UNVEILING THE ROLE OF PVDF AND ITS COPOLYMER ON THE OUTPUT PERFORMANCE OF THE PIEZOELECTRIC NANOGENERATOR

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Submitted by:

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CANDIDATE'S DECLARATION

We ALOK YADAV and DIBYAJYOTI GIRI, Roll No(s). 2K22/MSCPHY/02 and 2K22/MSCPHY/10 student(s) of M.Sc. (Physics), hereby declare that the project Dissertation titled "Unveiling the Role of PVDF and its Copolymer on the Output Performance of the Piezoelectric nanogenerator" which is submitted by us to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master's in Physics is original and not copied from any source without proper citation. This work has not previously formed the basis for awarding any Degree, Diploma Associateship, Fellowship, or other similar title or recognition.

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This is to certify that the student has incorporated all the corrections suggested by the examiners in the thesis and that the statement made by the candidate is correct to the best of our knowledge.

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CERTIFICATE

I hereby certify that the Project Dissertation titled "Revealing the Impact of PVDF and its Copolymer on the piezoelectric nanogenerator's Output Performance" which is submitted by DIBYAJYOTI GIRI, Roll No. (s) 2K22/MSCPHY/10 and ALOK YADAV, 2K22/MSCPHY/02, Department of Applied Physics, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the students under my supervision. To the best of my knowledge, this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi **Dr. BHARTI SINGH**

Date: 07/06/2024 **SUPERVISOR**

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ABSTRACT

Herein, we have systematically investigated the impact of polyvinylidene fluoride (PVDF) and its copolymer on the piezoelectric properties of the nanogenerator. For this, PVDF, polyvinylidene fluoride-cotrifluoroethylene (PVDF-TrFE), and polyvinylidene fluoride-cohexafluoropropylene (PVDF-HFP) films were synthesized by drop casting method, and their piezoelectric response was analyzed. The experimental results show that the PVDF-TrFE films-based nanogenerator outperforms all other fabricated nanogenerators in terms of piezoelectric performance. In comparison to other polymers, PVDF-TrFE has a maximum output voltage (V_{OC}) and short circuit current (I_{SC}) of 23.6 V and 3.7 μA, respectively. This enhanced performance of PVDF-TrFE-based PENG is attributed to the highest β-phase in comparison to PVDF and PVDF-HFP. For potential application, the PVDF-TrFE film-based PENG was demonstrated to harvest energy from the human body movements, and the energy is also stored by charging a 1μF capacitor. This study contributes to the fundamental understanding of PVDF-based materials for mechanical energy harvesting applications, thereby, paving the way for advancements in self-powered systems.

Keyword: - PVDF-TrFE; PVDF and its copolymers; Piezoelectricity; Nanogenerator; Energy Harvesting

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LIST OF SYMBOLS AND ABBREVIATIONS

EH	Energy Harvesting
2-D	2-dimensional
DI water	Deionised water
DMF	N, N dimethyl formamide
PENGs	Piezoelectric Nanogenerators
PVDF	Polyvinylidene fluoride
PVDF-HFP	polyvinylidene fluoride-cohexafluoropropylene
PVDF-TrFE	polyvinylidene fluoride-cotrifluoroethylene
XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared
V_{OC}	Open circuit Voltage
I_{SC}	Short circuit Current

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1. INTRODUCTION

Human invention and progress are frequently responsible for the rapid advancement of technology. The idea of nanotechnology was introduced to us by that improvement. Nanotechnology is the study of materials with dimensions ranging from 1 to 100 nm. The scientist who won the 1965 Nobel Prize in physics, Richard Feynman, is credited with creating modern nanotechnology. In a 1959 American Physical Society meeting at Caltech, he first proposed the idea of manipulating matter at an atomic level, when he gave a paper titled "There's Plenty of Room at the Bottom". The term "nanotechnology" was first used in 1974 by University of Tokyo researcher Norio Taniguchi to refer to the ability to create materials at the nanoscale size precisely[1].

In around 50 years, nanotechnology has grown to become the foundation for incredible industrial applications and exponential growth[1]. Because of their special structure, nanoparticles can have remarkably large surface areas. Nanostructures are very different from their bulk counterparts in these aspects and can exhibit exceptional optical, mechanical, electrical, catalytic, and magnetic properties. The properties of nanomaterials can be precisely tailored to meet particular needs by carefully controlling their size, shape, synthesis conditions, and appropriate functionalization[2].

In recent years, with technological advancement, there is an upsurge in the usage of wearable, portable electronics which has led to an increase in energy demand [3, 4]. Till now, batteries are used to provide power to these electronic devices but due to their bulky nature and, limited life span, it is difficult to incorporate them into wearable technology [5, 6]. Thus, there is an urgent demand for designing self-powered devices that are compact, lightweight, and environmentally friendly [7, 8]. One of the possible ways to do so is to harness the energy from the ambient source of the energy present in our surroundings such as solar, thermal, mechanical energy, etc. Among all sources of energy mechanical energy is of utmost importance because of its ubiquitous nature which is present in the environment in several forms. Piezoelectric nanogenerators (PENG) are devices that can transform mechanical energy with good power density into electrical energy for self-powered power sources in various settings for which we require piezoelectric materials [9, 10]. In this context, several piezoelectric materials have been explored, such as, ZnO, rGO, MoS_2, SnS_2 etc [11, 12]. Among the various piezoelectric polymer materials, PVDF is one of the most explored piezoelectric polymer materials owing to its excellent piezoelectric properties, ferroelectric, low density, flexibility, and thermal stability [13, 14]. PVDF is a semi-crystalline structured polymer comprising of -(CH_2-CF_2)- repeating units. It has a regular structure and can display five various crystalline forms: α, β, γ, δ, and ε, with the α-, β-, and γ-phases being the most commonly researched [15, 16]. In PVDF α-phase is non-polar, whereas β-phase is polar. Therefore, increasing the content of β-phase in the PVDF matrix is crucial to boosting PVDF's piezoelectric ability. Furthermore, polyvinylidene fluoride-hexafluoropropylene (P(VDF-HFP)) has a comparatively higher piezoelectric response than PVDF (but your perforce is low in comparison to

PVDF). Adding HFP components in the P(VDF-HFP) copolymer greatly improves the mechanical flexibility of the materials [17]. For example, the traditional PVDF film has an elastic modulus of about 2200-2600 Mpa, thus it only has an inverse piezoelectric coefficient of about 25 pm/V, while the elastic modulus of copolymer PVDF-HFP film is 360-440 MPa, and the inverse piezoelectric coefficient is also much higher than that of PVDF [18]. In addition, the trifluoroethylene (TrFE) monomer was added to the PVDF chain segment in 1979 to create the binary copolymer polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE). Several fluorine atoms are incorporated by P(VDF-TrFE), whose van der Waals force atomic radius is larger than that of H atoms. As such, when the content of TrFE exceeds a certain amount, -CHF-CF_2 - and -CH_2 -CF_2 -, the rotation barrier between block polymer TGTG,' is formed within the molecular chain structure, which is beneficial for the β-crystal phase [19, 20]. Several studies have been done on flexible PVDF-based PENGs. The majority of them focused on improving the piezoelectricity of flexible PVDF-based PENGs. Investigations have been conducted on the impact of various manufacturing techniques on flexible PVDF-based PENGs. For example, melt spinning, solution spinning, electrospinning[21, 22], and 3D printing[23].

Herein, we have studied flexible piezoelectric nanogenerators based on PVDF, PVDF-HFP, and PVDF-TrFE films. The application of PVDF and its copolymer films in nanogenerator systems is highlighted to specify the perspectives of PVDF, PVDF-HFP, and PVDF-TrFE films in the advancement of flexible and wearable technologies. The electric performance of the fabricated PENG devices with PVDF and its copolymer flexible films has been obtained by periodic tapping of the nanogenerator using an electrodynamic shaker. The experimental results show that the PVDF-TrFE

films-based nanogenerator outperforms all other fabricated nanogenerators in terms of piezoelectric performance. In comparison to other polymers, PVDF-TrFE has a maximum V_{OC} and I_{SC} of 23.6 V and 3.7 μA respectively, the maximum V_{OC} is 1.5 times more in PVDF-TrFE as compared to PVDF and twice as compared in PVDF-HFP (at a frequency of 7 Hz). Moreover, experiments were carried out that combined PENGs with human activity to study the device's capacity to gather and transform various types of mechanical energy.

1.2. LITERATURE REVIEW

1.2.1. Energy Harvesting

The limited supply of energy in today's world limits human and economic advancement. Investigating clean and sustainable energy sources should be one of the main approaches to this problem. Furthermore, carbon emissions from renewable energy sources, such as solar or mechanical power, do not contribute to global warming or environmental degradation and only very slightly do so. There's always more energy than we could ever need in the ecosystem, yet it gets “wasted”[24]. Due to its ability to transform mechanical energy from the environment into usable electrical energy, piezoelectric nanogenerators have garnered a lot of attention lately. So far, a variety of piezoelectric materials have been studied, such as BaTiO3, ZnO, PZT, etc[25].

Energy harvester architecture: Energy harvester architecture is classified into two classes:

I. Harvest-use (just-in-time) architecture: An operational model where resources, data, or components are collected and utilized precisely when required, ensuring efficiency and minimizing waste. This architecture supports real-time processing, reduces storage needs, and improves responsiveness to changing demands.

II. Harvest-store-use architecture: An operational model where resources, data, or components are collected and stored for future use, ensuring availability and stability in operations. This architecture supports strategic planning, inventory management, and consistent supply, balancing the need for readiness with the costs associated with storage.

1.2.2. Energy Harvesting Techniques

The following are some of the most frequent energy-harvesting techniques:

- Piezoelectric Energy Harvesting
- Triboelectric Energy Harvesting
- Pyroelectric Energy Harvesting
- Photovoltaic Energy Harvesting
- Thermoelectric Energy Harvesting
- Electromagnetic Energy Harvesting

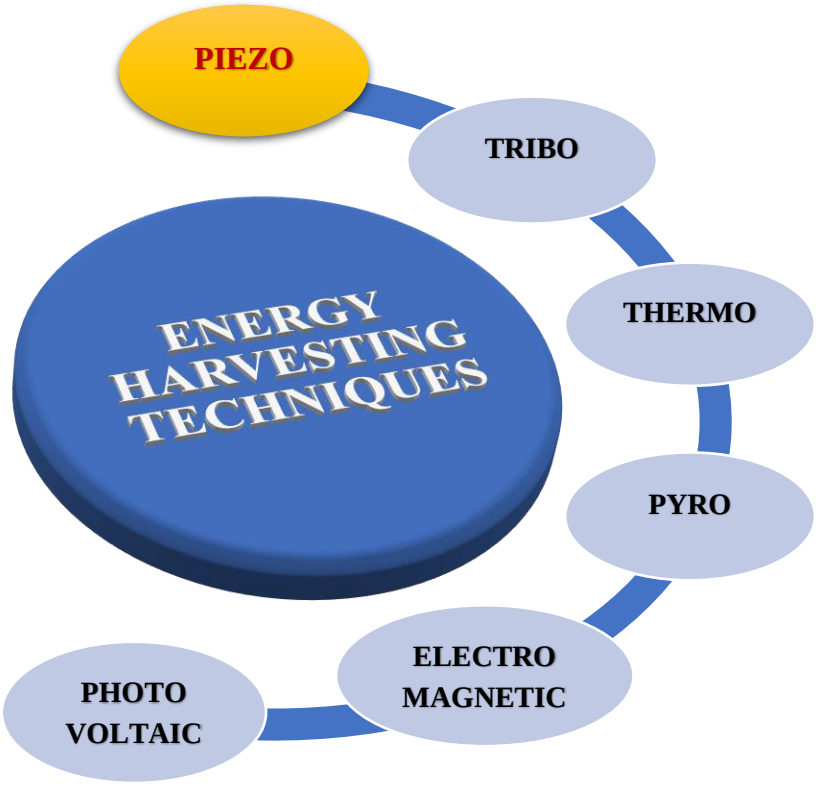

Figure 1.1: Energy Harvesting Techniques

1.2.3. Piezoelectric Nanogenerators (PENGs)

In the past 10 years, there has been substantial advancement in devices that rely on functioning piezoelectric materials, including piezoelectric and sensing devices. Piezoelectric nanogenerators are new devices being created using nanometre-scale piezoelectric materials. PENGs can transform available mechanical energy into useful electrical energy. Compared to chemical batteries, they are more environmentally friendly and able to provide a reasonable amount of electrical energy. They are therefore seen to be promising options for applications in renewable energy[26].

1.2.4. Working principle of PENGs

Even though they are not symmetrically distributed, the charges in a piezoelectric crystal are often perfectly balanced. Piezoelectricity is the process of creating a voltage between two opposing sides of a crystal by applying pressure on it.

- The piezoelectric material undergoes structural deformation when an external force is applied to it. The material's charge centres are displaced by the deformation. The polarization caused by this displacement produces an electric field inside the nanostructure.
- When the material is stretching, the portion of the structure that is under positive strain will display a positive electrical potential; conversely, when a material is compressed, the portion that is under negative strain will display a negative electrical potential.
- When the piezoelectric material is subjected to an external load, such as a circuit, electrons start to flow out of it to create a new equilibrium. What we know as an electric current is this movement of electrons[27].
- The tiny, wirelessly autonomous devices, like wearable electronics and wireless sensor networks, can then be powered by the electric current produced.

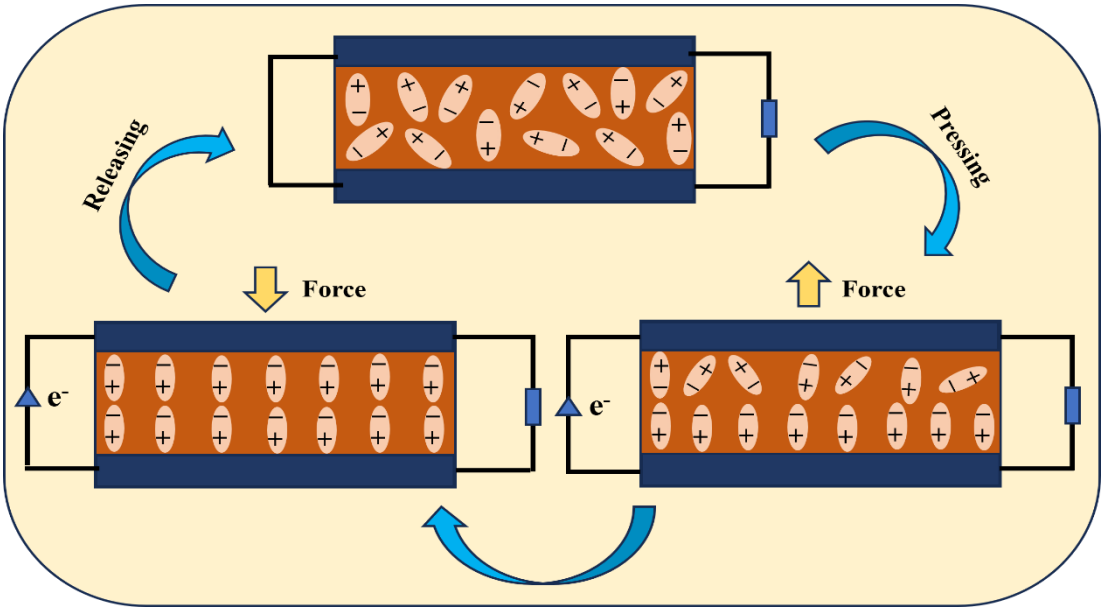

Figure 1.2. Piezoelectric Nanogenerators

1.2.5. Advantage of Piezoelectric Nanogenerators (PNs)

For the purpose of transforming mechanical energy into electrical energy, PENGs are a promising nano power source.

- Mechanical vibrations, pressure, or strain can be effectively converted into electrical energy using PENGs.
- The effective harvesting of energy from the surroundings is guaranteed by their high efficiency.
- PENGs may be fabricated without the need for costly materials or intricate procedures. They are appropriate for widespread adoption due to their reasonable cost.
- PENGs minimize their negative effects on the environment and depend less on batteries because they run without the need for external power sources.

1.2.6. Disadvantage of Piezoelectric Nanogenerators (PNs)

Although piezoelectric nanogenerators have the ability to harvest energy, they do have significant drawbacks:

- Piezoelectric nanogenerators typically have a lower output current than electromagnetic micro-power generators.
- The output impedance is likewise higher with them.
- A higher power density is required for piezoelectric energy harvesters because they usually produce low-power outputs.

1.3. Polyvinylidene Fluoride (PVDF) and its copolymer

Recently, there has been a lot of interest in piezoelectric polymers, including polyvinylidene fluoride (PVDF) and its copolymers, hexafluoropropylene (HFP), trifluoroethylene (TrFE), bromotrifluoroethylene (BTFE), and chlorotrifluoroethylene (CTFE). Of these, TrFE has gotten the most attention[28]. A higher level of crystallinity in the copolymer unit cells leads to a stronger piezoelectric response, even though the unit cells of the copolymers are less polar than those of pure PVDF. Thus, in piezoelectric applications, copolymers are made[29]. When pressure or mechanical stress is applied, the non-toxic, flexible, and reasonably priced polymer polyvinylidene fluoride (PVDF) exhibits a piezoelectric effect. PVDF polymer has four unique crystalline phases: α, β, γ, and δ. These phases may be interconverted with the application of pressure, heat, and an electrical field. In terms of thermodynamics, the α-phase is the most stable and non-polar phase, while the β and γ phases are polar phases. Polar PVDF is used in electronics, sensors, actuators, and other applications to

gather energy. The β phase is the most significant of all the crystalline phases because of its increased polarization and piezoelectric sensitivity[30]. Owing to this characteristic, several attempts have been undertaken to improve the β phase of PVDF's thermal, mechanical, and chemical characteristics[31]. PVDF has strong film-forming qualities that make it equivalent to applications for nanogenerators. Nevertheless, pure PVDF produces very little electrical energy in real-world applications. They so require certain procedures like poling and the addition of filler materials, among others. The primary reasons we think about introducing nanofiller materials are their many benefits, which include reduced costs, easier production, and higher electrical output.

CHAPTER - 2

MATERIALS AND METHODS

2.1. Materials

Polyvinylidene fluoride (PVDF) powder (Alfa Aesar, CAS: 24937-79-7, molecular weight: 64.012456 g/mol), Polyvinylidene fluoride-trifluoro-ethylene (PVDF-TrFE), Polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) are procured from sigma Aldrich and we purchased N, N dimethyl formamide (DMF) from Fisher.

2.2. Preparation of thin films

We have prepared thin films of PVDF and its copolymer (such as PVDF-TrFE, PVDF-HFP), by using 1g of PVDF and 1g of PVDF-TrFE powder by dissolving separately in 10 ml of DMF. After that, the solutions were stirred continuously for 30-40 minutes over a magnetic stirrer at room temperature. Further, to make the solution of PVDF-HFP, 1g of PVDF-HFP material was dissolved in 10 ml of DMF, and magnetic stirred at a temperature of 55ºC for 3 hours to prepare a solution. Then, all three solutions were separately dropped onto a glass substrate by using the drop-casting method through a micropipette and are put into the oven at 70º C for 2 hours. After the natural cooling down of the oven, films were taken out from the oven and immersed in DI water to get freestanding films. Thus, we finally obtain the thin films of PVDF and its copolymers.

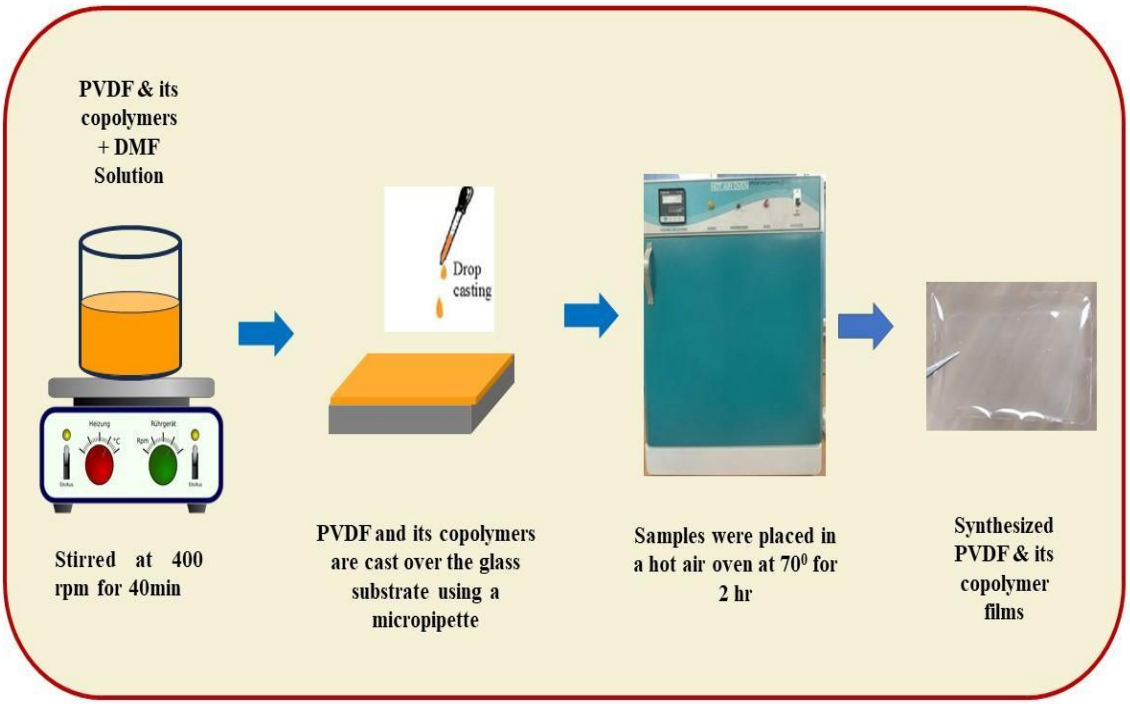

Figure 2: Schematic fabrication process of PVDF films

2.3. Fabrication of PENG

PVDF and its copolymer films were used to create the PENG devices. For this initially, the films were cut into the requisite shape and the aluminium tapes were attached on both sides of the films as an electrode. Then, for the external connection, two copper wires are pulled from top and bottom aluminium electrode surfaces, and lastly, the complete apparatus is encapsulated with Kapton tape.

CHAPTER - 3

CHARACTERIZATION AND RESULTS

3.1. Characterization Techniques

Firstly, the crystallinity of the prepared PVDF, PVDF-HFP, and PVDF-TrFE films has been studied using an X-ray diffractometer (Rigaku, Ultima-IV) in thin film mode, using a Cu K_α radiation source (1.54 Å). The β-phase content of thin films has been studied using PerkinElmer FTIR (Fourier Transform Infrared) Spectroscopy spectrum-II. Using a Marine India P-E loop tracer, the P-E loops of thin films were obtained at an applied voltage of as high as 80 kV/cm. The dielectric measurements were performed in the frequency range of 20 to 10^4 Hz using an LCR meter. The synthesized films, which had a thickness of around 100 μm, had been placed between Al electrodes to create nanogenerators. Finally, an electrodynamic shaker (Micron MEV-0025) was utilized to apply an external force to the nanogenerator using the functional generator (Micron MPA-0200) at various frequencies to record the piezoelectric response. An oscilloscope (Tektronix MDO34) was used to measure the (V_{oc}), and a Keithley digital multimeter (Keithley DMM7510) was used for measuring the (I_{sc}).

3.2. Results and Discussion

3.2.1. XRD

The crystallinity of the prepared PVDF, PVDF-HFP, and PVDF-TrFE films has been studied using an X-ray diffractometer (Rigaku, Ultima-IV) in thin film mode, using a Cu K_α radiation source (1.54 Å) in scattering range (2θ) of 10-80° at room temperature. Deposited PVDF film has both an alpha phase that is non-polar and an electroactive

beta phase, this is due to the alignment of the fluorine atoms in a regular pattern relative to the core of the polymer chain. The alpha phase shows an XRD peak of around 17.6° and the corresponding plane is (100), whereas the beta phase shows a peak of around 20.5°, but two planes have been assigned together for this peak position i.e. 110/200 planes. The figure shows the XRD pattern for PVDF, PVDF-TrFE, and PVDF-HCP showing two standard characteristic peaks located at 17.57° and other at 20.14° corresponding to the non-polar α-phase and electroactive β-phase, respectively. The intensity of the electroactive β-phase is highest for PVDF-TrFE.

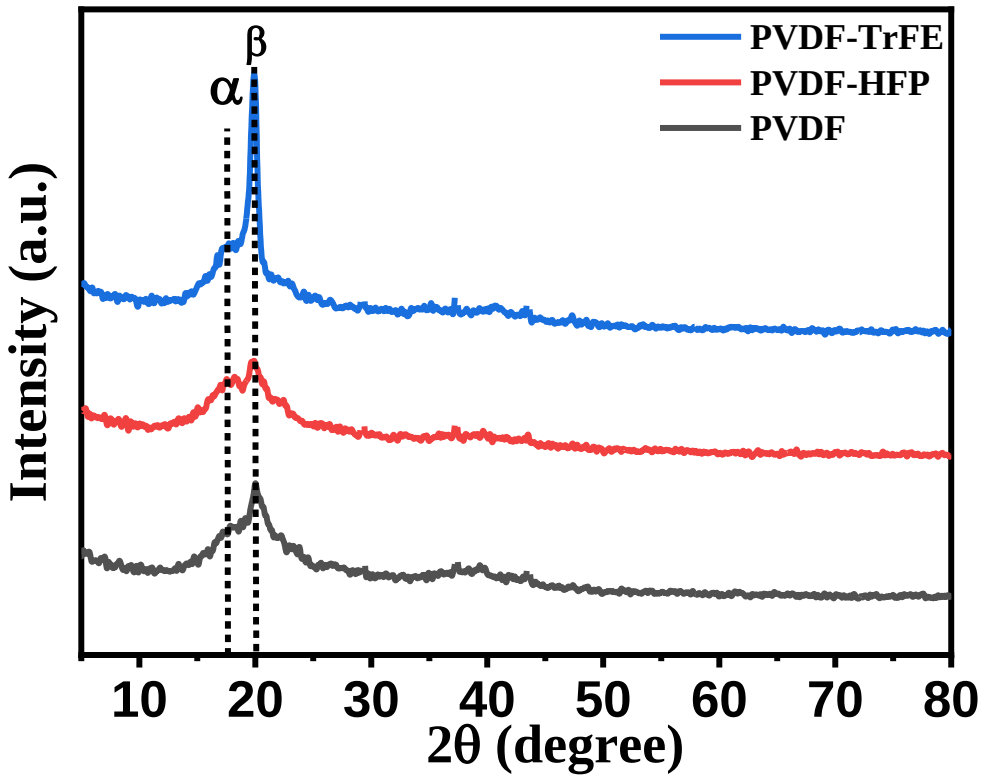

Figure 3.1. XRD Pattern of PVDF and its Copolymers

3.2.2. FTIR analysis of thin films

Figure 3.2 shows FTIR absorption spectra of the synthesized thin films, which are utilized to determine the PVDF-based thin film β-phase percentage. The peaks at 840, 1278, and 1400 cm^{-1} correspond to the polar β-phase of the PVDF. The α-phase is associated with the peaks at 762, 795, 974, and 1382 cm^{-1}. The equation may be utilized to determine the relative content of β-phase by the application of the Lambert-Beer law[15, 32-34].

$$F(\beta) = \frac{A_\beta}{(k_\beta/k_\alpha)\times A_\alpha + A_\beta} \times 100\ \%$$

Where, $K_\alpha = 6.1\times10^4$ cm^2/mol is the absorption coefficient at ~762cm^{-1}, $K_\beta = 7.7\times10^4$ cm^2/mol is the absorption coefficient at ~840 cm^{-1},[35] The calculated β-phase content was observed to be 61% for bare PVDF, 58% for PVDF-HFP, and 71% for PVDF-TrFE. All the above results indicate that beta-phase is present in all copolymers and FTIR studies also complement the XRD results, where PVDF-TrFE is enriched with an electroactive phase.

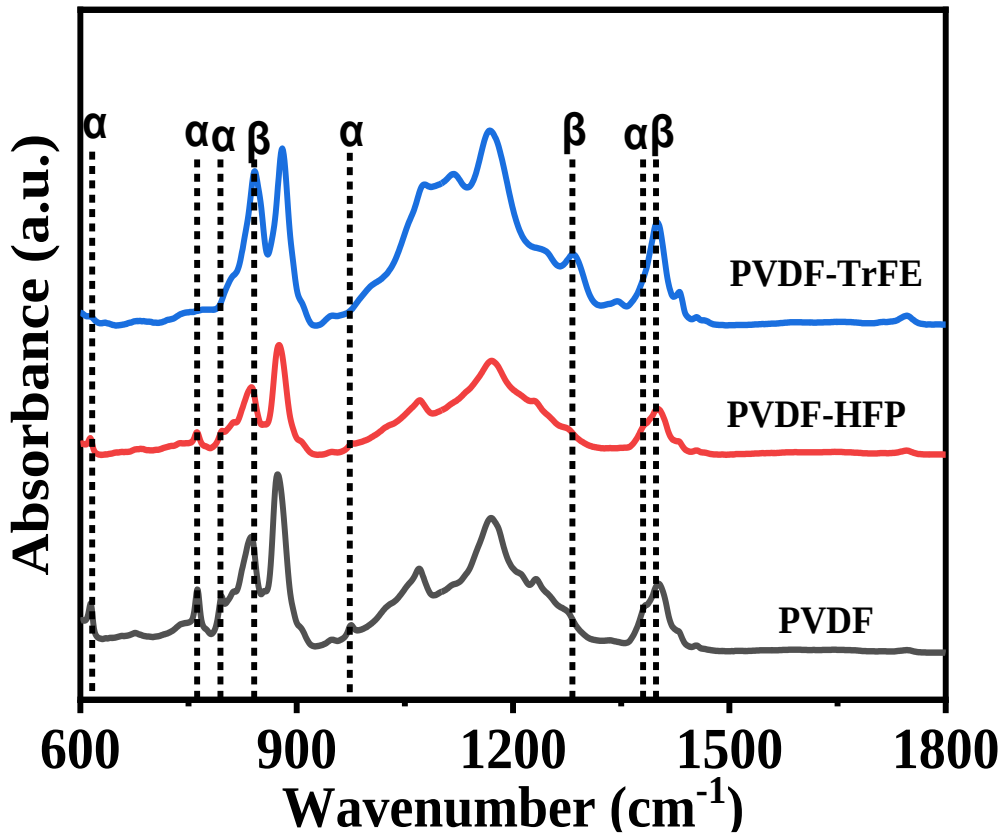

Figure 3.2. FTIR Analysis of PVDF and its copolymers

3.2.3. P-E loop analysis

Measurements of PVDF and its co-polymer films polarisation versus electric field (P-E) are done to investigate the ferroelectric characteristics of PVDF, PVDF-TrFE, and PVDF-HFP, as shown in Figure 3.3. The findings of the P-E measurement confirm that PVDF and its copolymers exhibit ferroelectric behaviour. The remanent polarisation (Pr) for PVDF, PVDF-TrFE, and PVDF-HFP are 0.093, 0.102, and 0.034μC/cm^{-2}, respectively.

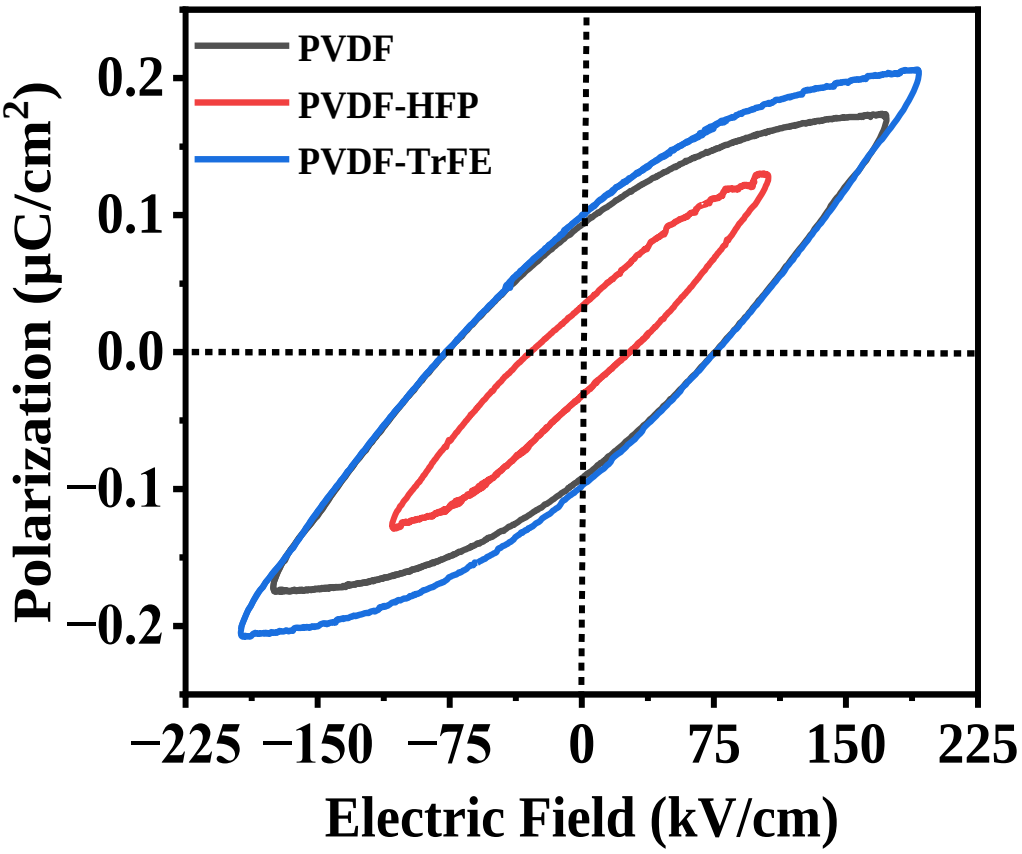

Figure 3.3. P-E Loop Polarisation of PVDF and its copolymer films

3.2.4. Dielectric Measurement

The dielectric constant measurement of PVDF and its copolymer films is given in Figure 3.4. Dielectric measurements of PVDF (Polyvinylidene fluoride) and its copolymer films are important in understanding their electrical properties and their potential applications in various electronic devices. Dielectric measurements involve studying the material's reaction to an applied electric field. PVDF and its copolymers display intriguing dielectric characteristics because of their polar nature. Here are some of the key points that dielectric measurements of PVDF and its copolymer films may

reveal: Dielectric Constant, Dielectric Loss, Ferroelectric Properties, and Temperature Dependence. The graph shows a noticeable increase in the dielectric coefficient values from PVDF, PVDF-TrFE, and PVDF-HFP have dielectric constant values of 3.12, 3.77, and 2.44, respectively.

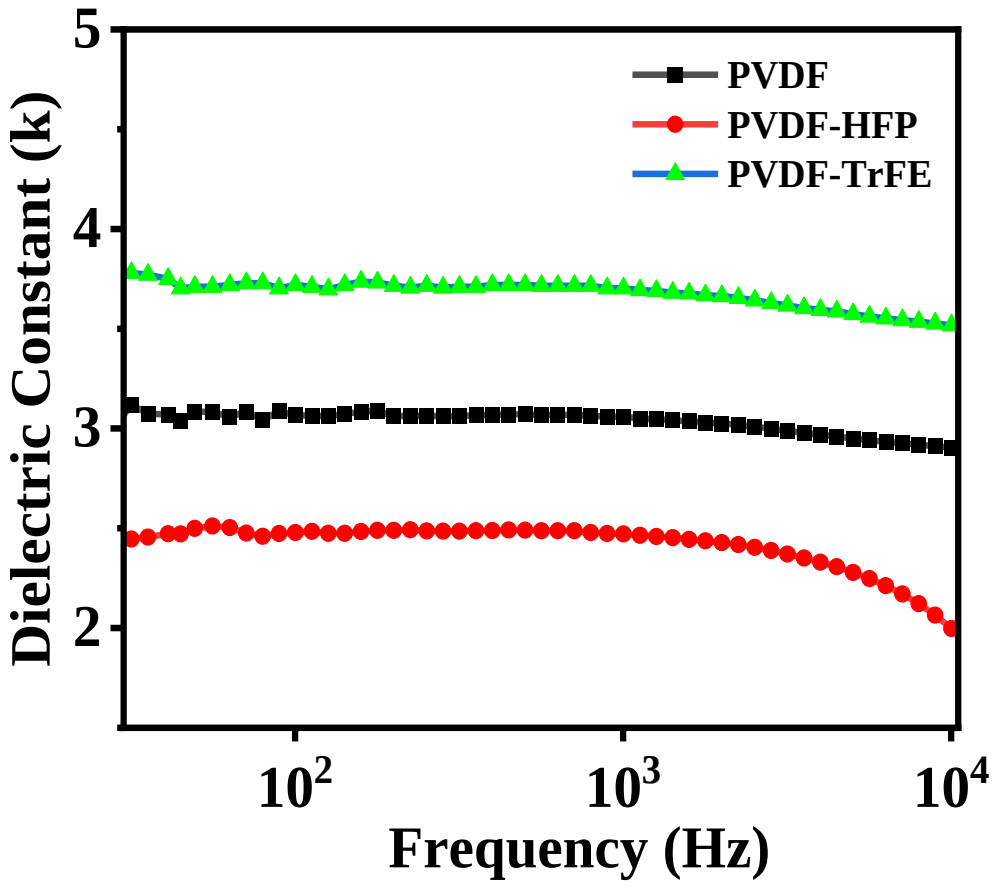

Figure 3.4. Dielectric Constant of PVDF and its Copolymers Films

3.2.5. Device Performance

Using an electrodynamic shaker machine as assistance that operates at frequencies ranging from 2-10 Hz, the piezoelectric response of the fabricated PENGs, which have dimensions of approximately 3 cm × 3 cm, has been studied through continuous tapping. The output performance of PVDF and its copolymers in terms of generated V_{OC} and I_{SC} has been shown in Figure 3.6. (a-f) at a tapping frequency of 7Hz. The obtained results demonstrate that nanogenerators based on PVDF-TrFE thin film produce the highest V_{OC} and I_{SC} with a magnitude of 23.7 V and 3.7 µA, respectively. The generated output parameters for various fabricated devices are shown in Table 1. Fig.4 shows the frequency response of all fabricated nanogenerators concerning the variations of V_{oc} at various tapping frequencies. All of the nanogenerators exhibit the same pattern, as given in the figure, in which the output voltage first rises to the tapping frequency of 7 Hz before beginning, to fall when the tapping frequency is increased further above 7 Hz [36].

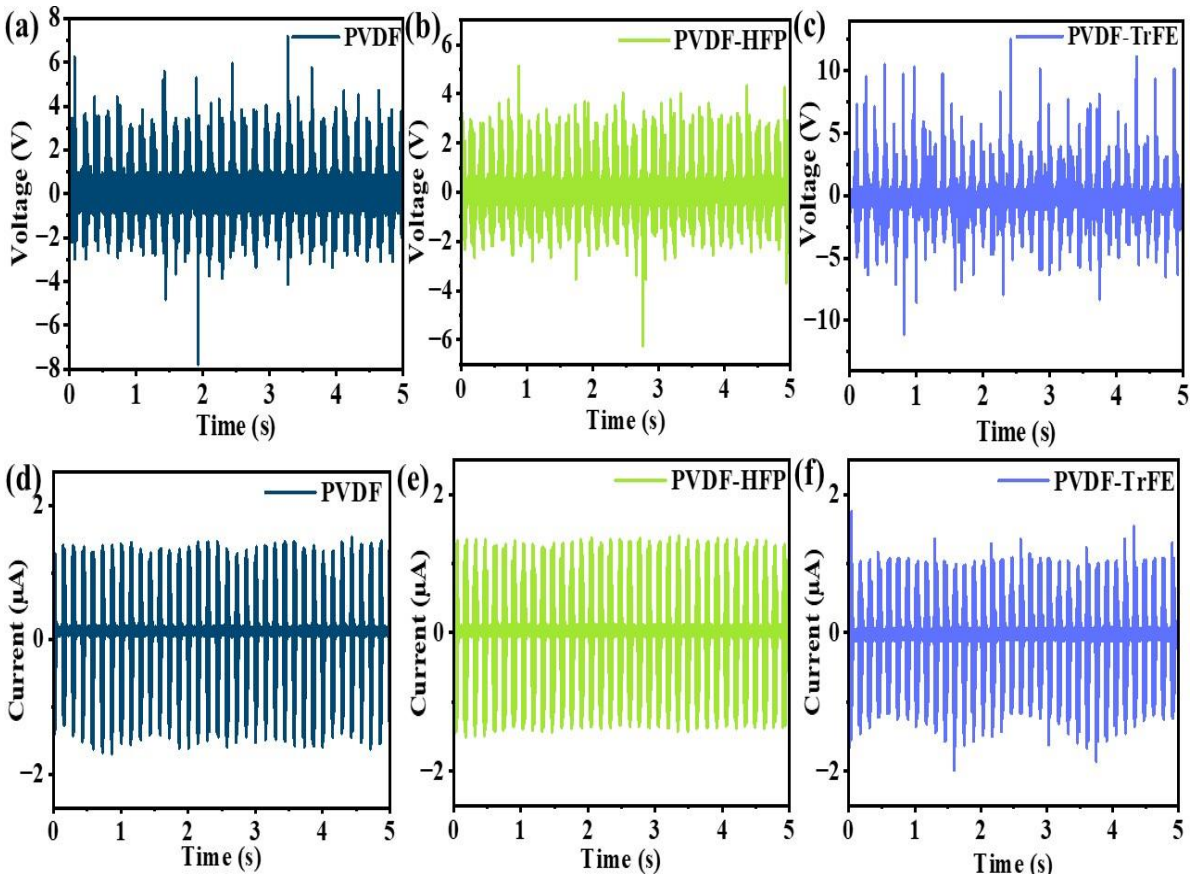

Figure 3.5. Electrical Output performance of PVDF and its copolymer films ((a), (b), (c)) shows open circuit voltage (V_{OC}) and, ((d), (e), (f)) shows short circuit current (I_{SC})

Table 1. PENGs generate an open circuit voltage and current from peak to peak at a 7 Hz tapping frequency.

S. No.	Nanogenerators	Peak-to-peak output voltage (V_{oc} in V)	Peak-to-peak output Current (I_{sc} in µA)
1.	PVDF-HFP	11.4	2.9
2.	PVDF	14.9	3.2
3.	PVDF-TrFE	23.6	3.7

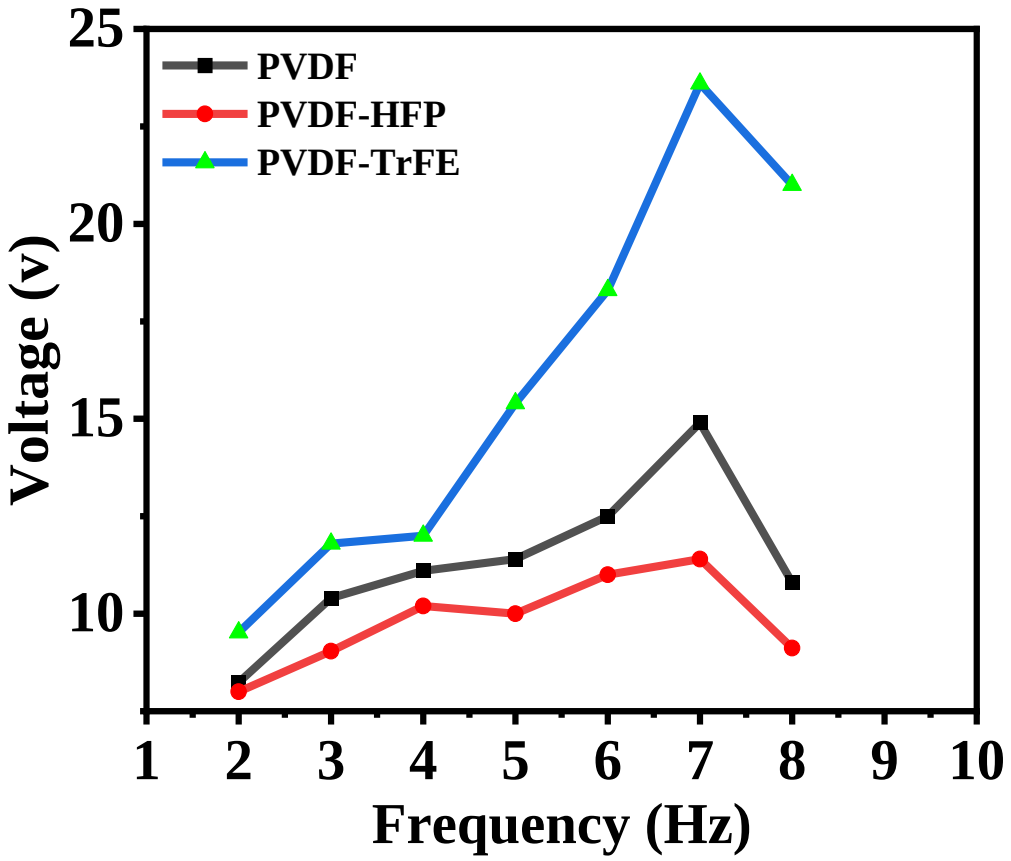

Figure 3.6. Voltage Output of PVDF and its copolymers at various frequencies.

3.2.6. Applications of PENG

Experiments were conducted that combined PENGs with human activity to study the device's capacity to gather and transform various types of mechanical energy. Here, we perform various types of tapping, Fig.5(a-e) shows the electrical output voltage is 4.96, 3.44, 3.20, 5.84 & 7.40 V for double-figure tapping, single-figure tapping, thumb tapping, knocking, and foot tapping respectively, and figure 3.7(f) shows the capacitor charging using the PVDF-TrFE film-based nanogenerator. At a 7 Hz frequency, the 1µF capacitor can charge up to 3.28 V. The formula for calculating the corresponding energy stored in the capacitor is $E=1/2*CV^2$, where E stands for stored energy, C for capacitance, and V for voltage, and the capacitor stores 1.64 µJ of energy, as per the formula[37]. Therefore, by using an efficient PVDF-TrFE polymer, the current study suggests a useful method to develop an energy harvester for self-powered devices.

Table 2. The output voltage of PVDF-TrFE Applications:

S. No.	PVDF-TrFE PENGs at different tapping	Electrical Voltage Output (V)
1.	Single-finger tapping	3.44
2.	Double-finger tapping	4.96
3.	Thumb tapping	3.20
4.	Foot tapping	5.84
5.	1 µF Capacitor charging at tapping frequency 7Hz.	7.40

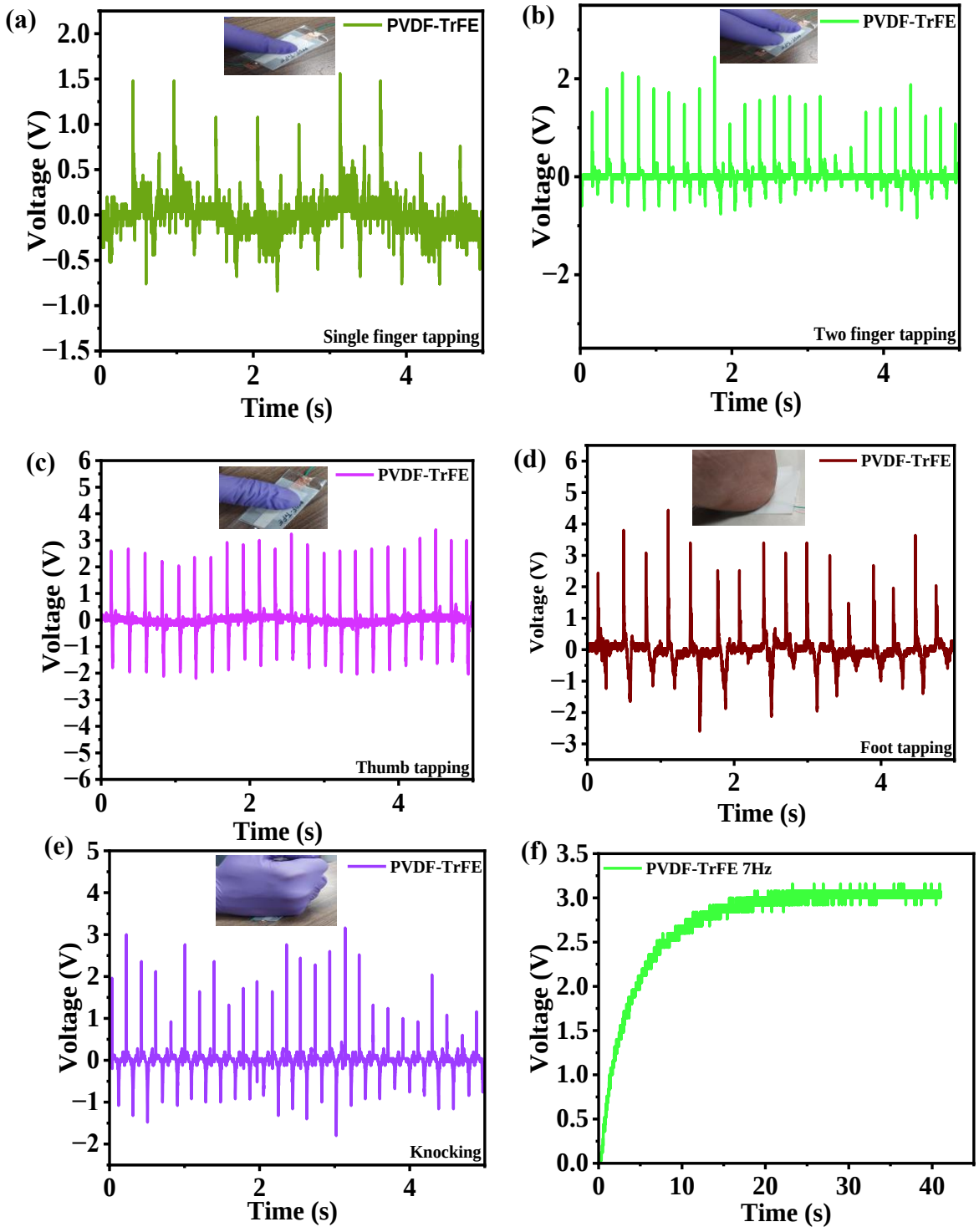

Figure 3.7. Illustration of Electrical Voltage Output of PVDF-TrFE film (a) single-finger tapping, (b) two-finger tapping, (c) thumb tapping, (d) foot tapping, (e) knocking, (f) capacitance of PVDF-TrFE film at frequency 7Hz.

Furthermore, to check the stability of the PVDF-TrFE-based nanogenerator, the output current measurements are carried out over 1100 cycles which shows a negligible change in the output current values, and Figure 3.8 shows the corresponding results.

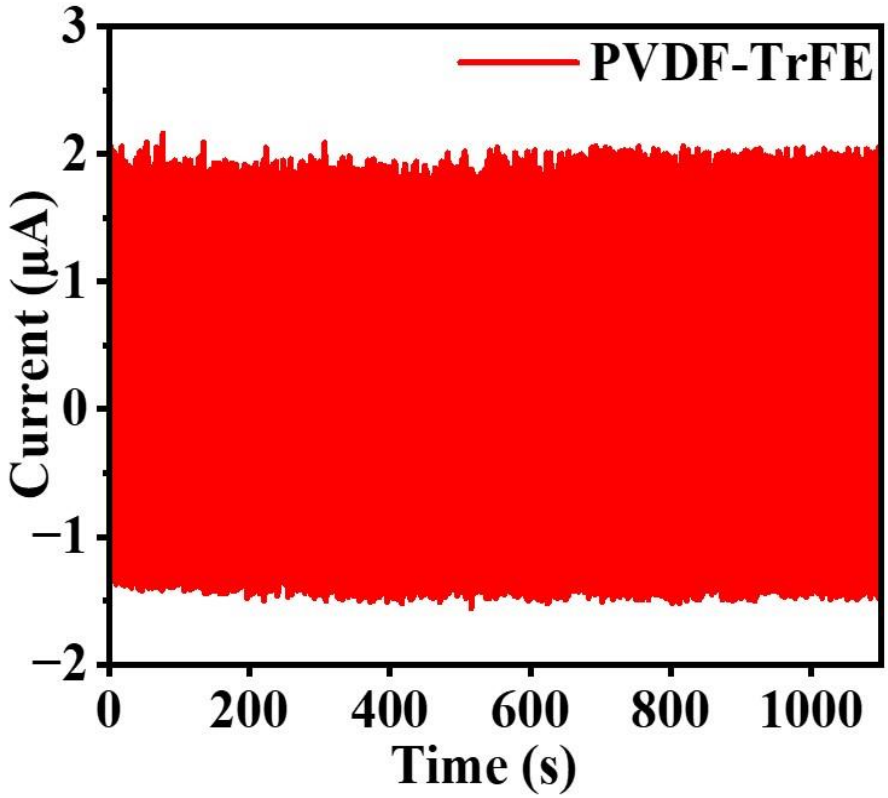

Figure 3.8. The stability test of PVDF-TrFE PENG over 1100 cycles, at a frequency of 7 Hz.

CHAPTER - 4

CONCLUSIONS AND FUTURE SCOPE

4.1. Conclusion

Lastly, we have methodically examined how the PVDF and its copolymer affect the nanogenerator's piezoelectric characteristics for mechanical energy harvesting. To do this, drop casting was used to create PVDF, PVDF-HFP, and PVDF-TrFE films, and their piezoelectric reaction was examined. The experimental results demonstrate that the PVDF-TrFE films-based nanogenerator performs better in terms of piezoelectric performance than any other fabricated nanogenerator. In comparison to other polymers, the output voltage and current of PVDF-TrFE are found to be at a maximum of 23.6 V and 3.7 μA. Compared to PVDF and PVDF-HFP, the PVDF-TrFE-based PENG exhibits a higher β-phase, which is responsible for its improved output. Potentially, the PVDF-TrFE film-based PENG was shown to capture energy from human motions such as tapping with two figures, one figure, tapping with one thumb, knocking, and tapping with the foot. The maximum output voltage from tapping with the foot was 7.4 V, and the 1.67 μJ energy was also stored by charging a 1μF capacitor at a frequency of 7 Hz, producing 3.28 V, as illustrated in Figure 3.6.

4.2. Future Scope

Although, PVDF and its copolymers-based PENG is a potential candidate for designing flexible piezoelectric devices but its performance still needs to be optimized for its practical application. Hence, the present study contributes to the fundamental understanding of PVDF-based materials for enhancing the performance of

piezoelectric nanogenerators, paving the way for advancements in self-powered systems and energy harvesting technologies.

The design objectives for flexible piezoelectric devices are high output performance, stability, cost-effectiveness, and simplicity in the manufacturing process. It is anticipated that flexible piezoelectric nanogenerators that satisfy the practical application requirements will emerge soon, propelling the commercial application of several new technologies like mechanical energy conversion and self-driven sensing. These developments are the result of new materials, structures, and techniques being successively applied to the design of flexible PVDF-based piezoelectric devices[38].

References

[1] J. Hulla, S. Sahu, A. Hayes, Human & experimental toxicology, 34 (2015) 1318-1321.

[2] R.R. Chandran, B.I. Thomson, A. Natishah, J. Mary, V. Nachiyar, Biosciences Biotechnology Research Asia, 20 (2023) 53-68.

[3] G. Chen, Y. Li, M. Bick, J. Chen, Chemical Reviews, 120 (2020) 3668-3720.

[4] H.H. Shi, Y. Pan, L. Xu, X. Feng, W. Wang, P. Potluri, L. Hu, T. Hasan, Y.Y.S. Huang, Nature Materials, 22 (2023) 1294-1303.

[5] W. Chen, Q. Zheng, Y.A. Lv, Y. Chen, Q. Fan, X. Zhou, H. Li, Q. Yu, H. Liu, Chemical Engineering Journal, 465 (2023) 142755.

[6] A. Tabak, B. Safaei, A. Memarzadeh, S. Arman, C. Kizilors, Journal of Vibration Engineering & Technologies, 12 (2024) 3155-3192.

[7] A.Ç. Seçkin, B. Ateş, M. Seçkin, Applied Sciences, 13 (2023) 10399.

[8] A. Ali, H. Shaukat, S. Bibi, W.A. Altabey, M. Noori, S.A. Kouritem, Energy Strategy Reviews, 49 (2023) 101124.

[9] P. Jiao, H. Hasni, N. Lajnef, A.H. Alavi, Materials & Design, 187 (2020) 108214.

[10] Z. Zhao, Y. Dai, S.X. Dou, J. Liang, Materials Today Energy, 20 (2021) 100690.

[11] Z. Huo, Y. Wei, Y. Wang, Z.L. Wang, Q. Sun, Advanced Functional Materials, 32 (2022) 2206900.

[12] K. Khan, A.K. Tareen, M. Aslam, R. Wang, Y. Zhang, A. Mahmood, Z. Ouyang, H. Zhang, Z. Guo, Journal of Materials Chemistry C, 8 (2020) 387-440.

[13] C. Ribeiro, V. Sencadas, J.L.G. Ribelles, S. Lanceros-Méndez, Soft Materials, 8 (2010) 274-287.

[14] P. Saxena, P. Shukla, Advanced Composites and Hybrid Materials, 4 (2021) 8-26.

[15] P. Martins, A.C. Lopes, S. Lanceros-Mendez, Progress in polymer science, 39 (2014) 683-706.

[16] A. Salimi, A.A. Yousefi, Journal of Polymer Science Part B: Polymer Physics, 42 (2004) 3487-3495.

[17] E. Kar, N. Bose, S. Das, N. Mukherjee, S. Mukherjee, Physical Chemistry Chemical Physics, 17 (2015) 22784-22798.

[18] M. Rahimabady, K. Yao, S. Arabnejad, L. Lu, V.P.W. Shim, D. Cheong Wun Chet, Applied Physics Letters, 100 (2012).

[19] P. Adhikary, S. Garain, D. Mandal, Physical Chemistry Chemical Physics, 17 (2015) 7275-7281.

[20] J. Nunes-Pereira, P. Martins, V.F. Cardoso, C.M. Costa, S. Lanceros-Méndez, Materials & Design, 104 (2016) 183-189.

[21] D. Ponnamma, H. Parangusan, A. Tanvir, M.A.A. AlMa'adeed, Materials & Design, 184 (2019) 108176.

[22] M. Kashfi, P. Fakhri, B. Amini, N. Yavari, B. Rashidi, L. Kong, R. Bagherzadeh, Journal of Industrial Textiles, 51 (2022) 531S-553S.

[23] H. Pei, J. Jing, Y. Chen, J. Guo, N. Chen, Nano Energy, 109 (2023) 108303.
[24] G. Gautam, M. Kumar, B. Singh, Materials Today: Proceedings, 62 (2022) 3239-3243.
[25] R.S. Sabry, A.D. Hussein, Polymer Testing, 79 (2019) 106001.
[26] D. Hu, M. Yao, Y. Fan, C. Ma, M. Fan, M. Liu, Nano Energy, 55 (2019) 288-304.
[27] O.Y. Pawar, S.L. Patil, R.S. Redekar, S.B. Patil, S. Lim, N.L. Tarwal, Applied Sciences, 13 (2023) 2891.
[28] M. You, X. Hu, Y. Xiang, IOP Publishing, pp. 012071.
[29] S.M. Nakhmanson, M.B. Nardelli, J. Bernholc, Physical review letters, 92 (2004) 115504.
[30] B. Bera, M.D. Sarkar, IOSR J. Appl. Phys, 9 (2017) 95-99.
[31] H. Pan, B. Na, R. Lv, C. Li, J. Zhu, Z. Yu, Journal of Polymer Science Part B: Polymer Physics, 50 (2012) 1433-1437.
[32] B. Jaleh, A. Jabbari, Applied Surface Science, 320 (2014) 339-347.
[33] S. Sarkar, S. Garain, D. Mandal, K.K. Chattopadhyay, RSC Advances, 4 (2014) 48220-48227.
[34] N. Soin, D. Boyer, K. Prashanthi, S. Sharma, A.A. Narasimulu, J. Luo, T.H. Shah, E. Siores, T. Thundat, Chemical Communications, 51 (2015) 8257-8260.
[35] D. Sengupta, A.G.P. Kottapalli, S.H. Chen, J.M. Miao, C.Y. Kwok, M.S. Triantafyllou, M.E. Warkiani, M. Asadnia, AIP Advances, 7 (2017).
[36] V. Singh, D. Meena, H. Sharma, A. Trivedi, B. Singh, Energy, 239 (2022) 122125.
[37] S. Rana, V. Singh, B. Singh, ACS Applied Electronic Materials, 4 (2022) 5893-5904.
[38] L. Lu, W. Ding, J. Liu, B. Yang, Nano Energy, 78 (2020) 105251.

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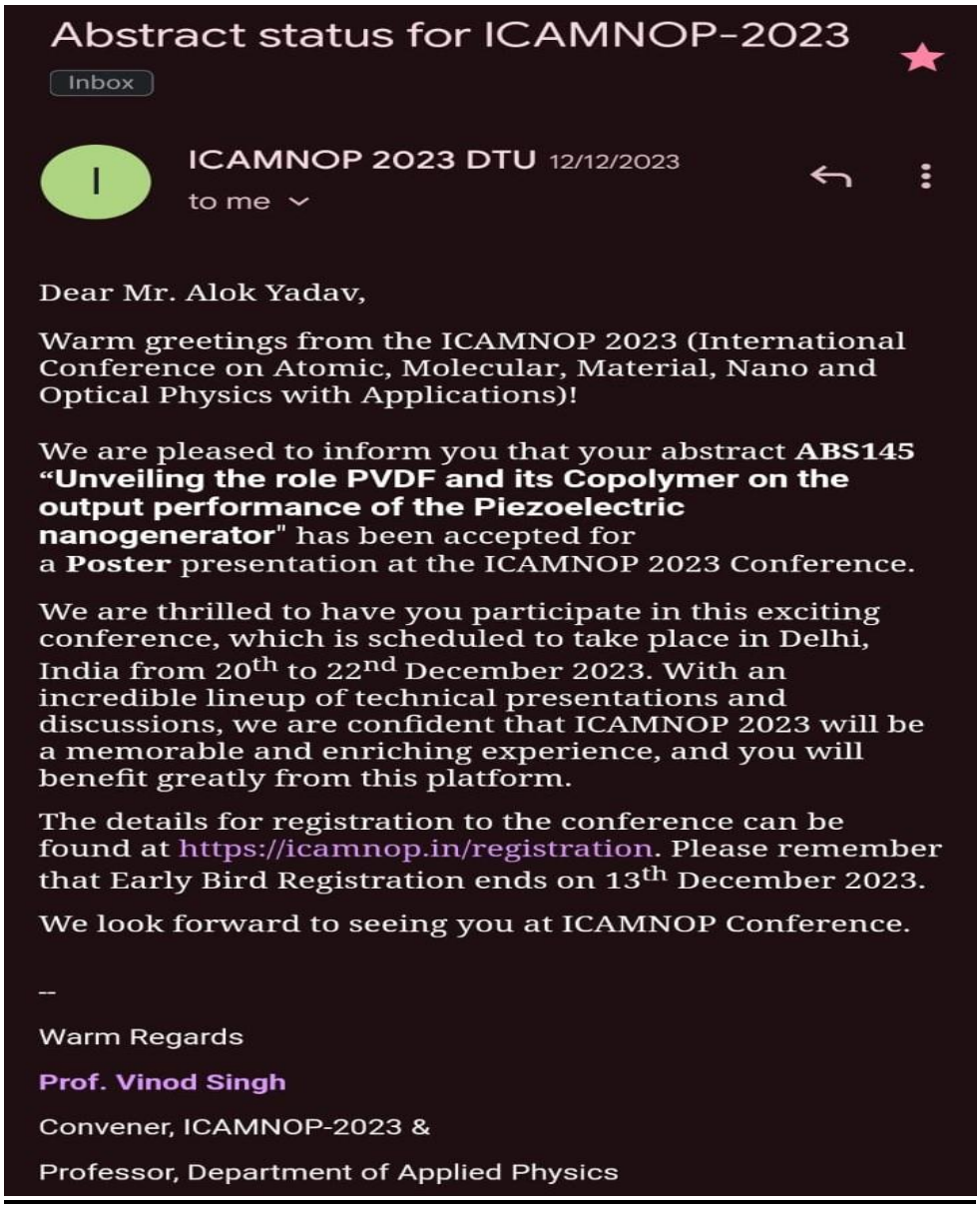

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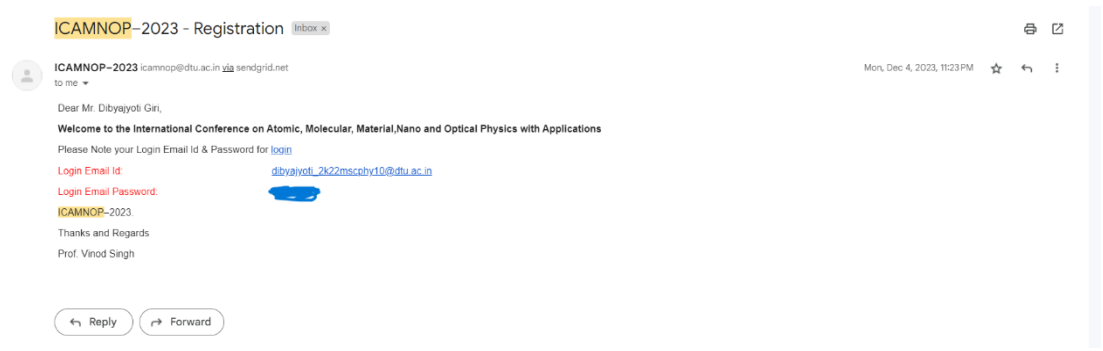

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Unveiling the role of PVDF and its Copolymer on the output performance of the Piezoelectric nanogenerator

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Abstract

Herein, we have systematically investigated the impact of polyvinylidene fluoride (PVDF) and its copolymer on the piezoelectric properties of the nanogenerator. For this, PVDF, polyvinylidene fluoride-cotrifluoroethylene (PVDF-TrFE), and polyvinylidene fluoride-cohexafluoropropylene (PVDF-HFP) films were synthesized by drop casting method, and their piezoelectric response was analyzed. The experimental results show that the PVDF-TrFE films-based nanogenerator outperforms all other fabricated nanogenerators in terms of piezoelectric performance. In comparison to other polymers, PVDF-TrFE has a maximum output voltage (V_{OC}) and short circuit current (I_{SC}) of 23.6 V and 3.7 μA, respectively. This enhanced performance of PVDF-TrFE-based PENG is attributed to the highest β-phase in comparison to PVDF and PVDF-HFP. For potential application, the PVDF-TrFE film-based PENG was demonstrated to harvest energy from the human body movements, and the energy is also stored by charging a 1μF capacitor. This study contributes to the fundamental understanding of PVDF-based materials for mechanical energy harvesting applications, thereby, paving the way for advancements in self-powered systems.