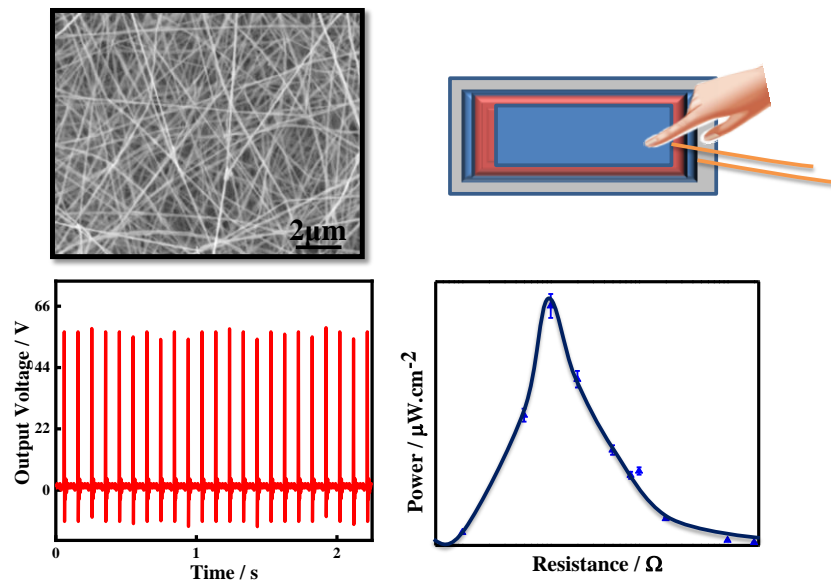


Chapter 4

Enhanced piezoelectric response in nanoclay induced electrospun PVDF nanofibers for energy harvesting



4.1 Introduction

Energy scavenging or harvesting is a process of using ambient power from the human movement, vibrations, mechanical loads and converting it to useful electrical energy. The energy procured is environment friendly and maintenance free as compared to other methods of energy generation. Several materials has been developed or investigated for such purpose and the most prominent of them is piezoelectric materials. Piezoelectricity is the internal property of the material which generates electrical potential upon the application of stress/strain. Among all developed materials, PVDF and its copolymers show the most efficient piezoelectric, pyroelectric and ferroelectric properties apt for energy harvesting [3][127][128][129][130]. PVDF possess some exceptional features such as biocompatibility [131], flexibility [101], chemically resistant [94], high mechanical strength, UV and nuclear radiation resistant [132], low dielectric constant [24] which makes it a versatile material for large number of applications *e.g.* actuators, sensors, biosensors and many more. Apart from the mentioned characteristic features, its excellent piezoelectric, pyroelectric and ferroelectric properties [133] makes it the most preferred material for the energy harvesting applications. Among the devices prepared using PVDF, piezoelectric nanogenerator is the one which has caught many researchers' eyes because of its low cost, good reliability, environment friendly and flexibility [101]. PVDF is a semicrystalline polymer [134] with an alternating hydrogen and fluorine units attached to the carbon chain. It consists of five different prominent crystal phases α , β , γ , δ and ϵ . Amongst them, α and δ phases possess $TGT\bar{G}$ type of configuration and β and γ has TTTT (all trans) and $T_3GT_3\bar{G}$ configuration, respectively [135]. α and δ -phases are non-polar and possess zero dipole moment due to its anti-parallel arrangement of $-\text{CH}_2/-\text{CF}_2$ unit along the

polar axis [35] whereas the β -phase having the parallel $-\text{CH}_2/-\text{CF}_2$ alignment possesses considerable electric dipole moment and the γ -phase is semi-polar with small dipole moment but exhibits more effective piezoelectric property than the α -phase [93].

The piezoelectricity of the polymer is accounted due to the presence of electroactive β -phase which possesses spontaneous polarization [136]. The other non-piezo phases have the tendency to get converted to the electroactive phase by poling or mechanical stretching [137] which leads to the alignment of the dipoles and enhances its electrical property. The conversion of the non-piezo phase to piezoelectric active phase can also be achieved through electrospinning; a process where poling and uniaxial stretching is performed under the influence of high electric field and produces fiber from microns to nanometer dimensions [138]. The electrospun fibers enhance the mechanical and electrical properties and also increase its surface to volume ratio [139] which multiplies its application field. Apart from deriving some remarkable applications from the pristine PVDF, its area of versatility is even more enhanced through the incorporation of some additives or fillers at certain range of concentration. The addition of these modifiers leads to increase in surface charge of the polymers, as a result, the electroactive β -phase gets enhanced and so does the piezoelectric property. Organic and inorganic fillers have been used to modify the functionality of PVDF polymer. The incorporation of filler is a very scalable, efficient [140] way to produce material for energy harvesting applications. Fillers like ZnO [141], BaTiO₃ [142], PZT [123], GaN [143], ZnSO₃ [144] were added because of their high permittivity and dielectric constant [145]. Carbon based additives like CNT [146], reduced graphene oxide [147] and layered silicates [138][148] were incorporated with the matrix to enhance the β -phase/piezoelectric response of the nanohybrid. In a recent study, metals

like Ni [149], Pd [150], Ce^{+3} [65] are also doped to the host matrix for better electrical and thermal properties and β -phase enhancement. To produce better response in the nanohybrid, the filler and the polymer should be highly interactive and compatible. The ceramic based piezoelectric materials possess higher d_{33} value [24] but they also have lower piezoelectric stress constant [136], brittle in nature [24], dimensionally constraint, and low electromechanical conversion efficiency than the organic/polymers. The organically modified polymers are scalable, easy to process, highly flexible (low elastic constant) and non-toxic than their counterparts [132]. Recent study in the field of energy harvesting has produced some extraordinary output with the electrospun nanofibers. Baozhang et al. [151] prepared a nanofiber through electrospinning of PVDF - reduced graphene oxide composite which led to significant rise in the β -phase and generated an output voltage of 46 V and power density of $18.1 \mu W/cm^2$. Siddiqui et al. [69] generated 3.4 V and $2.28 \mu W/cm^2$ of voltage and power, respectively, from finger tapping with P(VDF-TrFE)-BaTiO₃ nanohybrid. Electrospun nanofiber of PVDF-MWCNT at different concentration of MWCNT exhibit a maximum output voltage of 6V and power of 81.8 nW [57] and an output voltage of 1.6 V and $0.03 \mu W$ of power from electrospun PVDF-PZT nanohybrid was also reported [123]. PVDF composite with graphene along with Ce^{3+} as precursor for electrospinning showed a maximum output voltage and power of 11V and $6.8 \mu W$, respectively, through mechanical stress [65].

In this present work, a light weight, flexible and highly efficient electrospun nanofibers of PVDF with two-dimensional organically modified nanoclay have been designed for energy harvesting application. Miniaturized devices have been fabricated using hybrid nanofiber for energy production. Different kind of body movements are

applied to generate electricity and exhibit very high energy conversion using hybrid fibers with plausible explanation behind the huge improvement in device performance.

4.2 Methodology

The electrospinning was performed at 12.5 kV at the flow rate of 0.5 ml/h, after optimizing the fiber preparation method. The scaffold obtained after electrospinning was kept at ambient atmosphere to evaporate the remaining solvent and was used for the characterization purpose. The electrospun fibers from pure PVDF has been abbreviated as 'P', while that prepared from nanoclay at concentration of 5, 10, 15 and 20 wt.% are designated as C5, C10, C15 and C20, respectively.

4.3 Results and discussion

4.3.1 Influence of nanoparticle on morphology of nanofiber

The quality of fiber depends on the electrospinning parameters like applied potential, flow rate, concentration of solution, distance between spinneret and collector drum and the solvent or their ratio for mixed solvent system. These parameters are optimized to obtain good quality of fibers and 12.5 kV potential, 0.5 ml/hr flow rate, 10 wt. % solutions, 15 cm spinneret-drum distance and 2:8 ratio of DMF and acetone mixture have been found to be optimized for obtaining better quality of fiber **Figure 4.1**. Slightly thicker fibers are evident in optical images (**Figure 4.2a**) in presence of organically modified nanoclay dispersed in PVDF. Importantly, no bead formation occurs in presence of nanoclay which is further confirmed from the high magnified SEM images of fibers where clear beads are evident in fibers made from pure PVDF solution against very smooth surface morphology throughout the fibers made from composite solution (**Figure 4.2b**). The fiber diameter increases in presence of nanoclay

as evident from the histogram of fibers from pure PVDF and nanohybrid solutions (*Figure 4.2c*). Further, the quality and orientation of fiber improves with the enhancement of nanoclay content and 15 wt. % is found to be optimized as further increase of nanoclay reduces the quality of fiber prepared from 20 wt.% nanoclay solution.

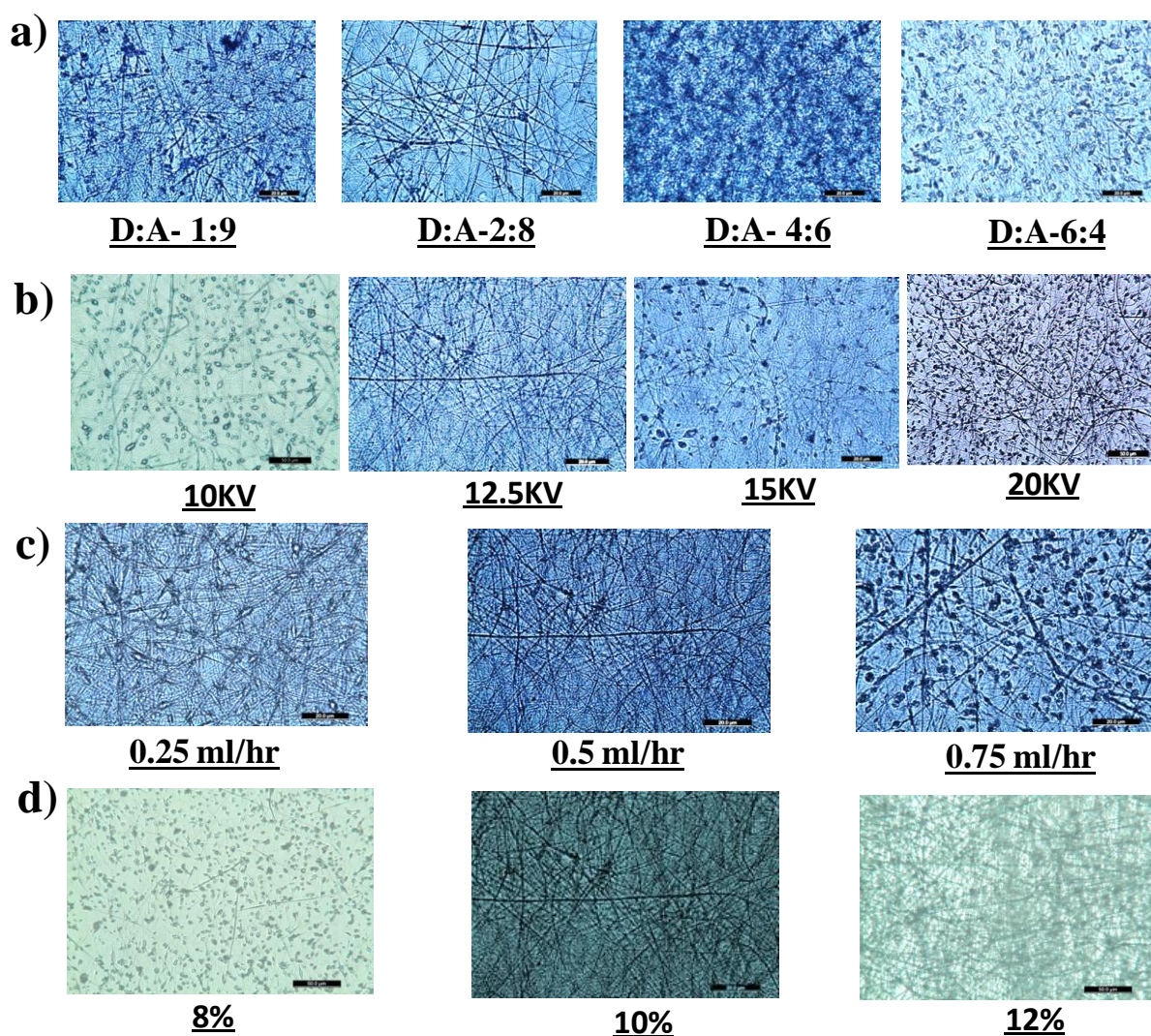


Figure 4.1: Optical Microscopy images showing the fibers obtained from electrospinning at different a) solvent ratio b) Voltage c) flow rate and d) solution concentration.

The average fiber diameter of 190 ± 20 nm is measured from pure PVDF solution vis-à-vis 330 ± 30 nm fiber diameters observed in C15 with the systematic increase of fiber diameter with increasing nanoclay content. The morphology through AFM also endorses the uniform and similar dimension of fiber (*Figure 4.2d*). However, the better quality of oriented fiber can be produced by incorporating organically modified nanoclay in PVDF under suitable processing conditions. Graphene is reported to increase the diameter of PVDF fiber slightly ($165 \rightarrow 230$ nm) while significant enhancement of alignment and fiber diameter occurs in presence of nanoclay presumably because of harder template of inorganic aluminosilicates [67][51]. The rise in average fiber diameter and alignment with the addition of nanoclay is due to the enhancement in viscosity and conductivity of the solution.

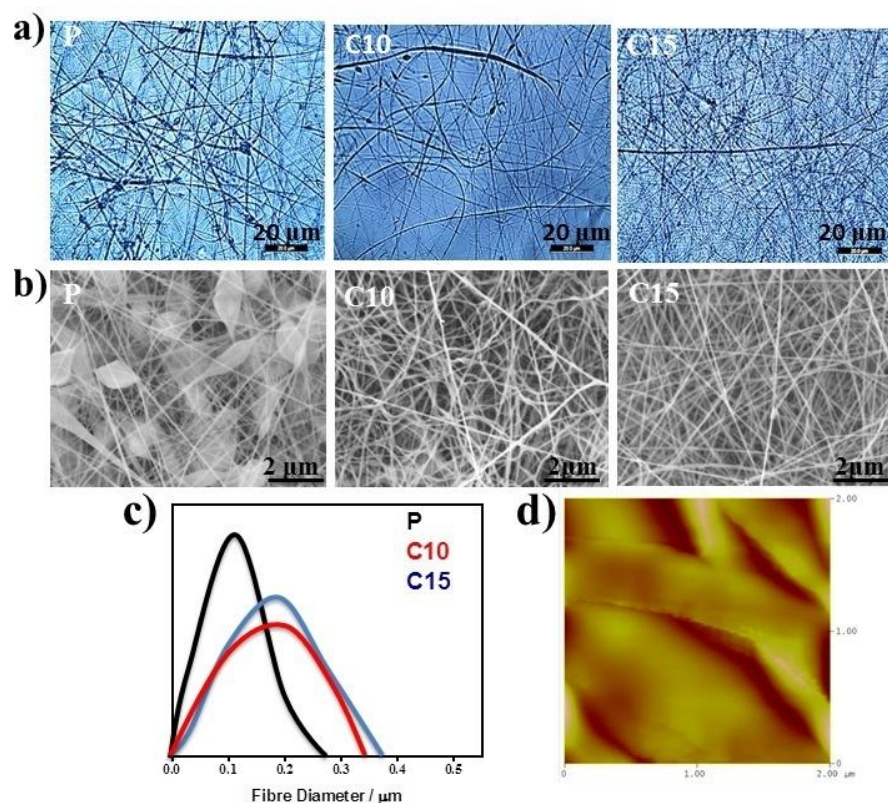


Figure 4.2: a) Optical images of fibers of indicated specimens (P, C10 and C15); b) SEM micrographs of the electrospun fibers of pure PVDF and its indicated nanohybrids; c)

comparison and distribution of fiber diameter of P, C10 and C15; d) representative AFM image showing the PVDF nanofibers

4.3.2 Structural, thermal and mechanical alteration of nanofiber

Now, it is pertinent to check the property improvement of fiber in presence of nanoclay. Pure PVDF crystallizes in α -phase (either from solution or melt) and the XRD peaks appear at 17.6° (100), 18.3° (020), 19.9° (110) (inset figure of **Figure. 4.3a**) while the electrospun fiber of pure PVDF exhibit considerable β -phase as evident from the strong peak at 20.2° (020/110) in addition to other α -phase peaks. On the other hand, β -phase peak enhances along with slight shifting of peak towards higher angle (20.4°) and α -phase peaks gradually disappear with the increase of nanoclay content in fiber (**Figure. 4.3a**). The shifting of peak position is also reported in literature in presence of nanoclay [152]. This is worthy to mention that β -phase is electroactive phase and exhibit piezoelectricity. Its content in the fiber dictates the nature of piezoelectricity developed in the material. The amount of β -phase is calculated from the deconvoluted XRD peak areas and found maximum β -phase content of 79% in C15 with some γ -phase (11%) as opposed to relatively lower β -phase ($\sim 66\%$) and 0.1% γ -phase in pure PVDF fiber (P) (**Figure. 4.3b**). Significant enhancement of electroactive phase ($\beta + \gamma$) occurs in C15 in presence of nanoclay while non-polar / non-electroactive α -phase gradually reduces with the increment of nanoclay content in fiber. The nucleation of electroactive phase in presence of nanoclay is also supported from FTIR intense band at $879, 1072, 1181, 1274$ and 1233 cm^{-1} , assigned as β/γ peaks, as compared to the peaks at $760, 792$ and 976 cm^{-1} for pure unprocessed α -PVDF (**Figure 3c**). Similar appearances of peaks are reported in presence of nanoclay [66] and Fe-doped RGO [50]. Pure PVDF nanofiber shows the melting temperatures at 170.2

and 175.1 °C due to β - and α -phase, respectively, while nanohybrid fibers (C10 and C15) exhibit the γ -phase peak at higher temperature (~ 179.1 °C) due to its higher content along with their ordered form in addition to β -phase peak at similar position as pure PVDF.

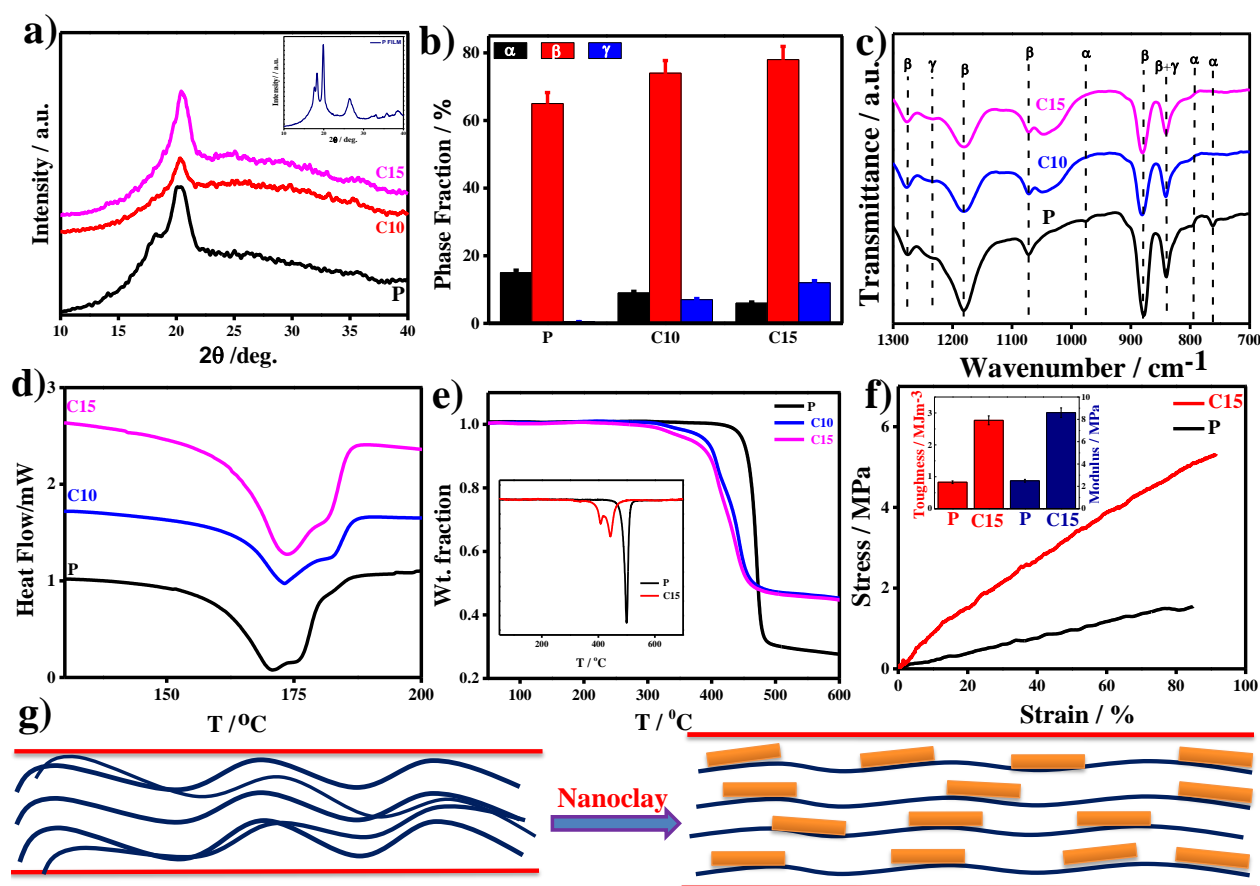


Figure 4.3: a) XRD patterns of electrospun indicated nanofibers (inset shows the XRD pattern of pure unprocessed PVDF film of α - phase); b) phase fractions calculated from the deconvoluted XRD patterns, α , β , γ \square represents the various phases obtained; c) FTIR spectra showing the presence of different phases in P, C10 and C15; d) DSC thermograms of pure PVDF and its nanohybrid fibers showing the change in melting temperature with nanofiller loading; e) TGA curve for P, C10 and C15 (inset figures show the DTG curves for understanding degradation temperature); and f) Stress – strain curves for pure PVDF

nanofibers and its nanohybrid fibers with inset bar diagram of modulus and toughness; g) schematic view of the fiber orientation obtained through electrospinning for pure PVDF fiber (P) nanohybrid fiber (C15) showing better alignment and thicker fiber in presence of nanoclay.

This is to mention that the first melting peak ~ 170 °C is a combined peak of α - and β -phase peaks and slightly higher melting temperature of β -phase as compared to conventional β -phase is due to close packing and greater orientation under high voltage electrospun condition. However, XRD, FTIR and DSC studies suggest the formation of electroactive phases ($\beta+\gamma$) in electrospun fiber whose quantity enhances considerably in presence of nanoclay leading to the creation of superior piezoelectric materials / fiber. Electroactive phase is usually generated either in presence of nucleating agent / template [133] or through regulated uniaxial stretching [132]. This method uses both by applying template system using two-dimensional platelets at very high stretching rate through electrospinning at high voltage generate $\sim 90\%$ of total ($\beta+\gamma$) electroactive phase to be used in energy harvesting device. The reduction of β -phase content at higher clay containing nanohybrid (say C20) is presumably due to the formation of bead at considerable high viscous liquid. The result supports that the interaction between the nanoclay and PVDF matrix is good and effective crystallization of β -phase arises on the top and bottom of the modified silicate layers of nanoclay. Further, the addition of nanoclay leads to the development of surface charge which interacts with the dipoles of PVDF segments in nanohybrids which leads to the stabilization of electroactive phases by aggregating the locally ordered *all-trans* conformation and thus enhances the piezo-phases to a great extent suitable for device application.

Device made of any material should be thermally and mechanically strong enough for its practical uses. Thermal stability is measured under the heat treatment of material through thermogravimetric analyser and 5% weight loss is considered as the degradation temperature. Even though there is slight reduction in degradation temperature of hybrid nanofiber vis-à-vis pure PVDF fiber, all the nanofibers are stable up to 350 °C (**Figure 4.3e**). The degradation temperatures are calculated from the DTG (derivative) curves and 500 and 405°C degradation temperatures are measured for P and C15, respectively (inset figure of **Figure 4.3e**). Slight reduction of thermal stability of hybrid nanofiber as compared to pure PVDF fiber arises due to better dispersion of catalyzed inorganic layers [153]. Stress-strain behavior of materials, under constant strain rate, signifies its strength and the representative curves are shown in **Figure 4.3f**. Slope of the linear region indicates its rigidity (Young's modulus) while area under the curves implies its toughness. Interestingly, the elongation at break for C15 enhances to 92 % as compared to 82 % for the pristine PVDF nanofibers leading to overall increase of toughness more than three folds. **Table 4.1** summarizes the mechanical strength of nanofibers and hybrid nanofiber exhibits superior stiffness and toughness vis-à-vis pure PVDF nanofiber. The increase in stiffness and toughness with the addition of nanoclay is shown in the inset figure of **Figure 4.3f** and better mechanical strength of hybrid nanofiber arise due to suppression of beads in the electrospun fibers, as confirmed from SEM images *c.f.* **Fig 4.2b**, along with better alignment and thicker fiber diameter. Nanoclay acts as a nucleating agent and strongly interacts with polymer chains [154][155] and form tiny mesh-like morphology which in turn inhibits the growth of cracks resulting in tougher fiber in presence of nanoclay. Thus, the dramatic increase in toughness and modulus can be attributed to the modification in morphology,

crystal structure and good dispersion of the layered silicates in polymer matrix. Thereby, thermally and mechanically strong hybrid nanofibers with its superior piezoelectric behavior is very much suitable for piezo-device including energy harvesting device.

Table 4.1: Comparison of mechanical strength of electrospun nanofibers (pristine vs. hybrid nanofiber)

Nanofibers	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
P	1.6	82	2.5 ± 0.5	0.8 ± 0.5
C15	5.3	92	8.6 ± 0.5	2.8 ± 0.5

4.3.3 Induced piezoelectricity for energy harvesting:

From the above discussion, it is evident that tougher, thermally stable and electroactive phase has been induced in electrospun nanofiber in presence of two dimensional clay platelets. Therefore, this material is suitable for piezo-devices especially for energy harvesting purpose to convert the mechanical form of waste energy into useful electrical energy. The developed nanofibers are fabricated in the form of device to measure the piezoelectric responses under the application of different human body movements. The nanofibers are encapsulated within the poly (dimethyl siloxane) (PDMS) to provide the nanofibers / device of sufficient stability and better rigidity. The encapsulated PDMS around the nanofibers along with the electrodes prevents the scaffold from direct impact. The output voltage as a function of time is measured through different modes of human movement. **Figure 4.4a** shows the output voltage using finger tapping. The output voltages are measured to be 20, 50 and 70 volts for P, C10 and C15, respectively, clearly indicating higher voltage output for greater nanoclay content fiber. However, maximum output

performance of very high (70 V) is obtained from 15% nanoclay containing hybrid fiber followed by decreasing tendency with even higher clay content (20 wt. %) fiber. The diminution in the energy harvesting property at higher filler loading is due to the outflow of charges through the conducting network path between the electrodes and severe agglomeration at higher clay content. The addition of filler loading beyond a certain concentration (15%) results in increase in beads and decrease in fiber quality, as also seen from the morphology and phase fraction distribution, and thereby drop in ultimate electroactive phases. The application of periodic mechanical force (press/release) leads to the generation of charge which flow back and forth between the top and bottom electrode through external circuit. The mechanical strain induces polarization (piezoelectric bound charges) in the fabricated device which creates a potential difference at the two ends of the nanogenerator [156]. The induced polarization generates a piezoelectric potential inside the fiber / hybrid fiber which causes the electron to flow from the electrodes towards the external load in order to balance the electrical field and, thus, results in the positive signal. During the removal or release of strain, the piezoelectric potential gets diminished immediately and the electron/charge gathered to the nearby electrode flows back to the other electrode causing a negative signal [60].

The power density for the fabricated devices are measured across load resistance using the formula, $P = V^2 / (R_L \times A)$, where, P is the power density, V is the maximum output voltage, R_L is load resistance applied parallel across the device and A is area of the device [99][106]. Similar to the output voltage data, the power density too increased with the increment of nanofiller loading (**Figure 4.4b**). The maximum output power density is recorded at $68.0 \mu\text{W}\cdot\text{cm}^{-2}$ from the device made of C15 nanofiber. Alluri et al. [131]

reported the maximum output voltage and power density of 37.8 V and $6.3\mu\text{W}/\text{cm}^2$ using PVDF-activated carbon composite film, whereas a peak to peak voltage of $\sim 60\text{V}$ for UV resistant Ce^{3+} -PVDF system is reported [158] while unidirectional aligned PZT fibers generate 0.75 mW power under 180 MHz vibration frequency [159]. Li et.al [160] obtained $2\text{mW}/\text{cm}^3$ of power from PVDF film through cross-flow fluttering. In contrast, the current device exhibits the highest energy output from energy harvesting device especially using polymeric materials. The output power densities of 23.2 and $44.0\mu\text{W}\cdot\text{cm}^{-2}$ are measured from the devices made of pure PVDF nanofiber (P) and 10% clay content hybrid nanofiber (C10), respectively.

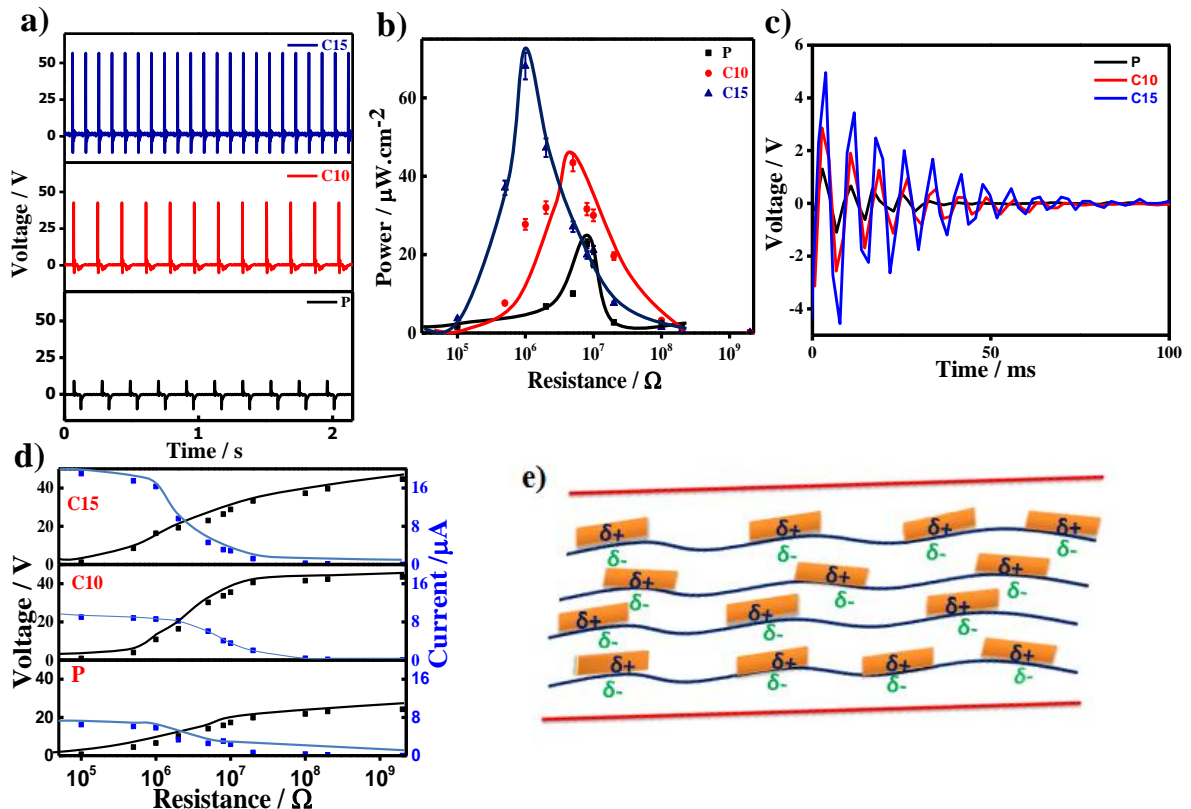


Figure 4.4: a) Stacked arrays of output voltage responses from indicated nanofibers namely P, C10 and C15 produced through finger tapping under multiple hits; b) Comparative study

of power density generated using nanofibers like P, C10 and C15 as a function of resistance; c) Comparison of output voltage measured through instantaneous load on the prepared unimorph (P, C10 and C15) as a function of time for a single hit; d) Voltage and current vs. resistance curve for devices using P, C10 and C15 nanofibers; and e) Schematic representation of charge separation in templated system to understand the mechanism behind the enhanced piezoelectricity for the developed device using hybrid nanofiber.

On application of external force to the nanogenerator, the crystal structure of the nanofibers gets deformed resulting in the induced piezoelectric response through transformation of the deformed structure to a stable one or vice-versa. The mechanical stress applied on the nanofibers results in displacement of the electric dipoles which becomes anti-parallel and generates a net dipole moment in the system. When the pressure is applied through the finger tapping or any other mode of human body movement, it is transferred to the electroactive hybrid nanofibers encapsulated by PDMS which results in charge generation through external circuit. The mechanism of press and release to the nanogenerator creates a voltage difference between the electrodes through charge separation. When the strain is held constant, the net charges and the in-built potential diminishes to zero as the free charges are balanced by the piezoelectric bound charges [123]. To understand the stability of the device and its role in the energy harvesting, voltage response under single impulsive load is shown in **Figure 4.4c** from the unimorph comparing pure and hybrid nanofibers (C15). The output voltage is 5.1 V from the device made of C15 vis-à-vis 1.5 V using pristine PVDF nanofiber. Importantly, the response time for the generated output under the single impulsive load is ~100 ms for the device made of C15 against 50ms time for pristine PVDF nanofiber, after which the output signals decay out. Thus, the developed device (made of

C15 nanofiber) is very much suitable for energy harvesting application due to its enhanced piezoelectric responses. A comparison is drawn between the voltage and calculated current with respect to resistance in **Figure 4.4d**. The voltage starts to rise initially and after attaining a maximum it becomes almost saturated upon increase of resistance while the current measured across the resistance decrease with increasing resistance. It is evident that hybrid fiber provides better response in terms of current and voltage than that of neat PVDF fiber.

Now, it is evident that the increment in output voltage and power has enhanced significantly in presence of nanoparticle in nanofibers [52] where epitaxial crystallization of PVDF chains occurs on top of the layered silicates due to their intimate interaction. The greater charge separation in template system under loading/strain is visualized through a schematic model (**Figure 4.4e**) where polymer chains aligned on top of nanoplatelets in its electroactive form (β -phase) with $>CH_2$ group towards the platelet surface with its partial positive charge while $>CF_2$ group having partial negative charge stay away from the platelet surface. The alignment of several chains over any single platelet cause separation of charge, arising from *all trans* configuration, undergo more charge separation on application of load/strain and causes the generation of colossal piezoelectricity in hybrid nanofibers as opposed to pristine PVDF fiber and explain the unique phenomena of energy harvesting device using hybrid nanofibers.

The output voltage generated via other modes of human movement like walking, foot tapping, twisting and bending are also performed. The maximum output voltage (peak-to-peak) produced via walking and foot tapping are found to be ~10 and 15 V, respectively (**Figure 4.5a**). The output voltage (peak-to-peak) recorded for the fabricated device under

bending and twisting modes of force application are around 8.2 and 6.1 V, respectively (*Figure 4.5b*). The generated power density values for walking and foot tapping mode are measured to be 5.8 and 8.5 $\mu\text{W}\cdot\text{cm}^{-2}$, respectively, as shown in *Figure 4.5c*, whereas the twisting and bending mode of force application produces a maximum power density of 3.8 and 5.3 $\mu\text{W}\cdot\text{cm}^{-2}$ respectively (*Figure 4.5d*). Under bending and twisting process, the development of piezoelectric potential is less as compared to that of finger tapping due to less number of charge generations on the two electrodes under comprehensive strain.

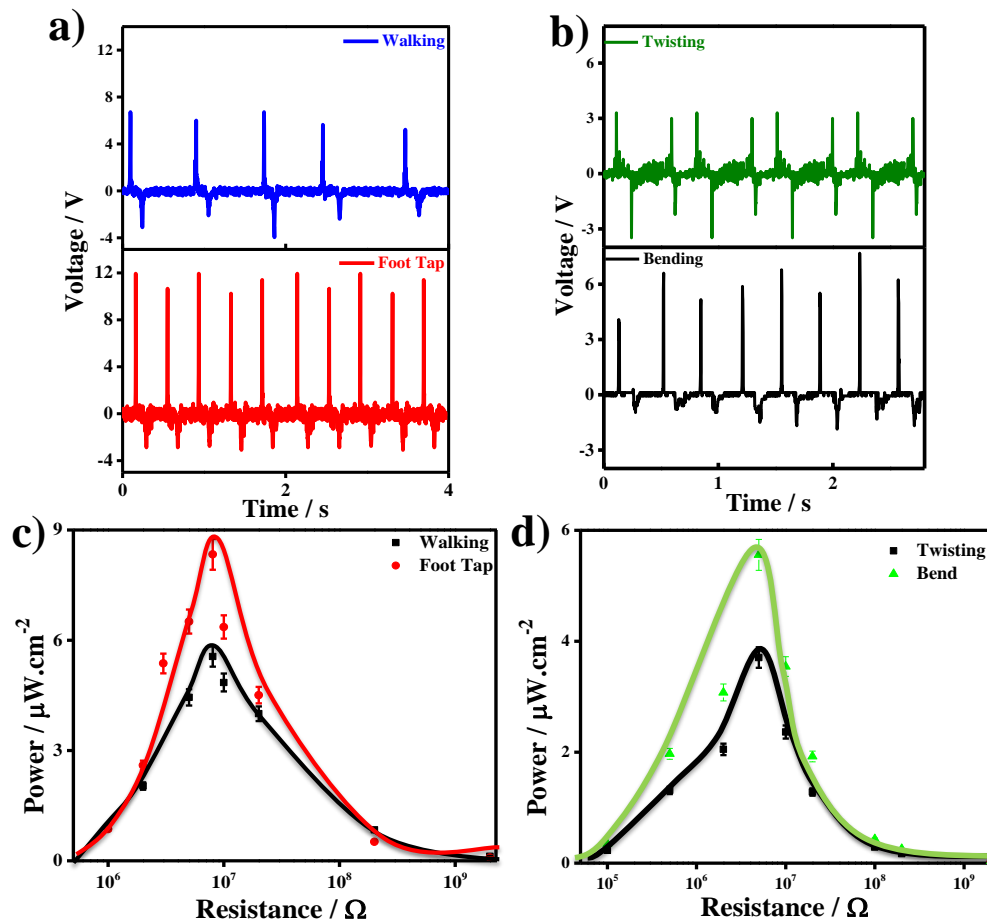


Figure 4.5: a) Comparison of output voltage generated from other modes of vibration like walking and foot tapping; b) voltage generation from twisting and bending type of

force application; comparison of the power output of C15 obtained through different human movement c) walking and foot tapping d) torsional or twisting and bending.

Moreover, greater toughness and thermal stability of the hybrid nanofibers add the feather to new device for energy harvesting applications using all types of body movements. Thus, the developed superior device having greater electroactive phase is able to convert waste mechanical energy into useful electrical energy which can be stored for sensor or biomedical applications.

4.4 Conclusions

Electrospun nanofibers of PVDF and organically modified nanoclay are prepared using different nanoclay content and optimized the processing condition to obtain better quality of fiber. Morphological analyses report the thicker and uniform nanofiber (330 nm diameter) in presence of nanoclay against thinner fibers (190 nm) with considerable bead formation in pure PVDF fiber. Optical image, high resolution SEM and AFM micrographs support the fiber formation. The structural changeover is analyzed through XRD and FTIR studies and up to 90% electroactive phase have been measured in presence of 15 wt. % of nanoclay, supported by heating isotherm measured through DSC. Considerable stiffer and tougher (>300 %) hybrid nanofiber is measured using tensile test while the fibers are stable up to 350°C, thereby suitable for most device applications. Devices are fabricated with structural and piezoelectric layer (unimorph) to measure the piezoelectric response produced by different human movements showing response time of ~100 ms for hybrid nanofiber against less than 50 ms tenure for pristine PVDF fiber. Piezo-device using hybrid nanofiber exhibits very high output voltage (peak-to-peak) of 70 V and power density

$68.0\mu\text{Wcm}^{-2}$, significantly higher than the literature reported value for energy harvesting application. Various modes of human movements like walking, bending, twisting, foot and finger tapping are found to be suitable for generating electrical power using the devices along with the superiority of device made of hybrid nanofiber. Mechanistic pathway of charge separation in hybrid template nanofiber has been revealed which explain well the high conversion of energy using hybrid nanofibers. This tiny device has potential for its use in sensor and biomedical arena as the matrix polymer is biocompatible.