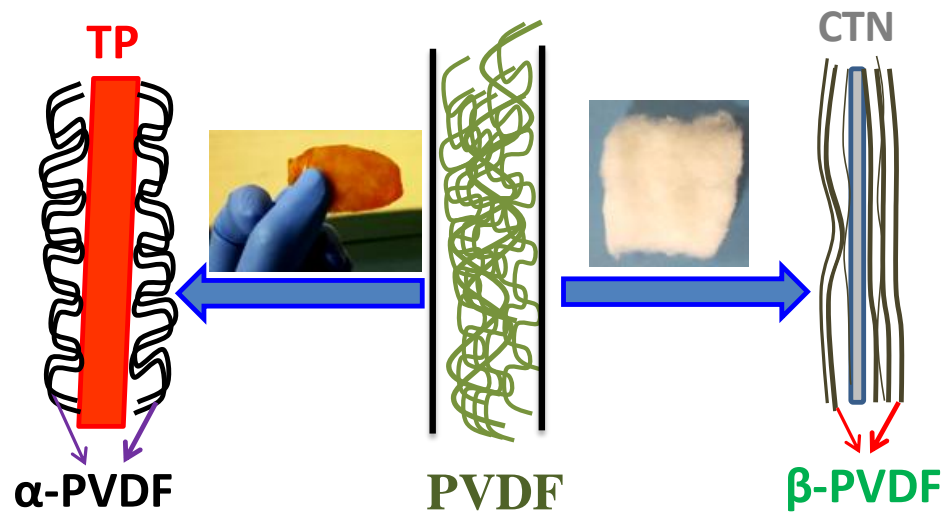


Effect of induced piezoelectric phase in the PVDF based hybrids for energy harvesting applications



3.1 Introduction

The constant depletion of the conventional energy sources and the rising environmental pollution are one of the major challenges the world is facing and is the driving force for the development of the alternative sustainable energy sources [78][79][80][81]. Several approaches have been developed in the prospect of the alternate energy like fuel cells [82], solar cells [83], supercapacitor [84] which is continuously being modified to enhance their efficiency. Energy harvesting is one of the alternate sources, which capitalizes the waste or unused mechanical or vibrational energy sources and convert them into productive electrical energy [3]. Mechanical or vibration energy based harvesting is of interest due to its clean, sustainable and efficient nature [85]. The energy produced from the harvesting of mechanical or vibrational sources is used for the low power based electronic devices or sensors [29]. Human body is rich source of mechanical energies which goes wasted in the form of running, walking, heart beats, breathing, finger motion which on proper integration can be harnessed to productive electrical output in some small portable electronics which can be an alternative to the batteries [87][88]. Different mechanism is applied to generate power from the mechanical or vibrational sources of which piezoelectric based energy harvesting (PEH) is of higher interest due to the higher power storage ability and scalability, simple design, high energy efficiency as compared to other mechanisms [4][89]. Piezoelectric based energy harvesting provides a sustainable solution by harnessing the waste or unused energies to easily convertible electrical energy. When an external stress or pressure is subjected to the piezoelectric materials, the electrical charges are accumulated over the two ends which lead to generation of the electrical output [90]. The common piezoelectric materials used for these applications are piezoceramics due to their higher performance. The major demerit of these ceramic materials is their brittle nature and the

toxicity which restricts its usage in the biocompatible applications [91]. Piezoelectric polymers are one of the most effective and efficient materials for the piezoelectric based energy harvesting due to their enhanced mechanical properties, durability and biological viability [92]. Poly (vinylidene fluoride) or PVDF is one of the remarkable polymers in terms of the piezoelectric applications. PVDF mainly consists of three active phases α , β , and γ ; of which the β -phase is polar in nature with all trans (TTTT) configuration and is of higher interest for piezoelectric based applications due to its higher spontaneous polarization and greater piezoelectric sensitivity [35]. Implementation of different processing techniques generates the piezoelectric active phase in the PVDF such as mechanical stretching [93][94], poling [40], electrospinning [95][96] and addition of electroactive filler to form polymer composites [97][98]. Gaur et.al [99] showed the effect of the mechanical stretching and poling in the PVDF polymer which led to higher content of the piezoelectric phase as compared to the pristine polymer. Polymer based composites and nanocomposite with the incorporation of the polar fillers is highly favorable in the PEH applications. The electroactive fillers generally induce the piezoelectric active phases on to the PVDF matrix which leads to higher crystallization and hence increases the content of the polar phase. Several studies has been reported where the fillers like ionic liquids [100][101], nanoclay [102][103], carbon fillers [104][105], metal salts [106] has been incorporated to the polymers which induces the piezoelectric phase into the composites and generates higher response. Bio-based fillers have been of greater interest towards the development of the biodegradable and bio-compatible piezoelectric materials for the green and sustainable energy harvesting. Karan et. al [72] developed a bio-piezoelectric nanogenerator of egg shell membrane which generated maximum output voltage of 26.4 V

and current of 1.45 μA under mechanical stress. Maiti et.al [61] prepared a nanogenerator from the onion skin which was able to generate maximum output voltage, current, power density and piezoelectric coefficient of 18 V, 166 nA, 1.7 $\mu\text{W}/\text{cm}^{-2}$ and 2.8 pC/N respectively. Recent works of PVDF and bio-based biodegradable fillers like DNA[64], fish scale [107], peel of fruits [108][109] has been of interest among researchers which showed better piezoelectric response and were used to analyse the electromechanical response from different motions of human body. Cellulose is one of the most abundant natural polymers with better piezoelectric property due to the presence of the non-centrosymmetric arrangement of the hydroxyl groups [110]. Ram et.al [111] prepared a Nylon 11 and biomass derived cellulose nanocrystal composite using the solution casting process which generated maximum output voltage of 6.95 V at ~ 23 N forces. Fashnadi et.al [112] prepared electrospun fibres of PVDF and cellulose nanocrystal at different concentration of the cellulose nanocrystal (CNC). The maximum output voltage generated was 6.3 V at 5 wt. % CNC and PVDF nanocomposites which also was able to store charge in capacitor and glow up LEDs.

In this present work, easily processable, flexible polymer based hybrids using two different types of electroactive fillers with the PVDF is prepared for energy harvesting applications. Tomato peel and cotton template based PVDF hybrids are prepared through which the effect of induced piezoelectric effect is being demonstrated. A novel approach to fabricate the scaffold is used and its alteration in the structure and morphology is being studied towards the piezoelectric energy harvesting applications. A device is being fabricated to observe the electromechanical response from different external stress applied over the

device which supports the efficacy of the material and corresponds as the potential material for sustainable green energy harvesting.

3.2 Experimental

PVDF-Tomato peel powder film preparation: The tomato bought were washed with water and then was kept in hot water at 50 °C for 30 minutes and then placed into normal water. Then the tomatoes were peeled off using sterilized doctor's blade and are the peels were then dried at room temperature. The dried peels were then powdered using the liquid nitrogen and then the powdered material was placed in vacuum oven at room temperature to remove any traces of the moisture.

The powdered tomato peel is abbreviated as 'TP' and is taken in different weight percentage with respect to the PVDF to develop a film through solution cast process. The PVDF was initially dissolved in DMF solvent with constant stirring at 60 °C till a homogeneous solution is formed. The sonicated TP and DMF is then poured into the PVDF solution and was kept at similar conditions till a viscous solution is formed which was then dried at 50 °C in air oven to get dried composite film. The air oven dried film was then kept at vacuum oven overnight to discard any traces of the solvent from the film. The developed film is abbreviated as P+TP-x%; where P is the pure PVDF polymer and x denotes the weight fraction of the TP w.r.t the PVDF.

PVDF-Cotton based hybrid preparation: Initially the PVDF is dissolved in presence of DMF as mentioned in section above. The dissolve PVDF is then drop casted over the cotton pad (35 weight percentage w.r.t. PVDF) to form a homogeneously casted PVDF over the cotton. The PVDF-cotton combination is dried at 40 °C in air oven followed by

drying in presence of vacuum. The pure cotton is abbreviated as CTN, while the PVDF-Cotton hybrid is symbolized as P+CTN.

3.3 Results and Analysis

The change in the structure and morphology is an indication of the transformation of the non-polar α -phase to the polar and piezo-active β -phase. The XRD curve shown in **figure 3.1a** shows the characteristic peaks of the pure α -phase at 17.6° (100), 18.3° (020), 19.9° (110) and 26.5° (021) which has been reported in previous literatures [107][108]. On the incorporation of the TP to the PVDF matrix the induction of piezoelectric phase is very minimal which is understood by the retaining of the α -phase peaks with a slight shift. Since TP is an electroactive material as reported in previous study [62], the addition of the TP generates some polarity in the PVDF which is attributed by the crystalline peak at 20.2° (200) which resembles the characteristic peak of the β -phase. Here the contribution of the polar filler is the highlighting point in development of the piezo-active phases. The curve with TP and PVDF shows that the addition of the TP does not transform to polar phase due to the significant presence of the α -phase peaks as seen in the pristine PVDF. On the contrary, CTN based PVDF hybrid shows a remarkable alteration in the structure where the crystalline peak for the β -phase is seen at 20.7° (200) which suggests the induction of the piezoelectric phase through the cellulose dominant cotton pad. A small hump is visible at the 19.2° (110) which represents the presence of the semi-polar γ -phase that further assures the role of induction of electroactive phase to the PVDF matrix [94][113]. The confirmative peak of cellulose is seen at 23.1° which confirms the role of it in the induction of polar phase phenomenon [114]. The epitaxial crystallization of the PVDF over the surface of the

cotton results in higher content of the polar phase which demonstrates the piezoelectric based application of the prepared material.

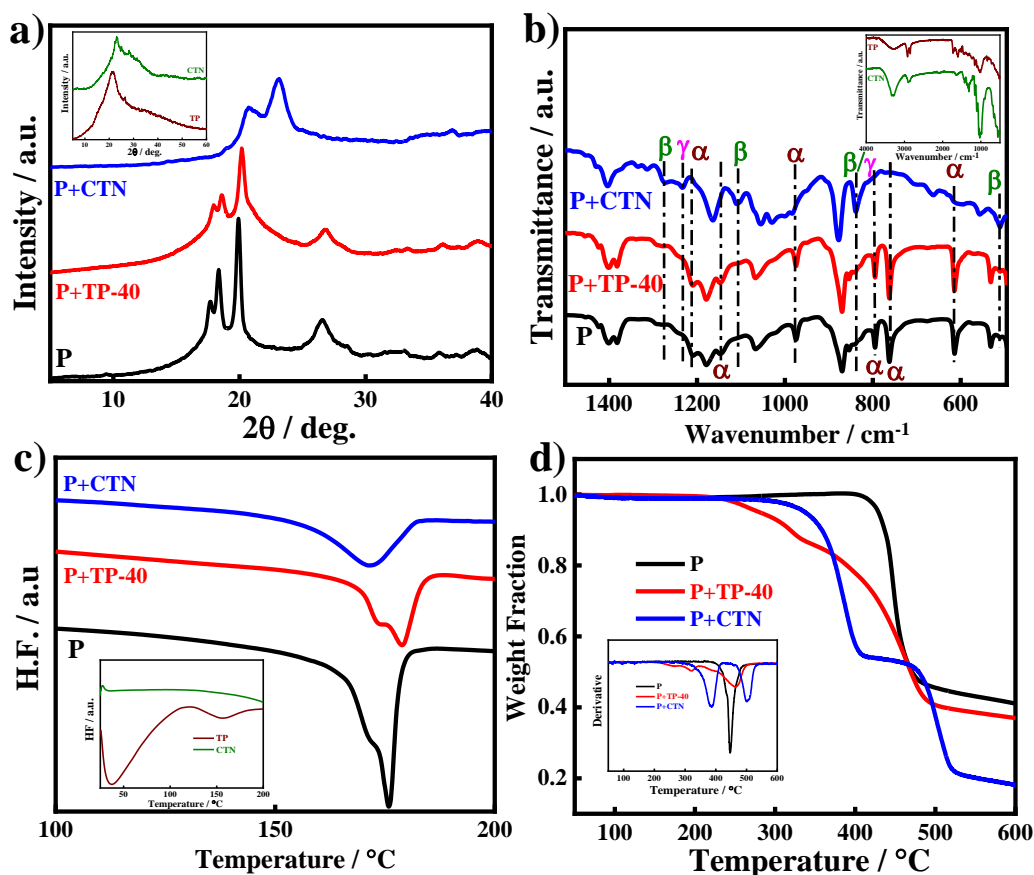


Figure 3.1: a) XRD study of the prepared PVDF hybrids from TP and CTN (inset shows the XRD curve for the CTN and TP); b) FTIR-ATR spectra of the P, P+TP-40 and P+CTN (the FTIR-ATR spectra for the TP and CTN); c) DSC thermograms of the PVDF and its hybrids (inset showing the DSC curve of the CTN and TP) and d) TGA plot of the PVDF and its hybrids (DTG plot of the PVDF and its hybrid).

FTIR-ATR study further affirms the effect of induced piezoelectric phase on the PVDF based hybrids as depicted in the **figure 3.1b**. The pristine PVDF film shows the major

peaks at 615, 760, 795, 975, 1146 and 1210 cm^{-1} which is the main peak of the non-polar α -phase. P+TP-40 shows some variations in the FTIR peaks with some shifting in the wavenumber. For the P+CTN, the intensities of the α -phase peaks gets reduced or diminished and new peaks are seen at 512, 839, 1277 cm^{-1} which signifies the presence of the polar β -phase and the confirmative peak of the γ -phase is seen at the 1231 cm^{-1} which is in accordance with the previous literatures [115] Hence a novel method to impregnate the electroactive phase is being clearly demonstrated from the structural analysis. To further stamp the presence of the polar electroactive phases the thermal study has been carried out which is shown in the **figure 3.1c, d**. **Figure 3.1c** shows the DSC thermogram where the effect of induced crystalline phase is clearly visible. The neat PVDF shows the melting temperature (T_m) at 176 $^{\circ}\text{C}$ which is the melting peak of the α -phase. Two characteristic peaks are seen for the P+TP-40, the initial peak at 173.6 $^{\circ}\text{C}$ is the melting peak for the β -PVDF while the major and intense melting peak at 179.1 $^{\circ}\text{C}$ signifies the presence of α -phase. The lower transformation of the non-polar part to the electroactive part in the TP based film supports the results from the structural characterizations. The T_m for the P+CTN is observed at 171.5 $^{\circ}\text{C}$ which is the primary peak for the polar β -phase. The single melting peak with the shift in the melting point at the lower temperature suggests the induction of the crystalline β -phase which results in the diminution of the non-polar part with transformation to the piezo-active part [96][102].

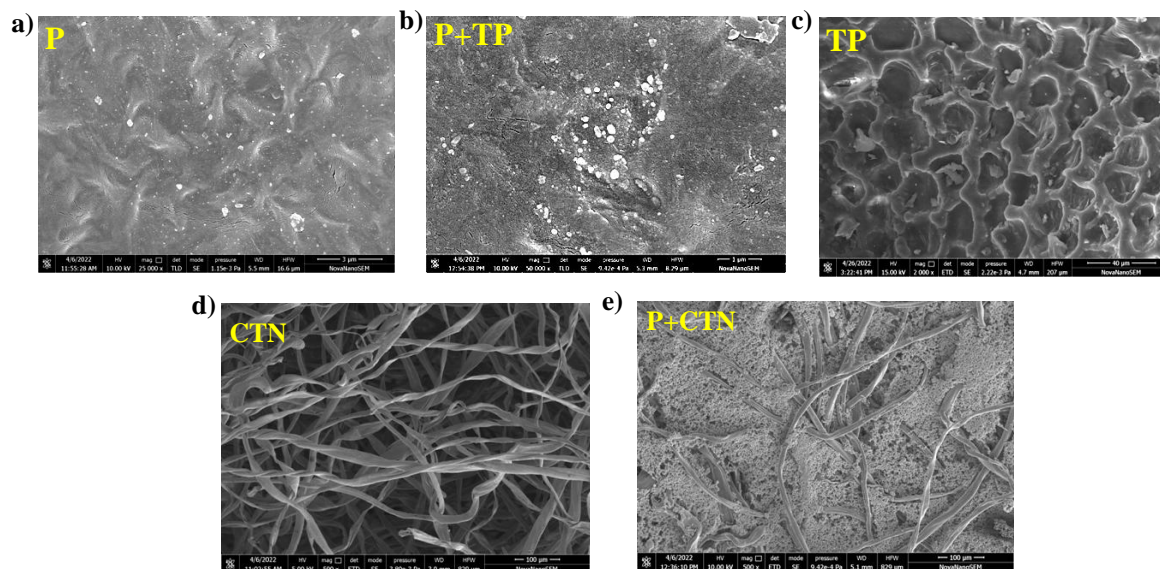


Figure 3.2: FESEM images of the a) pure PVDF film; b) P+TP-40 film; c) TP; d) pure cotton and e) PVDF-CTN hybrid.

The thermogravimetric analysis shown in **figure 3.1d** describes the thermal stability of the prepared hybrids and films. The pure PVDF film shows thermal stability till 400 °C after which the scission of bonds leads to the degradation of the material. When TP is added to the PVDF, the curve show two step degradation, the initial degradation starts at the 318 °C which denotes the cleavage of the functional group of the TP while the second degradation resembles the degradation of the carbon chains of the PVDF. In the case of the P+CTN, about 20-30% of weight loss is seen around 380 °C which is primarily due to the decomposition of the α -cellulose. The second degradation peak is the decomposition of the PVDF polymer which occurs at the higher degradation temperature due to better interaction of the polar cellulosic group with the PVDF. At 600 °C, almost 80 % of the P+CTN get decomposed while the P and P+TP-40 decompose to 60 and 65% respectively [116][117].

The morphological survey of the prepared hybrids and the pristine materials is shown in figure 2. **Figure 3.2a** depicts the morphology of the pure PVDF where the presence of the spherulitic structure is seen prominently which represents the presence of the α -phase. On the addition of the TP to the PVDF matrix, the content of the spherulites gets slightly disrupted but the presence is still persistent which suggests the presence of the α -phase as seen in **figure 3.2b,c**. **Figure 3.2d** shows the morphology of cotton, which possesses the fibrous nature; when PVDF is casted over the cotton pad, polymer gets embedded in between the fibres of the cotton as visible in **figure 3.2e**, which indicates the compatibility and better interactions with cellulosic groups that favors the conversion of the non-polar part to polar phase. Hence from the morphological point of view, the change in the structure is clearly demonstrated and the reason for the induction of the polar phase in presence of the CTN is well understood.

Hence the effect of the induced electroactive phenomenon in the CTN based PVDF hybrid is clearly understood through the structural, thermal and morphological analysis. TP based hybrids does not primarily favour the induction process in PVDF and the changes occurred in the system are due to prominent contribution of the piezoelectric filler. Based on the observations from the Figure 1 and 2, it is now pertinent to evaluate the piezoelectric based analysis to understand the electromechanical response of the fabricated device and its potential as an efficient energy harvester.

The chief component of the cotton is cellulose, which is a linear-chained polysaccharide with the repeating unit of the glucose. These repeating units are joined together through β -1,4-glucosidic bonds having three hydroxyl groups. The presence of the hydroxyl groups develops strong hydrogen bonds which makes the cellulose molecule highly crystalline in

nature. The triclinic and monoclinic structure of the cellulose having no centre of symmetry and the presence of the hydroxyl groups arranged in noncentrosymmetric way develops a net dipole moment in the cellulose which leads to the piezoelectric effect [110][118][119][120]. The major constituent of the tomato consists of lycopene, amino acids, zeaxanthin and lutein.

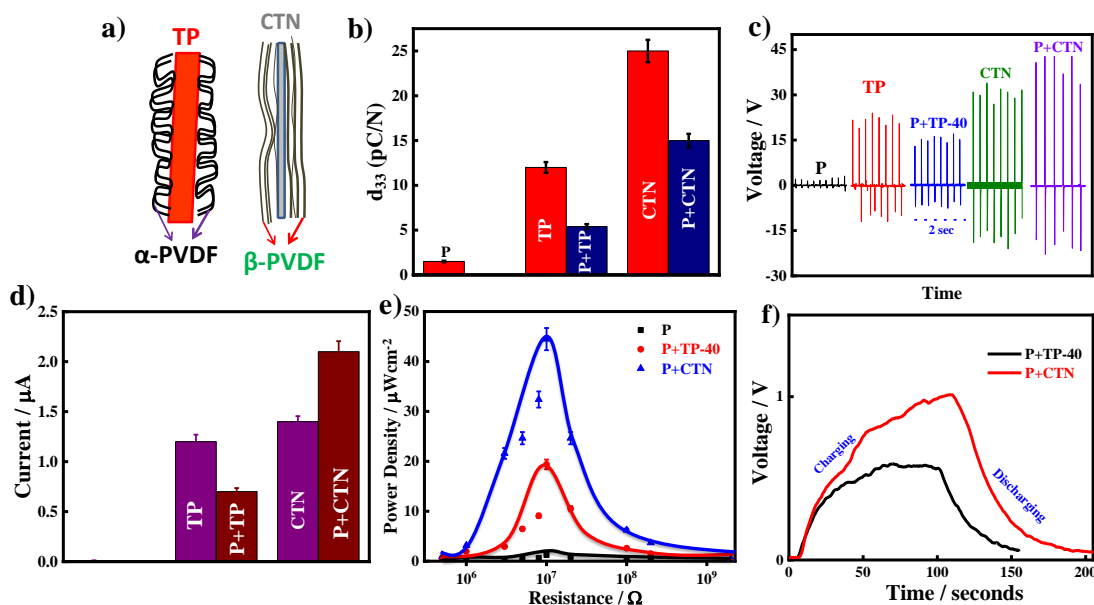


Figure 3.3: a) Schematic representation of the effect of filler addition onto the PVDF matrix; b) piezoelectric coefficient of the prepared PVDF and its hybrids and the fillers; c) output voltage generated through finger tapping mode on to the prepared device from PVDF, TP, P+TP-40, CTN and PVDF+CTN; d) output current obtained from the finger tapping on to the prepared samples as indicated on the bar; e) power density vs. resistance plot for the prepared device; f) charging – discharging plot of the device prepared from P+TP-40 and P+CTN for 2.2 μ F capacitor.

The monoclinic and low symmetrical orthorhombic space group present in the TP leads to the noncentrosymmetric features in the material. Also the presence of the electropositive hydrogen atoms and the electronegative oxygen atoms results in the hydrogen bonding that leads to piezoelectricity in the TP [62][121][122]. Hence it is conclusive that both the TP and CTN both have the piezoelectric property and hence addition of these into the PVDF results in enhanced piezoelectric response. But only addition of the piezoelectric filler does not enable to have high electrochemical response, another important factor is the induction of piezoelectric phase in the PVDF. PVDF being primarily non-polar in character but the highlighting characteristic of the polymer is the ability to get transformed into piezo-active phases (β and γ). The major contribution of the electroactive filler is the induction of the polar phase in the PVDF which makes it advanced material in the field of energy harvesting. **Figure 3.3a** depicts the schematic representation of the nucleation of the filler over the PVDF. The CTN crystallizes over the PVDF generating polar phase while the TP nucleates to the polar phase in relatively lower content that leads to lower piezoelectric phase. The piezoelectric coefficient (d_{33}) of the prepared samples is represented in the form of bar diagram in the **figure 3.3b**. The maximum d_{33} value obtained for the P, P+TP-40 and P+CTN is around 1.5, 5.4 and 15 pC / N respectively. The d_{33} value for the TP film (tomato skin) and the CTN is around 12 and 25 pC/N. Being a piezoelectric material, the TP and CTN shows high d_{33} value but when embedded into the PVDF the piezoelectric coefficient value gets lower which can be due to the non-piezoelectric property of the pristine PVDF. The content of the TP into the PVDF is 40%, hence from the obtained d_{33} value of the pristine TP which is 12 pC / N, the expected d_{33} for P+TP 40% should be 4.8 pC/N and from the obtained value of d_{33} is around 5.4 pC/N which supports the calculative

description and the rise in the piezoelectric coefficient value for the P+TP-40 is due to contribution of the TP and somewhat content of the polar phase generation as seen from the XRD study. Similarly for the CTN, the obtained piezoelectric coefficient value is 25 pC / N and that for P+CTN is 15 pC / N. The content of the CTN is 35% and thus the contribution of the CTN in P+CTN scaffold should be 8.75 pC / N but the obtained value for the P+CTN is 15 pC / N which is almost twice the expected contribution of the CTN. The rise in the d_{33} value can be attributed to the induced piezoelectric phase in presence of the CTN which enhances the electroactive content of the hybrid as evident from the structural changes in the **figure 1**. To quantify the induction of the piezoelectric phase through the electroactive filler is demonstrated in the **figure 3.3c-e**. The prepared scaffold is designed to a device form which is then subjected to external stress and is analysed for the electromechanical response. When an external pressure is applied to a piezoelectric energy harvester, there occurs a change in the crystal structure due to the deformation which leads to the alignment of the dipoles resulting in a net dipole moment into the system. On application of the external stress through different modes to the piezoelectric device, the load gets distributed over the material and the charge separation phenomenon takes place. When stress is applied and released to the device, a potential difference is created which leads to flow of charges across the electrodes and hence an output signal is received due to the electromechanical response [3][123]. The maximum output voltage (peak-to-peak) generated through finger tapping mode for the P, TP film, P+TP-40, CTN and P+CTN is 2.2, 35, 23, 50, and 65 V respectively as shown in the **figure 3.3c**. Zhang et.al [124] developed a paper based nanogenerator using barium titanate and bacterial cellulose and obtained open circuit voltage of 14 V. The finger tapping mode is chosen as a way to

demonstrate the practical applicability and efficacy of the device to generate a response on variable load which is evident from the non-uniform signal for the output voltage. The output voltage for the P+CTN is higher as compared to the TP and its PVDF based hybrids. On the similar note, the output current produced from the finger tapping mode is higher in case of P+CTN as visualised in the **figure 3.3d**. The maximum output current for P, TP film, P+TP-40, CTN and P+CTN is nearly 0.01, 1.2, 0.7, 1.4 and 2.1 μA respectively. The power density calculated across the variable resistance is depicted in the **figure 3e**. The equation used to evaluate the power density is:

$$\mathbf{P} = \mathbf{V}_m^2 / (\mathbf{R} \times \mathbf{A}_d) \quad (3.1)$$

where, P is the power density across the material, V_m is the maximum output voltage, R is the load resistance across which the output voltage is measured and A_d is the active area. The maximum power density for the P, P+TP-40 and P+CTN is 1.2, 19.8 and 44.7 μWcm^{-2} respectively. In a recent work, Wang et.al. [125] prepared a device from cotton cellulose interfaced maleic-anhydride-grafted PVDF and obtained maximum power density of 1.72 μWcm^{-2} . To further exhibit the efficacy of the developed material, the fabricated device is subjected to external stress and is analysed for its storage capabilities as revealed in the **figure 3.3f**. The maximum output voltage stored in the 2.2 μF capacitor for P+TP-40 and P+CTN is 0.6 V and 1.1 V respectively. When an external stress is applied onto the device, the energy stored in the capacitor is in the form of the generated output voltage which is measured through a bridge rectifier circuit. When no external pressure is applied onto the device, discharging phenomenon takes place [126][65]. Hence it is confirmed that the prepared cotton based PVDF hybrid has better electromechanical and storage properties which is attributed to the better induction of the piezoelectric phase in the material.

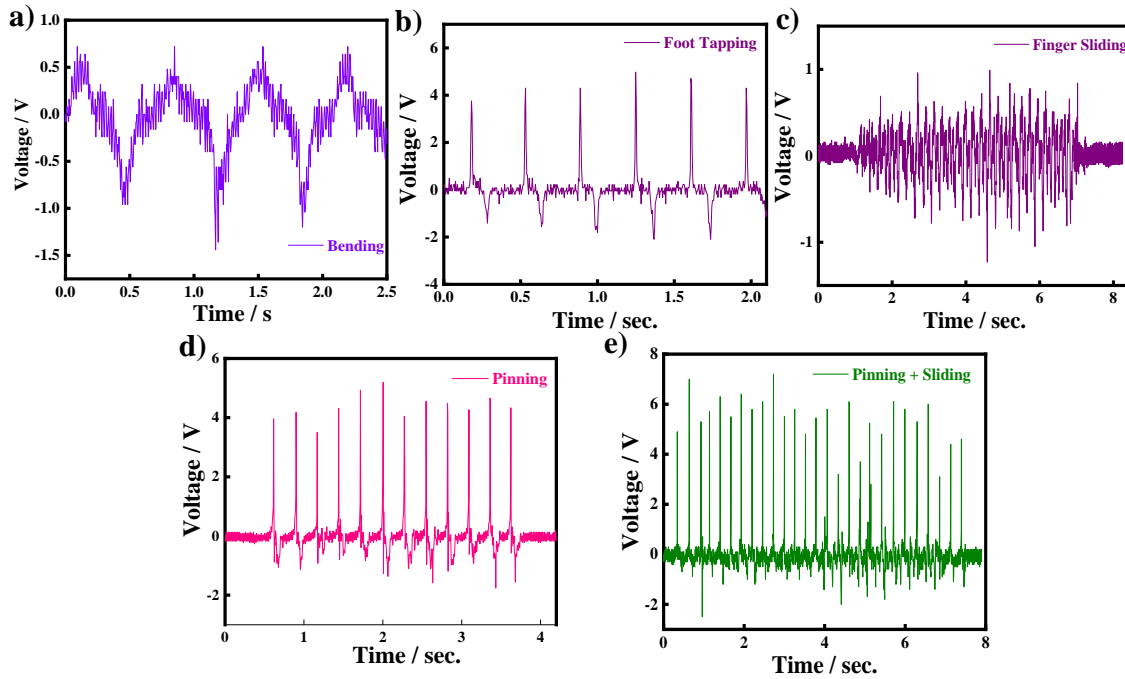


Figure 3.4: The output voltage generated from different motions namely a) bending; b) foot tapping; c) finger sliding; d) pinning with glass rods and e) pinning and sliding.

The changes in the structure and the piezoelectric coefficient support the rise in the output voltage and hence the effect of the induced piezoelectricity is well aligned with these electromechanical responses. The designed device (P+CTN) is further used to measure the output against different human motions like bending through fingers of palm and foot tapping as shown in **figure 3.4a-b**. The maximum output voltage (peak-to-peak) generated through the bending of the device is around 2 V and through foot tapping is nearly 7.1 V. The piezoelectric device prepared should be able to convert any kind of external stress applied over it. The fabricated device is subjected to the external stress in the form of sliding with the finger (**figure 3.4c**) and pinning with glass rods (**figure 3.4d**) which generated highest voltage (peak-to-peak) of ~2 V and ~ 6.5 V respectively. The repeated

application of stress over the device did not generate any cracks which explain the stability of the fabricated device. The tribological force or mechanisms lead to substantial rise in the output voltage. When the external pressure is provided in combination of sliding and pinning as shown in **figure 3.4e**, it results in the maximum output voltage of ~ 9.1 V, which is higher as compared to the individual modes. Thus the device possess the ability to generate considerable amount of electromechanical response through different kind of external mechanical stress, which suggests the efficacy and the potential of the material to be used as sustainable green energy harvester that can be a small contribution towards the alternate energy fulfilling future energy demands.

3.4 Conclusions

A novel approach to induce the piezoelectric phase in the PVDF based hybrids is being demonstrated in presence of bio-based fillers. Natural piezoelectric materials cotton and tomato peel are used with PVDF and their role in induction of polar phase is studied. The contribution of the electroactive content is higher in presence of cotton as compared to the tomato peel based hybrids which is confirmed with the structural and thermal analysis. The developed materials are formed to a device form which is then analysed to understand the electromechanical response. The induction of higher piezoelectric content in P+CTN results in better piezoelectric coefficients, output voltage, current and power density which aligns with the structural and thermal studies. The device is then subjected to different mode of external stress which generates considerable amount of output voltage and is able to store charge through external pressure which suggests the potential of the material as a sustainable energy harvester.