology is also demonstrated in several studies. In one of the work [90], the hybrids of PVDF and 30B nanoclay has been prepared to induce piezoelectricity. The scanning electron microscopy images are shown in **Figure 1.10** in which we can see clear spherulite pattern that converts into needle like morphology after incorporation of nanoclay.

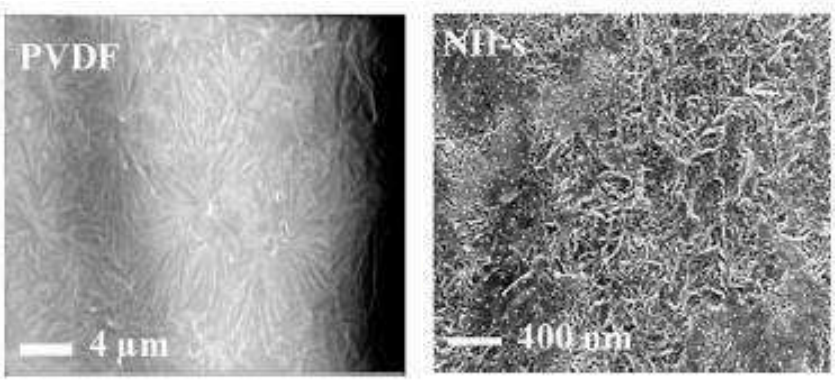


Figure 1.10: SEM images of pure PVDF showing spherulites and its hybrid with nanoclay showing needle like morphology [90].

There is always changes in structure and morphology of the material whenever there is induced piezoelectric phase in PVDF matrix. By using such piezoelectric hybrids we prepare the devices also known as nanogenerators for energy harvesting. Alamusi et al [91] prepared the hybrid of PVDF and rGO with 0 to 0.2 wt %. At an optimum filler content of 0.05% the maximum output of 3.28 V is obtained in vibration test at exciting frequency of 30Hz. Wu et al [92] prepared P(VDF-HFP)/ carbon black composite film and found that at 0.8 wt% ~81% β-phase is induced and at 0.5 wt% highest output voltage of 3.68 V and 30 W/m^3 power density in AC circuit is obtained. Garain et al [93] doped Cerium (III)-N,N-dimethylformamide-bisulfate [Ce(DMF)$(HSO_4)_3$] complex into PVDF and obtained high electroactive phase (β and γ) of 99%. On finger tapping it produces 32V of open circuit voltage and is able to charge 4.7 µF capacitor in 192 s. Alluri et al [94] prepared the composite of PVDF and activated carbon at 30 V/V% and 91.75% β-phase is found. After poling at 8 kV/24 hr at room temperature the output voltage, current and power density at 6.6 kPa pressure is ~49.6 V, ~1.63 µA and 63.07 mW/m^2 (**Figure 1.11a**). Nanofibers of

PVDF with $NiCl_2$ salt has been prepared [95] and 92% β-phase is obtained. In a free vibration test, the voltage generated per unit microstrain for pure PVDF was 0.119 mV, while for nanofibers with salt was 0.548 mV. Maity et al [96] prepared nanofibers of PVDF and natural sugar (12% w/v) to prepare a piezoelectric nanogenerator, which on human finger impact of 10 kPa produces ~100 V, ~9 μA current and power density of 33 mW/m^2 (**Figure 1.11b**). The nanogenerator is able to light up LED's and is able to produce voltage even after using up to ~10 weeks. Ceramic materials also have been used as filler in PVDF matrix to improve the efficiency. Ghosh et al [97] prepared ytterbium assisted porous composite film of PVDF, which is able to produce voltage on different mechanical motions and produces voltage of ~10 V and power density of 1 $\mu W/cm^2$ (**Figure 1.11c**). It can drive small electronics like LEDs and digital wrist watch. Many other different fillers have been used for the PVDF hybrid preparation, which is summarized in **Table 1.6**.

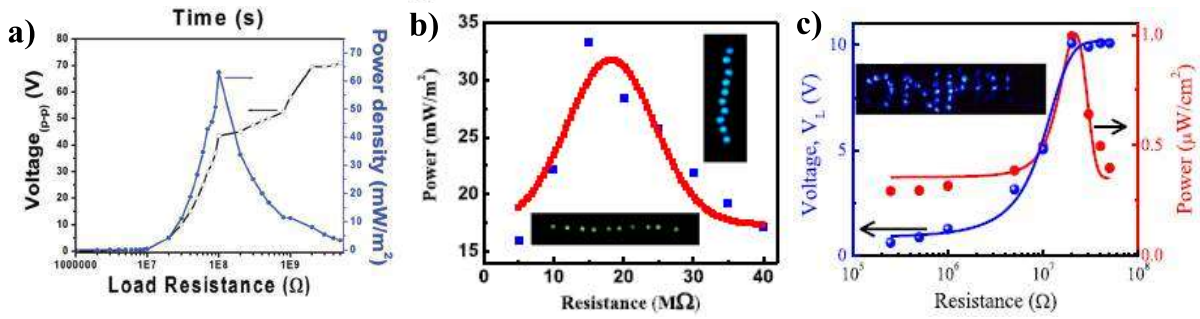


Figure 1.11: (a) output voltage and power density with respect to load resistance of PVDF-activated carbon composite [94] (b) Power density as function of load resistance for PVDF-natural sugar nanofibers, inset shows the glowing LED using the device [96] (c) output voltage and power density with load resistance for ytterbium-PVDF composite, inset shows the glowing LED's by device [97].

Table 1.6. Output voltage and power of the devices prepared by PVDF and its hybrids.

Material	**Processing**	**Others**	**Power**	**Reference**
PVDF/RGO 1wt%		Vpp= 0.9 V 150 nA	14 μW/cm^3	[98]
PVDF/30B clay 4%	Stretching at high temperature	Vpp 2.6V, 100nA	25 mW/cm^3	[99]
PVDF+rGO	poled at 900kV/cm	Max for 0.05 wt% rGO	3.5 V, 4.5 in AC, 2 W/m^3 in DC circuit	[100]
PVDF+ZnO nws (0.1/1)w/w	Uniaxial Pressing and releasing @50mm/sec		6.9 V, 0.96 μA 6.624 μW	[101]
Ce^{3+}-Doped Electrospun PVDF/GrapheneComposite Nanofibers	Concentrations of PVDF, CAS and graphene 12, 0.2, and 1 wt % with respect to the mixed solvent.	Able to sense 2Pa Musical vibration	11 V and 6.8 μW maximum power @ 6.6 kPa	[102]
PVDF/nanoclay nanofibers		0.83V on finger pressing	2.76V in free vibration damping test	[103]
PVDF+graphene nanoplateltes Electrospinning	0.1wt% graphene content		7.9V, 4.5μA @0.2MPa	[104]
$FaPbBr_3$ Nps+PVDF (12wt%)formamidinium lead halide perovskite nanoparticles	Drop cast, thermal annealing, poling 50kV/cm for 1 hr; Au/cr coated PET film as electrode	3.3μF cap charge in 200s upto 1.8V	30V, 6.2 μA/cm^2	[105]
PVDF+ZnO-etching-porous film		Finger pressing(0.36Mpa, ε=0.69%S^{-1})	9V, 1.3μA/cm^2 1.21mW/cm^2 @1kΩ	[89]
PVDF+BT nps electrospinning	Covered in PDMS Max @16wt% BT		0.48V @ 6mm deflection	[106]
PVDF-ZnO nps 50% suspension Composite film Acid etching	Proof mass (65 g) on mesoporous structure(2 cm x 1 cm x 28 μm)	11.0 V and 9.8 μA,@ 40Hz	0.16 mWcm^{-3} at 60 Hz	[107]
PVDF+ $BaTi_2O_5$ nanorods (5 vol%)	Cantilever beam mode (magnetic mass)	Max @ acceleration of 10g	27.4 μW/cm^3 Capacitor up to 3.72 V	[108]

PVDF-TrFE+MgO nanoparticles (2 to 8%)	PET then ITO coating then 2wt % composite then silver paste	Area 49 mm^2 thickness 20µm d_{33}~65 pm/V	2V max(4.5V pp) on bending On impact 0.4 V	[109]
PMN-PT+CNT+PVDF (30+1+69 vol%)	Mechanical and electrical properties Also measured	4V, 30nA		[110]
(PVDF+BT)-surface modified graphene-(PVDF+BT)	55% BT Poling 15MV/m 1hr @100°C Load 2N	10Vpp, 2.5 µA	5.8µW @1MΩ	[111]
PVDF/BT spin coating	20% filler with 10nm particle size	520mV	0.28µW max	[112]
PVDF+BT (ITO on PET as electrodes)	0.3g PVDF+0.7g BT	150V 1500nA @10MPa stress		[113]
PVDF+BT (Al and Ni as electrode) 40% BT		9.8V, 0.69µA On cyclic loading Micro battery charging	13.5µW/cm^2	[114]
PVDF-TrFE+BT nps (15 wt%) electrospinning	4.7µF capacitor charged in 72 steps	@ 600N, 06Hz frequency walking	25V, ~8µA	[115]
Zno nanowires on substrate then PVDF spin coated	On 3.2% strain (bending)	0.4 V, 30nA		[116]
PVDF+ BNZ-PT (30, 40, 50%)	On short time impact press (max with 50% filler)	16.75V, 7.8µA	163.63 µW/cm^2	[117]
PVDF-AlO-rGO	@1% filler loading 40V@46.8KPa	~36V, ~0.8 µA, 40V@46.8KPa	~27.97 µW/ cm^3	[88]
Fe-doped RGO/PVDF 2wt% loading	99% γ phase	energy density of ≈0.84 J cm^{-3} @537 kV cm^{-1}	5.1 V and 0.254 µA Finger pressing	[118]
DNA in TE buffer solution + PVDF-DMF mixed	6 Vand 0.088 µA @13 kPa	20 V, 0.184 µA @ 63 kPa	11.5 µW/cm^2 @ 9 MΩ.	[119]
PVDF-cellulose nanocrystal nanofibers	Bent by periodic external force with a fixed frequency 2 wt% CNC	β-phase-89.96%	Vpp~ 100V	[64]

Various bio-wastes and biological materials with polymer or in their pure form also have been used for energy harvesting as summarized in Table **1.7**.

Table 1.7: Output voltage and power of the devices prepared by bio-waste or natural materials.

Material	**Processing**	**Others**	**Power**	**Reference**
Bio Waste onion skin	PDMS encapsulation 0.053 μC/cm^2 Poled- 0.068 μC/cm^2	≈18 V ≈166 nA d_{33}= -2.9 pC/N calculated	≈1.7 μW/cm^2 at ≈20 MΩ	[120]
M13 bacteriophage (phage)		6 nA, 400 mV 7.8 pm/V		[121]
DNA in TE buffer solution + PVDF-DMF mixed	6 V and 0.088 μA @13 kPa	20 V, 0.184 μA @ 63 kPa	11.5 μW/cm^2 @ 9 MΩ.	[119]
Fish scale		4V, 1.5 μA 0.17 MPa. -5.0 pC/N.	1.14 μW/cm^2 @5MΩ	[122]
Prawn shell		Gentle human touch -2 pC/N	0.76 μWcm^{-2} @ 30MΩ	[123]
Fish swim bladder	Oven dried fish swim bladder	V_{OC}=10 V I_{SC}=541 nA ≈0.3% energy conversion efficiency	4.15 μW/cm^2	[124]
Taiwan localnephila pilipes spider silk	Reverse piezoelectricity filed 12kV/mm	Nonpolarized silk 13.4 mV, 70.6 nA with strain rate was 0.02/s	Polarized silk 46.7 mV, 105 nA with strain rate 0.02/s,	[125]
PVDF-cellulose nanocrystal nanofibers	Bent by periodic external force with a fixed frequency 89.96%	2 wt% CNC	Vpp- 100V	[64]

M13 bacteriophage (vertically aligned)		Phage nanopillers	Vpp=0.3V, 20nA after 7 cycles	[126]
Egg shell membrane	@81.6 kPa 131 V, 6 µA with 5 stacks	26.4 V, 1.45 µA 23.7 pC/N	~11.90 µW/cm^2 (~238.17 µW/ cm3)@15MΩ	[127]
Spider silk	@82.2 kPa, strain rate (ε) of 0.226% s^{-1}	21.3 V, 0.68 µA 66% energy conver. Eff 0.36 pm/V	4.56 µW/cm^2	[128]
Zno nanocoated on cellulose	Tensile load	d_{33}= 93.5 pC/N	908mV Vpp @14.2N	[129]

1.10. Objective of the work:

With the increment in energy consumption with each passing day, it is imperative to find an alternative energy source, which is economical, environment-friendly and easy to deploy. Also, on the other hand, there are lots of waste energy in various forms in our ambient that can be used. So, the main motivation for this work was to utilize the waste energy to reduce the dependency on conventional energy sources. This is where energy harvesting comes in. By using the harvested mechanical energy an effort has been made to power portable or small scale electronic devices.

The objective of the thesis is to develop the light-weight, low-cost and flexible PVDF hybrid materials for energy harvesting. Herein, we introduce a method to prepare piezoelectric polymer hybrids by solution route. The hybrids of PVDF with nanoclay and bio-wastes are prepared. The effect of mechanical processing on PVDF is also studied. The piezoelectricity in PVDF is induced by introducing filler in the PVDF matrix or by its mechanical processing. The prepared piezoelectric material is sensitive against external load and can be used to harvest different biomechanical energy.

The development, characterization, and application of the devices prepared by theses piezoelectric materials have been discussed in the thesis. The outlines of the thesis are:

- Synthesis of piezoelectric PVDF hybrids using nanoclay and bio-wastes as filler for energy harvesting.
- Improvement in the piezoelectric properties by mechanical stretching.
- Induction of the piezoelectric phase by incorporating the fillers.
- Characterization of prepared hybrids to study the changes in structure and in surface morphology.
- Fabrication of the device to measure the energy harvesting capability of the material.
- Measurement of output voltage and power density.
- To use these devices in practical applications.