

Performance Investigation of Piezoelectric PVDF-TrFE Polymer for It's Mechanical and Electrical Response and Use as Vibration Sensor

by

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Abstract

Piezoelectric polymers, such as PVDF-TrFE, are increasingly studied for their potential to replace traditional ceramic based piezoelectric materials due to their flexibility, ease of processing, and strong adhesion properties. This study focuses on PVDF-TrFE with a 75/25 molar concentration, emphasizing the enhancement of the β -phase to improve piezoelectric output. The research explores various techniques to increase the β -phase without requiring extensive stretching or polling processes. Notably, the addition of the TrFE co-polymer to PVDF negates the need for such processes, inherently boosting piezoelectric performance. The experimental study utilized PVDF-TrFE dissolved in two different solvents: MIBK (Methyl Isobutyl Ketone) and DMSO (Dimethyl Sulfoxide).

In the initial phase of the experiments, piezoelectric solutions based on MIBK and a combination of MIBK and DMSO were spin-coated onto flexible KAPTON cantilevers and annealed to form thin films. The mechanical properties were then assessed using a vibration test system. It was observed that films created with MIBK alone exhibited higher vibrational amplitudes than those formed with a mixture of MIBK and DMSO. Additionally, higher concentrations of PVDF-TrFE resulted in greater vibrational amplitudes, suggesting a direct correlation between polymer concentration and mechanical responsiveness. Notably, the films made by a 1.25% MIBK + DMSO based polymer solution produced an equivalent sensitivity to the films made by a 3% polymer solution. The equivalency is due to the presence of DMSO (polar nature) solvent and its ability to form long chains during the baking process. In contrast, the latter solution produced thicker films than the former due to the increased

quantity of polymer.

The performance of laboratory based vibration sensors fabricated using PVDF-TrFE was compared with existing ceramic based devices and commercial vibration sensors. The results indicated that PVDF-TrFE sensors generated comparable, if not higher, piezoelectric voltages than their ceramic counterparts. This finding underscores the potential of polymer based sensors in practical applications, offering advantages in flexibility and adhesion without sacrificing performance.

Further experiments involved fabricating a 5 x 2 mm cantilever on a PCB using a laser cut process. This cantilever responded to acoustic signals ranging from 400 Hz to 1200 Hz and produced a 0.011 V output voltage during vibration tests. Another U-shaped sensor, incorporating electroplated copper, spin-coated PVDF-TrFE, and silver sputtering, was tested as a Lorentz force actuator and sensor. The sensor exhibited responsiveness to magnetic fields and sinusoidal voltages, highlighting its multifunctional capabilities. Additionally, a vibration sensor was made on a bearing surface and subjected to motor induced vibrations, demonstrating a clear output signal, driven purely by the motor's rod vibrations.

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Publications

- Journal Publications:

1. **Naeem Riaz**, Nan Wu, and Cyrus Shafai, “Electrical and mechanical response of spin-coated PVDF-TrFE formed from MIBK and DMSO solvents under external excitations”, vol.10, p-125703, 2023, Materials Research Express: DOI 10.1088/2053-1591/ad14c1.

- Conference Publications:

1. **Naeem Riaz**, Nan Wu, and Cyrus Shafai, “Structural Response of Flexible Kapton Beam When Coated with Piezoelectric (PVDF-TrFE) Polymer,” in Proceedings of the Canadian Society for Mechanical Engineering International Congress 2022, <https://doi.org/10.7939/r3-dzb5-9187>
2. **Naeem Riaz**, Tao Chen, and Cyrus Shafai, ”A laser cut acoustic vibration sensor based on flexible-PCB spin-coated with PVDF-TrFE”, IEEE Canadian Conference on Electrical and Computer Engineering (CCECE),2024, DOI: 10.1109/CCECE59415.2024.10667270.

Chapter 1

Introduction

Pierre Curie and Jacques Curie discovered the direct piezoelectric effect in 1880, observing the electric charge in quartz (SiO_2) crystals resulting from mechanical stress. At the same time, the converse of the direct piezoelectric effect is the geometric strain when voltage is applied. After that, many of the polycrystalline piezoelectric ceramics in their oxides were discovered. During World War II, BaTiO_3 was first to be used as dielectric material on condensers [5]. But the complete picture of its piezoelectricity is unknown, which Robert found as 100 times higher than quartz when the crystal BaTiO_3 is poled using high voltage [6]. After that, BaTiO_3 ceramics have been widely used in transducers, sensors, etc. In 1952, Shirane et al. observed in 1952 that solid solutions between PbTiO_3 and PbZrO_3 can be developed [7, 8]. Ferroelectricity and antiferroelectricity were discovered in the solid solutions a year later [9]. The piezoelectric characteristics of PbTiO_3 - PbZrO_3 solid solution ceramics were examined by Jaffe et al. in 1954, showing that their piezoelectric constants were twice as high as those of BaTiO_3 and that their Curie temperature (beyond which the piezoelectricity disappears) was over 300°C [10]. Currently, the solid materials based on PbTiO_3 - PbZrO_3 are named PZT (piezoelectric ceramics) and are widely used in

various applications [11–14].

From the piezoelectric ceramics discovered so far, BaTiO_3 is lead-free, while the newly discovered PZT ceramic materials have lead. Still, the PZT materials dominate BaTiO_3 due to excellent and flexible properties, high Curie temperature, and low annealing temperature. As we know, the presence of lead in the environment causes health issues during handling, manufacturing, and disposal. That is why many countries have taken the first step to develop lead free piezoelectric materials [15–22]. However the industry can not change to lead-free piezoelectric material instantly. The amount has to be reduced as the research on alternative lead-free piezoelectric materials develops. After Kawai’s discovery of polyvinylidene fluoride (PVDF) polymer in 1969 [23], there is an increased interest in organic piezoelectric polymers.

These days, piezoelectric applications include innovative materials for vibration management, flexible surfaces and structures for aerospace and astronautical use, sensors for robotic applications, and creative methods for reducing vibration in sporting goods (tennis racquets and snowboards).

1.1 Motivation and Objectives of the Thesis

1.1.1 Motivations

There are several piezoelectric polymers available from different global suppliers, such as PVDF, PVDF-TrFE, P(VDF-HFP), P(VDF-CTFE), P(TFE-HFP-VDF) polymers. Several available molar concentrations of VDF/TrFE from PolyK labs are listed in table 1.1 [24]. Each molar concentration has a different percentage of PVDF and its copolymer TrFE. Due to this, the Curie temperature and its piezoelectric properties change. PVDF-TrFE (trifluoroethylene or VF3) copolymer resin

is a ferroelectric polymer that can produce piezoelectric or pyroelectric film and sensors. They are made by suspension polymerization with high melting temperature and high crystallinity degree, therefore, providing more robust piezoelectric and pyroelectric response.

Researchers are using different ways to increase the piezo-electricity and output efficiency by making hybrid structures, e.g., mixing different oxides like ZnO (Zinc Oxide), GO (graphene oxide). This may exhibit non-uniform properties due to additive dispersion and will increase the processing steps.

In this thesis, PVDF-TrFE polymer is used as a **sole polymer** in solvent base procedure to cover the comparison gap between inherent properties of PVDF-TrFE and solution with dopants. The 75/25 molar concentration of PVDF-TrFE (75% polyvinylidene fluoride, 25% trifluoroethylene) is preferred, because it achieves an optimal balance between crystallinity, piezoelectricity and mechanical flexibility. Here's why this specific molar ratio is better than other concentrations for piezoelectric applications. The below are few key properties of 75/25 as compared to other concentrations:

- The 75/25 ratio strikes a balance between crystallinity and amorphousness, ensuring sufficient crystallinity to maintain strong piezoelectric and ferroelectric properties.
- The 75/25 molar ratio facilitates easy film formation due to good solubility and processability in common solvents like DMF or acetone.
- The 75/25 molar ratio provides excellent thermal and mechanical stability, making it suitable for thin film applications.

- The Curie temperature of 75/25 molar concentration is high enough for most practical applications but not so high as to complicate processing.
- Due to its balanced ratio, some amorphous regions to retain flexibility and mechanical durability.
- Higher TrFE content (e.g in 65/35 or 50/50) increases amorphousness, which degrades the piezoelectric properties. Conversely, lower TrFE content (e.g/, in 85/15) results in overly rigid films with reduced flexibility.
- The 75/25 ratio reduces the coercive field required for poling. This facilitates easier and energy efficient electrical poling.

As per the product comparison data sheet on PolyK labs, in general, PVDF-TrFE (Polyvinylidene Fluoride-Trifluoroethylene) has shown good piezoelectric material due to its high piezoelectric coefficients, chemical stability, and high mechanical strength. That's why PVDF-TrFE is a preferred choice for various applications. Below are a few advantages and examples in industries for applications.

Table 1.1: Different Polar concentrations of PVDF-TrFE from PolyK labs.

Molar Concentrations	Curie Temperatures (°C)
80/20	135
75/25	112 - 121
70/30	104
65/35	72
55/55	66

1. High Piezoelectric Coefficients:

PVDF-TrFE has a high piezoelectric coefficient, meaning it can efficiently convert mechanical energy into electrical energy. Due to this property, it makes a suitable material for various applications, such as sensors, actuators, and energy harvesters.

2. Good Chemical Stability:

PVDF-TrFE has excellent chemical stability, which makes it suitable for use in challenging environments. PVDF-TrFE films are resistant to corrosion, radiation, and chemicals, making them an ideal choice for applications that require high durability and long-term stability.

3. High Mechanical Strength:

PVDF-TrFE has a high mechanical strength, so it can withstand high levels of stress and strain without breaking. Therefore, PVDF-TrFE films can be used in applications requiring high durability and mechanical stress resistance.

4. Versatility:

PVDF-TrFE films can be fabricated into various shapes, sizes, and thicknesses. It is suitable for a wide range of applications using different techniques such as spin coating, casting, and electrospinning.

Another advantage of having flexible a polymer material is that the film can be applied on a mechanical moving object. Traditionally, a patch of PZT materials is glued on the mechanically moving parts, but this increases mass.

1.1.2 Objectives

The novelty of this research work is to explore the inherent mechanical and electrical properties of a PVDF-TrFE piezoelectric polymer formulated from a **solvent base** formulation. Being a solvent based polymer solution, it is easier to handle than ceramic piezoelectric materials in various applications. It has also fewer processing steps than a hybrid solutions in which various compounds are used to increase the performance. In this solvent base procedure, the performance relies only on the in-

trinsic properties of polymer used without the influence of external dopants. The external dopants may exhibit non-uniform properties due to additive dispersion and can cause the environmental effects. Another advantage of solvent base formulation is that, the TrFE in PVDF promotes the stabilization of the β -phase without the need for extensive mechanical stretching or poling processes, which simplifies the fabrication process. And lastly, the β -phase can be tailored by changing the solvent nature and the polymer concentrations.

For the experimental purpose, the PVDF-TrFE was purchased in powdered form from PolyK labs along with Methyl Isobutyl Ketone (MIBK) as a non-polar solvent. To compare the performance, another polar solvent Dimethyl Sulfoxide (DMSO) was also used. Solutions of PVDF-TrFE was made by dissolving PVDF-TrFE in MIBK only and the combination of MIBK and DMSO of various polymer concentrations, so that it can be deposited on a surface to test.

The study is based on two substrates: a flexible Kapton substrate to analyze mechanical properties and a rigid aluminum base to evaluate electrical performance. The PVDF-TrFE solution was deposited on these substrates using the spin-coating technique, ensuring uniform thin films. Then used a ground-based shaker to test the material's response to vibrations and assess the differences between the two solvents.

The study revealed fascinating insights. MIBK, a non-polar solvent, demonstrated superior performance in mechanical applications due to its compatibility with flexible substrates. Conversely, DMSO, a polar solvent, enhanced the electrical output of PVDF-TrFE significantly, offering a deeper understanding of its potential for electronic applications. However, DMSO was found unsuitable for mechanical applications due to its limited compatibility with flexible structures. This differentiation underscored the importance of solvent choice in tailoring the material's properties

for specific applications. The findings were further validated through a series of experiments. A simple cantilever structure spin-coated with PVDF-TrFE was tested in response to acoustic waves, showcasing its potential in sound sensing technologies. Additionally, a U-shaped structure was used as a magnetic field sensor, demonstrating the material's ability to detect motion with precision. Another application involved coating PVDF-TrFE on a motor bearing to explore voltage generation from vibrations, emphasizing its role in monitoring rotational systems. These experiments highlighted the material's versatility and the transformative potential of solvent-based procedures in optimizing its performance. This solvent-based approach represents a novel methodology in the field of materials science, bridging the gap between mechanical and electrical research. By selecting the appropriate solvent, researchers can enhance specific properties of PVDF-TrFE, leading to the development of more efficient and versatile devices. These findings have broad implications, opening new avenues for the use of PVDF-TrFE in cutting-edge applications such as sensors, actuators, and flexible electronics.

1.2 Organization of the Thesis

Chapter 3-7 present the core contributions of this thesis. Chapter 3 explains the detailed initial preparation process of the PVDF-TrFE solution and the material characterizations explored using the FT-IR technique. Chapter 4 describes the test setup and comparison of two solution compositions in terms of electrical and mechanical properties. Chapter 5 shows the application of a simple cantilever design based on PVDF-TrFE to demonstrate the measurement of acoustic signals. In Chapter 6, the PVDF-TrFE based U-shaped sensor was explored as a Lorentz force actuator and sensor, while Chapter 7 describes the application of PVDF-TrFE in mechanical moving

parts, in which a bearing sensor's sensitivity was explored.

Chapter 2

Piezoelectric Materials

Piezoelectric materials are grouped into three main categories, defined by their atomic structures and how they respond to electrical and mechanical influences, with the concept of "poles" playing a key role. Poles refer to the directional arrangement of electric dipoles within a material. A dipole forms when positive and negative charges in the material are separated, creating a directional electric field.

The first category, dielectric materials, are electrical insulators that do not have permanent poles. However, when exposed to a high voltage, their atomic structure can shift slightly, temporarily creating dipoles, a process known as polarization. These materials are crucial for managing and insulating electric fields. The second category, ferroelectric materials, naturally possess permanent poles due to their organized dipole alignment. These poles can spontaneously reorient in response to an electric field, making ferroelectric materials highly adaptable and useful in applications requiring fast, reversible polarization. Finally, piezoelectric materials, a specialized type of dielectric material, generate electrical charges when subjected to mechanical stress. This is because the applied stress distorts their atomic structure, aligning the dipoles and producing poles that create surface charges. This unique

ability to convert mechanical energy into electrical energy makes piezoelectric materials vital for technologies such as sensors, actuators, and energy harvesting systems. Later sections provide a more thorough explanation of these materials.

2.1 Electric Polarization

The critical concept of dielectric, ferroelectric, and piezoelectric materials is understanding how these materials behave in the presence of the external electric field. When an external electric field is applied to a solid, the medium tends to shift the locations of the nuclei and electrons in response. As a result, the solid goes through the process of polarization by the formation of dipoles. So, polarization is a process in which dipoles are created, or the re-arrangement of existing poles occurs in the electric field's presence. There are four types of polarization: ionic, electronic, dipolar (or orientation), and interfacial space charge that occurs at electrodes and the heterogeneities such as grain boundaries. In the case of AC potential fields, each of the first three types contributes depending upon the applied field frequency as shown in figure 2.1.

Electronic polarization is caused by the electric field shifting the center of the negatively charged electron cloud in relation to an atom's positive nucleus. This scenario is most common in dielectric material only in the presence of the electric field. In ionic polarization, the applied electric field displaces cations and anions opposite each other to form a dipole. Dipolar or orientation polarization is observed in materials with dipoles and tends to rearrange themselves in the direction of the applied electric field. In general, the total electric polarization is equal to the sum of electronic, ionic, and dipolar polarizations, but there is a chance that one of them may dominate the others. The average polarization of the material can be calculated by equation 2.1

[25], in which $\vec{P}$ is the average polarization produced by N electric dipoles.

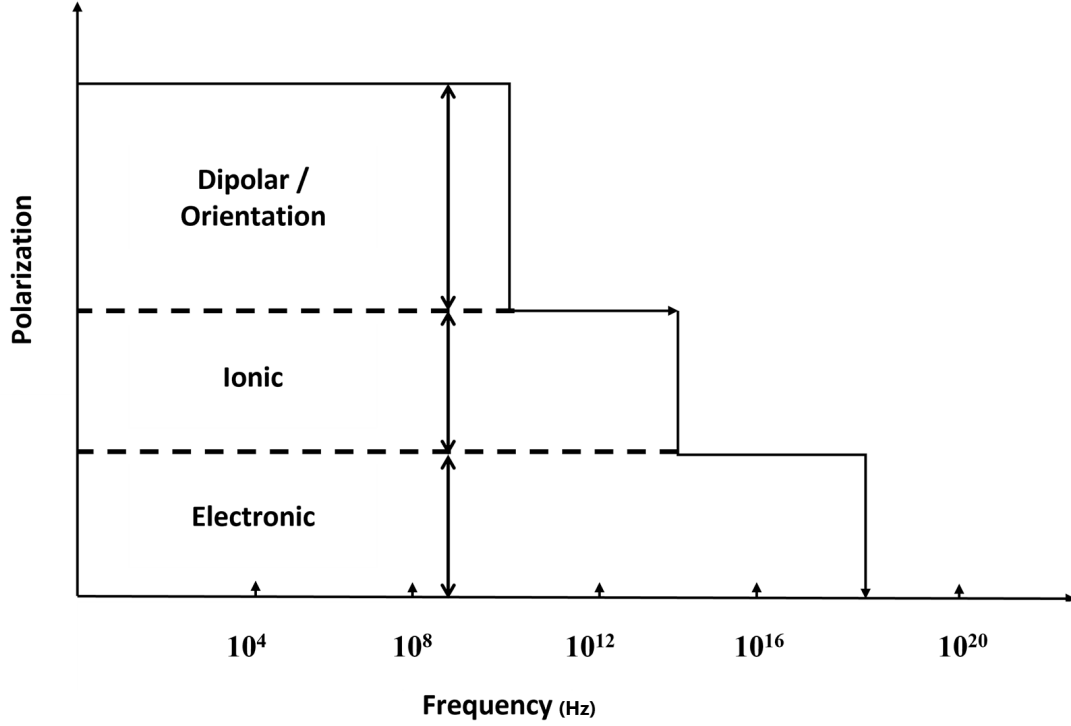


Figure 2.1: Frequency dependence of Dipolar, Ionic and Electronic polarizations.

$$\vec{P} = \frac{1}{Volume} \sum_{k=0}^N \vec{P}_k \quad (2.1)$$

2.1.1 Dielectric Materials

In general, the dielectric materials are electrically insulating but can polarize under the influence of an electric field, aligning their internal charges without conducting electricity. There are two main types of dielectric materials. One of them has permanent dipoles with random polarities without an electric field. This can be changed when the electric field is applied, but the alignment will not be perfect due to the thermal energy produced by the permanent polar moments. The second type of dielectric

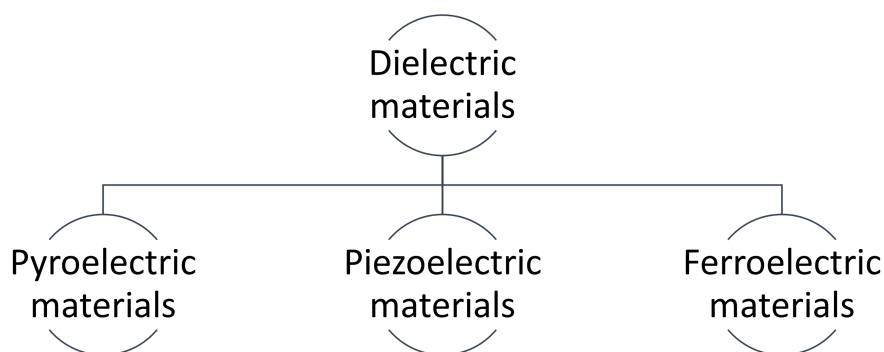
material does not possess permanent electric dipole moment, and the applied electric field can induce these electric dipole moments. Therefore, the dielectric materials can be polarized in the presence of an electric field, and this characteristic increases the storage capacity in terms of dielectric constants like in capacitors, as higher dielectric constants allow more charge storage for the same electric field [25].

2.1.2 Ferroelectric Materials

Ferroelectric materials are a category of dielectric materials that spontaneously polarize, even in the absence of an electric field, due to their natural dipole moment. When an electric field is applied, it alters the spontaneous polarization of ferroelectric materials, resulting in a phenomenon known as the P-E hysteresis loop. These materials undergo a structural transition from a high-temperature paraelectric phase to a low-temperature ferroelectric phase at the Curie temperature. In this way, ferroelectric materials resemble dielectric materials, which exhibit constant electric activity.

2.1.3 Piezoelectric Materials

Piezoelectric materials also fall under the category of dielectric materials in which the polarization can be produced by employing mechanical stress. This unique property in a few dielectric materials is named piezoelectricity. Piezoelectric materials also have two types: one has natural existing poles while the other has zero existing natural dipole moment [25]. Figure 2.2 shows the relationship of dielectric materials with ferroelectric and piezoelectric materials.



the material is polarized and the effect is called direct piezoelectric effect. This polarization is responsible of the transformation of mechanical energy into electric field. Conversely, mechanical strain is produced when an electric field is applied, called the indirect piezoelectric effect. The direct piezoelectric effect is used for sensor applications, while the indirect one is used for actuation applications. The types are shown in figure 2.4(a) and figure 2.4(b).

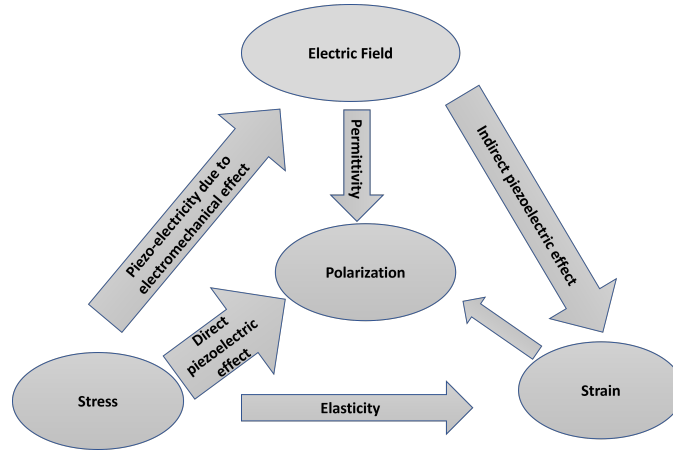


Figure 2.3: Piezoelectricity model. [25]

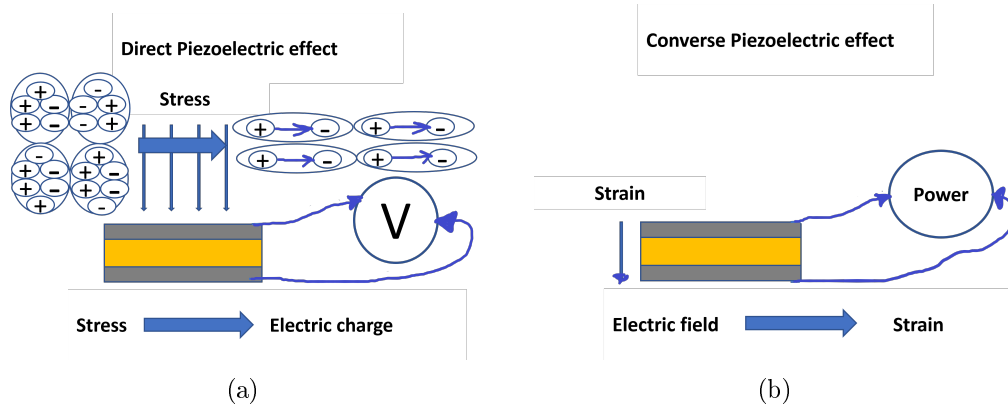


Figure 2.4: (a) Direct piezoelectric effect due to applied stress. (b) Indirect piezoelectric effect leads to strain due to applied electric field.(Reproduced from [21])

From figure 2.4(a), we can see that before applying the mechanical stress on a material, the positive and negative charges are randomly placed in an atom. This

has many usable applications, such as a simple vibration in the material can generate an electrical charge, which can be stored in attached storage devices or used to run a small device that requires a small immediate pulse. On the other hand, in the converse piezoelectric effect (figure 2.4(b)), the electric field is applied to the piezoelectric material, which results in deformation is called actuation. This shows that in actuation, small objects can be displaced in small distances by generating strain.

Piezoelectric materials can not be poled above the Curie temperature (T_{Curie}) because the material will lose their permanent electric properties and in case of polymers they will melt/deform. So, they are handled at Curie temperature and below Curie temperature. While the Curie temperature represents the critical point at which the thermal energy within a material becomes sufficient to overcome the forces aligning the electric domains, causing the material to lose its electrical properties due to weak attractions and unpaired electrons. When a ferroelectric crystal cools below its Curie temperature, it undergoes a structural phase transition, creating polarization through ion displacement, which distorts the crystal lattice, shown in figure 2.5(c) [26]. This process divides the crystal into regions called domains, where polarization is uniform, separated by thin boundaries known as domain walls. The saturation polarization (P_S) occurs when nearly all domains align with an applied electric field. Some domains retain their alignment even after the field is removed, resulting in remnant polarization (P_r), which is the remaining macroscopic polarization in the material. This retained polarization is crucial for applications requiring stable, long-term polarization.

To align the domains and activate the piezoelectric properties of ferroelectric materials, electrical poling is required. During this process, a strong electric field greater than the coercive field (E_C) is applied (figure 2.5(b)) [26]. The coercive field is

the minimum electric field strength needed to reorient the domains and overcome their natural resistance to switching. Without this alignment, randomly oriented domains cancel each other's charges, producing no piezoelectric response as shown in figure 2.5(a) [26]. After poling, the material retains significant remnant polarization, enabling it to generate electrical charges under mechanical stress and exhibit piezoelectric functionality.

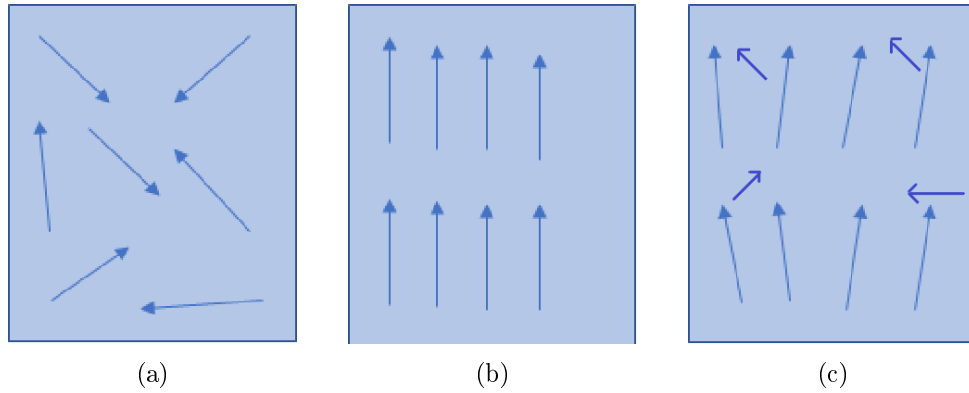


Figure 2.5: Poling process in piezoelectric material. (a) Before polling $T < T_{Curie}$. (b) At polling $T = T_{Curie}$. Saturation state. (c) After polling $T < T_{Curie}$. Remanent state.

2.3 Piezoelectric Constants and Coupling Modes

Different piezoelectric materials are commonly used for research purposes and are commercially available as well. For example, single crystal (e.g., quartz), piezoceramic (e.g., lead zirconate titanate or PZT), thin-films (e.g., sputtered zinc oxide), screen printable thick-films of piezoceramic powders and polymeric materials such as polyvinylidene fluoride (PVDF) [27]. Lead zirconate titanate (PZT) is the most commonly used piezoelectric ceramic for energy harvesting. This is because PZT has high power conversion efficiency and a high Young modulus. However, extreme brittleness and weakness under tensile stresses make it unsuitable for some situations

where a high curvature in the piezoelectric material is required [28]. On the other hand, Polyvinylidene fluoride (PVDF) is a piezoelectric polymer with quite impressive flexibility. One disadvantage of PVDF is that the conversion efficiency is quite low compared to PZT, because PVDF (Polyvinylidene Fluoride) is a lightweight and flexible polymer with piezoelectric properties, but its piezoelectric conversion efficiency is significantly lower compared to ceramic-based materials like PZT (Lead Zirconate Titanate). This is due to PVDF's lower piezoelectric coefficients and weaker ability to generate an electric charge under mechanical stress. Applying initial stress or deformation to PVDF improves its alignment of dipoles and enhances the piezoelectric response. This results in better charge generation and increases its power generation efficiency. However, even with these improvements, PVDF's efficiency typically remains much lower than that of PZT, which has inherently stronger piezoelectric properties. [27]. For comparison, PZT materials can have piezoelectric coefficients (d_{33}) in the range of 300-600 pC/N, while PVDF coefficients are around 20-30 pC/N.

Equation 2.2 shows the key factors upon which a piezoelectric material is categorized. The piezoelectric strain constant d , which shows the relation between strain m produced concerning the applied electric field V .

$$d = \frac{\text{strain produced}}{\text{applied electric field}} = \frac{m}{V} \quad (2.2)$$

For piezoelectric materials, the linear constitutive piezoelectric equations for extensive strain x , electric displacement D (the same as polarization P in ferroelectric) and the intensive stress X and the electric field E can be expressed in equation 2.3 and 2.4 [29].

$$x = s^E X + dE \quad (2.3)$$

$$D = dX + \epsilon_0 \epsilon^X E \quad (2.4)$$

where s^E and $\epsilon^X = \epsilon^r$ are the elastic constants and the relative permittivity, d is the piezoelectric constant. The two common piezoelectric constants are d_{31} or d_{33} , where d_{33} shows the coupling between stress and polarization in same direction, while in d_{31} the electric field polarization is aligned along the 3-direction, through the thickness of the beam and the mechanical vibrations cause strain in the 1-direction. While the ϵ_0 is the permittivity in vacuum. Equation 2.3 is used for the direct piezoelectric effect in which stress is applied, and electric charge is produced in the output. In this study, equation 2.3 will be used. A few constants are explained below, called figures of merits, which are important to consider.

2.3.1 Piezoelectric Strain Constant d

When external electric field E is applied on a piezoelectric material then as a result a strain x is induced, this is important in actuator applications. So, the equation 2.3 can be expressed as equation 2.5.

$$x = dE \quad (2.5)$$

2.3.2 Piezoelectric Voltage Constant g

In contrast to the strain constant, when external stress is induced then as a result electric charges will appear at output. These charges are called piezoelectric voltage, and this constant is named g . This is important when the device is used as a sensor. So, the equation 4 can be expressed as equation 2.6.

$$E = gX \quad (2.6)$$

Taking into account the relation, D (or P) = $d X$, we obtain an important relation (equation 2.7) between g and d .

$$g = \frac{d}{\epsilon_0 \epsilon_r} : \text{where } \epsilon_r \text{ is relative permittivity} \quad (2.7)$$

2.3.3 The Electromechanical Coupling Factor k (Energy Transfer Coefficient)

The energy transfer coefficient can be expressed as the ratio of stored mechanical energy to the input electrical energy (equation 2.8), or it can also be expressed as stored electrical energy to the input mechanical energy ((equation 2.9).

$$k^2 = \frac{\text{stored mechanical energy}}{\text{input electrical energy}} \quad (2.8)$$

$$k^2 = \frac{\text{stored electrical energy}}{\text{input mechanical energy}} \quad (2.9)$$

For sensor applications, we use equation 2.9, when external stress X is applied to the piezoelectric material, charge displacement occurs, generating an electric field E . This field remains unless charge is lost through leakage or an external circuit. If the material is then relaxed, the displaced charge and electric field naturally return to zero. However, if charge is removed while under mechanical load, it will reappear when the material returns to its relaxed state. This process highlights the interaction between mechanical stress and electrical energy storage in piezoelectric materials. In equation 2.9, the input mechanical energy will be $\frac{1}{2S^E X^2}$ per unit volume, and the stored electrical energy per unit volume under zero electrical field (short circuit shown in figure 2.6(left) can be obtained integrating the equation 2.4, we get the result in equation 2.11, which is based on the piezoelectric constants. Then equation

2.9 becomes as equation 2.11:

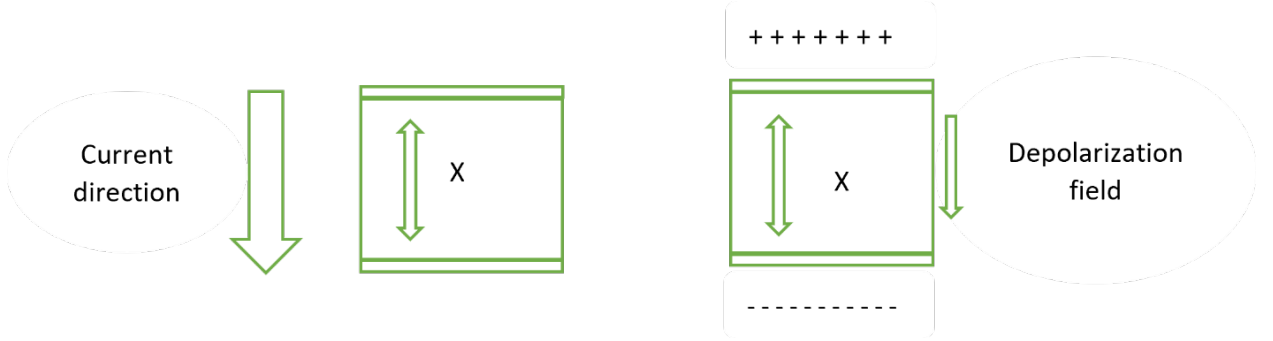


Figure 2.6: (Left) Short circuit case, and (right) open circuit case.

$$\frac{1}{2} \frac{D^2}{\epsilon_0 \epsilon_r} = \frac{1}{2} \frac{(dX)^2}{\epsilon_0 \epsilon_r} \quad (2.10)$$

$$k^2 = \frac{\text{stored electrical energy}}{\text{input mechanical energy}} = \frac{\frac{1}{2} \frac{(dX)^2}{\epsilon_0 \epsilon_r}}{\frac{1}{2} S^E X^2} \quad (2.11)$$

$$k^2 = \frac{d^2}{\epsilon_0 \epsilon_r} S^E \quad (2.12)$$

In the case of the open circuit shown in Figure 2.6 (right), when a mechanical stress is applied, the piezoelectric material generates an internal electric field, resulting in a surface charge buildup. This charge creates a 'depolarization field' that opposes the polarization caused by the mechanical stress. However, since the circuit is open, there is no external path for the charge to flow and neutralize. Instead, the accumulated surface charge gradually leaks away due to the material's inherent conductivity and imperfections, leading to charge dissipation over time. This leakage causes the internal electric field to diminish, and the material returns to a relaxed state, minimizing the net polarization and displacement (D). The displacement (D) eventually approaches zero, indicating that the electric field has reached equilibrium, hence $D = 0$. The

equation 2.4 becomes [29].

$$E = -\frac{d}{\epsilon_0 \epsilon_r} X \quad (2.13)$$

The relation for the open circuit case can also be derived using general equations. We know that the polarization is directly proportional to the induced stress X where d is the piezoelectric strain constant, as shown in equation 2.14. We know from the general equation of a capacitor 2.15, the polarization equation where P is inversely proportional to area A and the equation for stress in equation 2.16 and 2.17 respectively. Substituting equation 2.16 and 2.17 in equation 2.14. We get another equation for Q shown in equation 2.19.

$$P = dX \quad (2.14)$$

$$Q = CV \quad (2.15)$$

$$P = \frac{Q}{A} \quad (2.16)$$

$$X = \frac{F}{A} \quad (2.17)$$

$$\frac{Q}{A} = \frac{dF}{A} \quad (2.18)$$

$$Q = dF \quad (2.19)$$

From equation 2.19 we can conclude that the accumulated charge Q is independent of area A . The electric field is constant in equation 2.13, so voltage depends upon induced stress X , therefore open circuit voltage will also be constant as shown in equation 2.7. In sensor applications, open circuit voltage is measured to justify the performance. Therefore, an equation for voltage is required. Substituting equation

2.15 into 2.19, we get equation 2.20.

$$CV = dF \quad (2.20)$$

We know that the equation for the capacitance of a parallel plate capacitor shown in equation 2.21.

$$C = \frac{\epsilon_0 \epsilon_r A}{t} \quad (2.21)$$

where t is the thickness of the layer. Placing the value of C in equation 2.20, we get the open circuit voltage (equation 2.22). Where d is the piezoelectric constant (in our case: d_{31}) and ϵ_r is the relative permittivity of the piezoelectric polymer (in our case: $\epsilon_r = \epsilon_{PVDF-TrFE}$) and the stress X . If the X and strain constant d do not change, then we get a linear relationship between the open-circuit voltage and the thickness of the piezoelectric material in equation 2.23.

$$V_o = \frac{dFt}{\epsilon_0 \epsilon_r A} = \frac{dX}{\epsilon_0 \epsilon_r} t \quad (2.22)$$

$$V_o \propto t \quad (2.23)$$

2.3.4 Difference between d_{31} and d_{33}

As piezoelectric materials are anisotropic, the constant's (d_{31} and d_{33}) values are not fixed but vary with time, applied stress, and temperature. Also, the constants have different values in different orientations related to different poling directions and the applied mechanical stress direction. This results in piezoelectric coupling modes, i.e., 31, 33. As shown in figure 2.7.

Figure 2.7(left) shows the d_{31} mode on a block where the applied force is perpen-

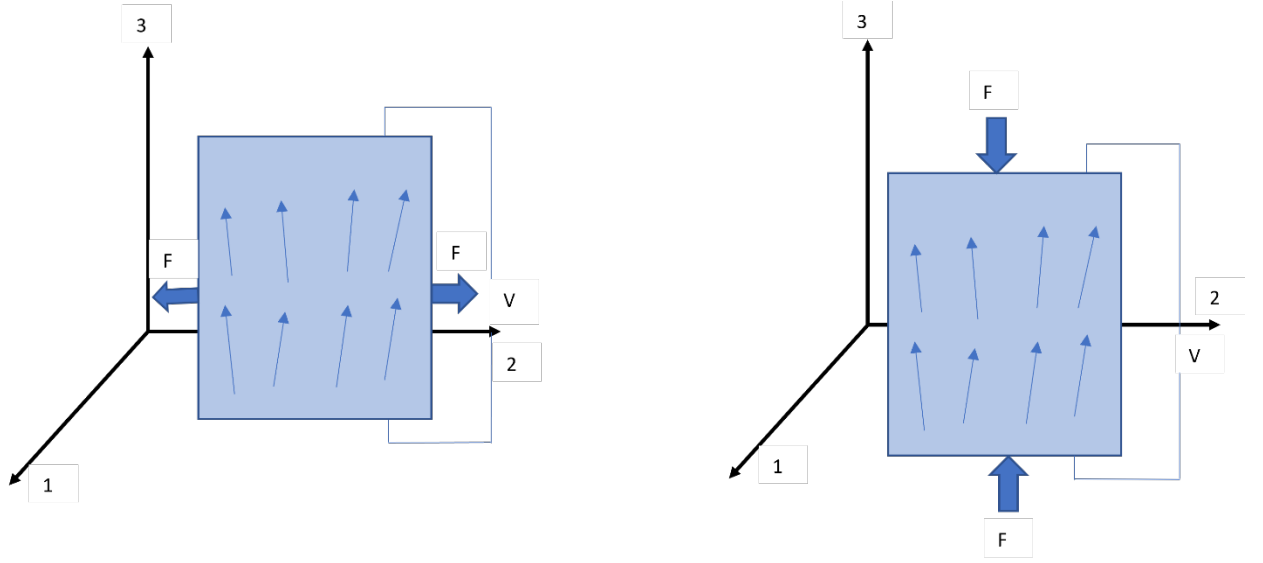


Figure 2.7: Two modes of operation of piezoelectric materials depending on direction of polarization, and mechanical stress (left) 31 mode (right) 33 mode.

dicular to the poling direction. This is an example of bending deformation. In figure 2.7(right), it is clear that in d_{33} modes, the applied force is parallel or anti-parallel to the poling directions. This is an example of piezoelectric block compression poled on its top and bottom surfaces.

Electro-mechanical coupling is higher in d_{33} modes, but the d_{31} mode is better than d_{33} . Because in d_{31} modes, low resonant frequencies can be achieved easily, which is a better match with the ambient vibration frequencies of the natural environment. Also, small applied forces can results in large mechanical strains to increase the performance. Based on the these advantages, in the d_{31} mode, practical energy harvester designs like bimorph or unimorph can perform better [30,31].

2.3.5 Piezoelectric Molecular Structure

Applied stress can cause aging in ceramic materials compared to ceramic and polymer materials. Soft piezo-ceramic materials like PZT-5H are more prone to stress

than harder PZT-5A. Additionally, temperature is a limiting factor because polling tends to decrease above the Curie temperature, reducing the piezoelectric properties. Crystal formation varies in terms of crystal orientation and ion spacing between different crystals. However, carbon-based long-chain polymers exhibit excellent flexibility compared to single-crystal ceramics. Due to long chains, polymers can withstand higher induced strain, which gives them superiority over ceramic materials. Extensively studied polymers are PVDF, PVDF-TrFE, and its derivatives like polylactic acids (PLA). Figure 2.8 shows PZT, PVDF, and PVDF-TrFE crystal and molecular structure [1]. Table 2.1 [1,27,32] lists some important piezoelectric properties. The table highlights the differences in the properties among common piezoelectric materials. PZT-5H exhibits the highest piezoelectric coefficient d_{33} , making it highly effective for applications requiring strong piezoelectric responses, while ZnO has lowest d_{33} , limiting its performance. PZT materials also have significantly higher relative permivity compared to PVDF, which makes PZT suitable for applications requiring high dielectric constants. However, PVDF stands out for its outstanding mechanical flexibility, ideal for flexible applications, while PZT materials are brittle. The significant difference in their Curie temperatures changed the nature of their applications. PZT is well suitable for high temperature environments like aerospace, industrial monitoring systems or engine sensors, while PVDF or its co-polymers are ideal for flexible customer based applications. And lastly PVDF based materials shows high g_{33} , which favors energy-harvesting applications, while PZT material requires high force for vibration.

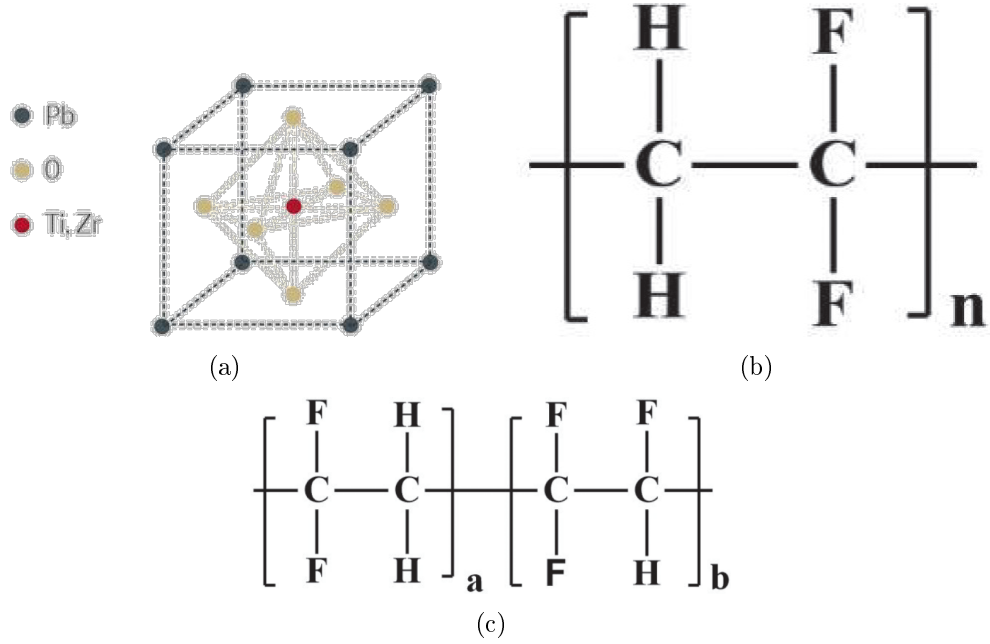


Figure 2.8: (a) Single crystal structure of PZT. (b) Molecular structure of PVDF. (c) Molecular structure of PVDF-TrFE [1].

2.4 PVDF-TrFE (Copolymer of PVDF) and Importance of β -phase

PZT is the most used piezoelectric material because of its high piezoelectric properties. Depending on applications, piezoelectric materials can be tailored to enhance their performance. In the case of ceramic materials, a tailored composite material is called multi-phase, which shows constituent phases for the original crystal and the doped crystal. Two phases make up a composite material: the first one is called "matrix, which surrounds the other phases and is continuous, while the second is the dispersed or discrete phase, which is more often known. The composite materials' characteristics depend on the components' characteristics, their relative quantities, and the geometry of the dispersed phase. The dispersed phases' geometry depends on the particles' form, size, distribution, and orientation. Nowadays, the interest is shift-

Table 2.1: Coefficients of common piezoelectric materials.

Property	PZT-5H	PZT-5A	BaTiO ₃	ZnO	PVDF	PVDF-TrFE
d_{33} (pC N ⁻¹)	593	374	149	14.3 - 2.67	-33	-25 - 40
d_{31} (pC N ⁻¹)	-274	-171	78	-5.43	23	12 - 25
g_{33} (Vm N ⁻¹)	19.7	24.8	14.1	1.7	330	380
g_{31} (Vm N ⁻¹)	-9.1	-11.4	5	0.36	216	232
k_{33}	0.75	0.71	0.48	-	0.15	0.29
k_{31}	0.39	0.31	0.21	0.33	0.12	0.16
Relative permittivity (ϵ/ϵ_0)	3400	1700	1700	-	12	18
Piezoelectricity	High	High	-	-	Low	-
Mechanical flexibility	Poor	Poor	-	-	Outstanding	-
Curie temperature (°C)	386	386	-	-	80	-

ing towards polymer-based materials. PVDF and its copolymers have shown great potential due to their unique properties, such as flexibility, environmental friendliness, chemical stability, and versatility. In performance, the output results of PVDF-based polymers are relatively lower than PZT-based ceramics, but there is a need to enhance the piezoelectricity of polymer composites. So, for the first time, the term crystal phase was introduced for polymers to explain the unit cell formation to define the piezoelectricity [2].

In pure form, PVDF is a thermoplastic piezoelectric polymer that can be crystallized into at least four distinct forms. The most common form is its non-polar form, which is usually obtained after the melting of PVDF. Stretching the polymer results in the electro-active crystal structure of PVDF. On the other hand, the copolymer P(VDF-TrFE) crystallizes into a piezoelectric form directly from the melt without the need for stretching [33].

There are five known phases that the PVDF exhibits, i.e., α , β , γ , δ , and ϵ . From these, the polymers commonly exist in α -phase. At the same time, β is the

most important phase, which is responsible for the piezoelectricity. The presence of β -phase activates the piezoelectricity. The α -phase crystals are called monoclinic and are in the formation of TGTG, in which the piezoelectricity is inactive. In the *beta* phase, the unit cells form orthorhombic TTTT formation, which activates the piezoelectricity. γ -phase also has an orthorhombic unit cell with T3GT3G formation. δ -phase is the polar analogue of α -phase, while ϵ -phase is the anti-polar analogue of δ -phase [34,35]. In PVDF-based polymers, the transformation or formation of β -phase from α -phase has its significance. Figure 2.9 shows a molecular structure of α and β phases. In the α -phase, the polymer chains exhibit a non-polar zig-zag conformation due to the symmetrical distribution of fluorine and hydrogen atoms around the carbon, resulting in weak or no piezoelectricity. In contrast, the β -phase features an all-trans polar conformation with aligned dipoles, where the fluorine atoms are oriented on one side of the chain. This structure enhances the piezoelectric and ferroelectric properties, making the β -phase more suitable for piezoelectric applications.

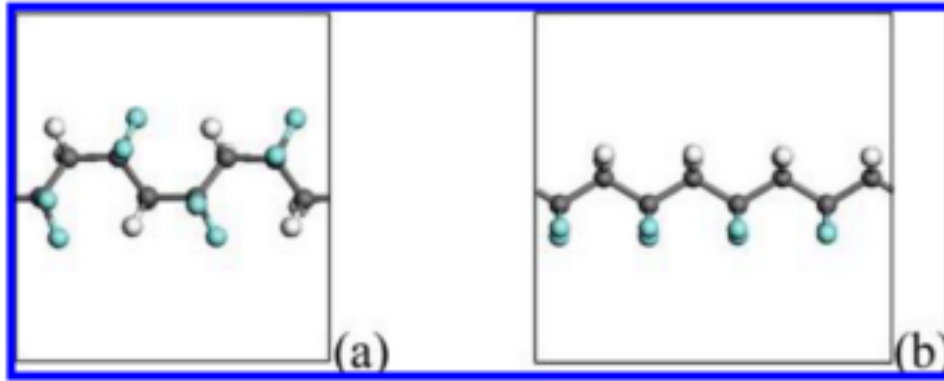


Figure 2.9: Molecular structure of [2] (a) α -phase. (b) β -phase.

Chemically, TrFE can be explained as $CH_2=CH_2$, while VDF consists of $CF_2=CH_2$. PVDF-TrFE is the copolymer of PVDF, and different molar concen-

trations of PVDF and TrFE are available. VDF (vinylidene fluoride) and TrFE (trifluoroethylene) can be obtained by the polymerization process. Basically, in PVDF-TrFE, the unit cells repeat in a chain formation. Figure 2.9 (a, b) shows the molecular structures for PVDF and PVDF-TrFE. At the same time, figure 2.10 shows the simple polymerization process of PVDF-TrFE. The molecular structure of PVDF-TrFE

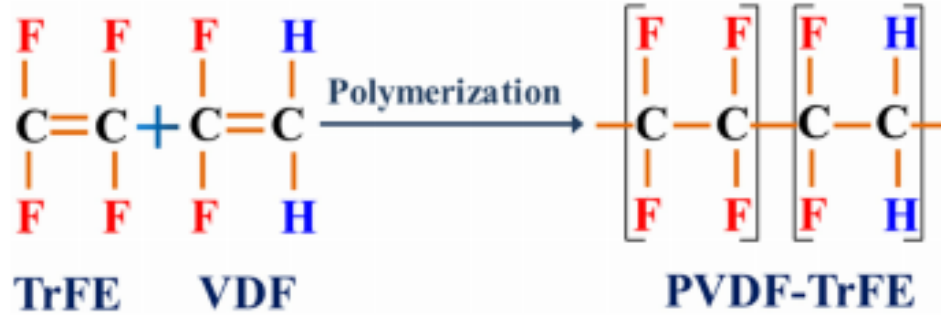


Figure 2.10: Polymerization process of PVDF-TrFE [2].

has a chain structure as compared to PVDF. This means that PVDF-TrFE is more crystalline, responsible for higher couple factor [36]. The molar ratio of VDF/TrFE also plays a vital role in piezoelectricity. The bonding of TrFE with VDF leads to the β -phase. This means the film can be polarized without stretching [28, 37]. So the more the presence of β -phase, the more it has piezoelectricity [38]. Further, the piezoelectricity can be increased by different methods, e.g., annealing at various temperatures, applying DC voltage, etc. The vital thing is that PVDF-TrFE should be annealed below its melting temperature, as at Curie temperature, its phase changes from ferroelectric to paraelectric [39]. This is why a two step annealing process is recommended, that in the first step anneal it below 80°C and to have smooth layer and then the annealing the film below it's annealing temperature [47]. At Curie temperature it may be helpful to increase it's piezoelectricity but annealing close to the Curie temperature range and beyond will cause the crystal structure to change and

will result in melting.

2.5 Applications of PVDF-TrFE

piezoelectric polymers have relatively less piezoelectric output than PZT, but the polymers have high dielectric breakdown strength, cost-effective fabrication, and, most importantly, flexibility. This makes it more prominent in various biomedical, mechanical, and flexible electronics applications.

Researchers have managed to store energy as an energy storage device from the ambient vibrations produced by the polymer films, which are widely used in electronic devices such as sensors, actuators, and transducers, as well as in biomedical applications. Figure 2.11 shows some applications commonly used in industry and research.

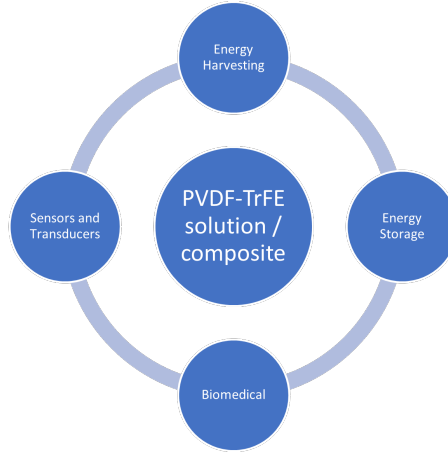


Figure 2.11: Applications of PVDF-TrFE.

2.5.1 Energy Harvesting / Energy Storage Applications

Self-powered electronic gadgets operate by converting external kinetic energy to electrical energy. Piezoelectric energy harvesters have established a solid place among

different energy-seeking methods because of their flexibility, small size, and straightforward processing methods. One reason for polymers' widespread application, especially PVDF-TrFE, in energy harvesting is their superior piezoelectric and electrostatic qualities.

Researchers are finding ways to increase the performance of PVDF-TrFE, by employing hybrid material solutions instead of using PVDF-TrFE alone. A hybrid solution of PVDF is used to enhance its piezoelectric properties while retaining its flexibility, chemical stability, and ease of fabrication, making it suitable for advanced applications like sensors and energy harvesting. A hybrid solution consists of a mixture of PVDF-TrFE solution and metal oxides such as zinc oxide (ZnO), graphene oxide (GO), multi-walled carbon nanotubes (MWCNTs), etc... In [62], Wang et al. used PVDF-TrFE nano-fibers and mixed with PDMS/MWCNT to make a hybrid solution. That solution was then used to fabricate a flexible nano-generator. Under a force of 5 N, the device produced a 25 V output peak to peak voltage with a 98.56 μW power. Similarly, in [63], Turdakyn et al. fabricated a nano-generator based on PVDF-TrFE polymer. The device produced 25 V peak-to-peak voltage when 3N force was applied and the power density of 125 nW cm⁻² at 6N load.

2.5.2 Sensor Applications

A sensor fabricated using piezoelectric material is called a piezoelectric sensor. Which can work in both piezoelectric and pyroelectric domains. The applications include pressure sensors, temperature sensors, and measurement of physical quantities due to their comprehensive frequency response.

Sharma et al. [64] fabricated a PVDF-TrFE-based pressure sensor using standard lithographic steps. The sensor has a fast recovery time of 0.17 seconds and covers

a broad pressure range of 0-300 mmHg. For E-skin applications, a PVDF-TrFE-based non-contact temperature sensor was fabricated by Marchiori et al. [65]. Adding PEDOT: PSS enhanced the stretching capability and produced a 13 mV pyro-electric voltage in 5 mW at 830 nm infrared illumination.

2.5.3 Bio-Medical Applications

PVDF-TrFE-based devices are also being used in biomedical applications. For example, Li et al. [66] made structural support for bone using the electro-spinning method for neural tissue engineering. Mechanical deformations produce an electrical charge used to repair defective bones and tissues. Similarly, PVDF-TrFE-based scaffolds were fabricated for cardiac tissues in [67]. The function of this sensor was to support the cardiac myocyte culture and increase the efficiency in the assembly of cardiac tissues.

Chapter 3

Design and Fabrication of Cantilever Based Structure

This chapter focuses on the general theory of forced excited devices and design of piezoelectric based devices. The materials required to form a piezoelectric solution and the deposition process of the solution onto a host. In this chapter the important aspect β -phase of the piezoelectric materials are also explained in detail.

A standard cantilever beam is generally used as a base to demonstrate the working principle of a sensor. For thick polymer films, the base for the piezoelectric film may not be required. However, a base is needed for a few micron-thick polymer films and scales of cm in length. In a typical piezoelectric sensor, the piezoelectric film is sandwiched between two electrodes, serving as connections and charge collectors. When a sinusoidal excitation force is applied to the free end of the cantilever beam. A voltage signal is produced by the vibrating cantilever beam, which contains piezoelectric material. Piezoelectric materials are used in engineering applications under both open-circuit and closed-circuit conditions, each serving different purposes. In open-circuit conditions, the electrical circuit is incomplete, so no current flows, but

the material generates an electric charge or voltage in response to mechanical stress. This property is utilized in applications like vibration sensors, where the voltage indicates mechanical forces, and in actuators, where an applied voltage causes mechanical movement. In closed-circuit conditions, the circuit is complete, allowing current to flow, which is essential for applications like resonators, where oscillations at specific frequencies are sustained, and ultrasonic motors, which use mechanical vibrations for motion. Thus, open circuits are ideal for sensing and signal generation, while closed circuits are suited for energy transfer and continuous operation.

3.1 Lateral Vibrations in Cantilever Beams

There are, in general, two conditions of vibration; in the first condition, the structure vibrates freely by distributing from its state of equilibrium and vibrating with its own natural frequency without employing external force, while in the second condition the structure vibrates under forced excitations. In the following case, the forced excitation method will be discussed in detail [40].

When a piezoelectric material is deposited on a host structure, then that structure is called a coupled structure. The deformation of the coupled structure by applying external force or by voltage produces shear force. In a free body diagram of an element of a beam shown in figure 3.1 [40], in which a shear force is represented by $V(x,t)$, which causes the bending moment $M(x,t)$ and $f(x,t)$ is the external force excitation, where $w(x,t)$ represents the displacement. Due to force, the inertia will be produced in the beam element mentioned in equation 3.1.

$$\rho A(x) dx \frac{\delta^2 w}{\delta t^2}(x, t) \tag{3.1}$$

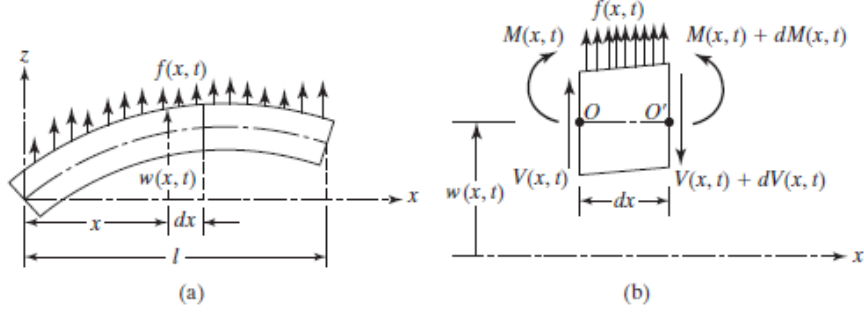


Figure 3.1: (a) Free body diagram of bending beam. (b) segment of beam. [40]

After solving this equation in the z -direction, we get equation 3.2, which explains the relationship between bending moment M , and the force excitation $f(x, t)$ [40].

$$-\frac{\delta^2 M}{\delta x^2}(x, t) + f(x, t) = \rho A(x) \frac{\delta^2 w}{\delta t^2}(x, t) \quad (3.2)$$

From the Euler-Bernoulli equation, we have the expression for the bending moment and deflection as shown in equation 3.3: where E is the Young's modulus and I is the moment of inertia of the uniform beam [40].

$$M(x, t) = EI \frac{\delta^2 w}{\delta x^2}(x, t) \quad (3.3)$$

By substituting the equation 3.3 into equation 3.2, we get equation 3.4 for forced lateral vibration of a uniform beam.

$$EI \frac{\delta^4 w}{\delta x^4}(x, t) + \rho A \frac{\delta^2 w}{\delta t^2}(x, t) = f(x, t) \quad (3.4)$$

In case of free vibration $f(x, t) = 0$. The superposition principle determines the natural frequencies in a forced vibration solution. Therefore, the deflection can be expressed as equation 3.5, where $w_n(x)$ is the n th normal mode and $q_n(t)$ is the

generalized coordinate in the n th mode equation 3.6 represents the modes of the uniform beam [40].

$$w(x, t) = \sum_{n=1}^{\infty} w_n(x) q_n t \quad (3.5)$$

$$EI \frac{\delta^4 w_n(x)}{\delta x^4} - w_n^2 \rho A w_n(x) = 0; \text{ where } n = 1, 2, 3 \dots \quad (3.6)$$

3.1.1 Frequency Modes using COMSOL Simulation

Considering the Euler-Bernoulli equation of forced excitation, the cantilever dimensions presented in this thesis for the experimental study were solved for the mode shapes and natural frequencies. The cantilever beam has length $l = 5 \text{ cm}$ and width $w = 2 \text{ cm}$, is fixed at one end $x = 0$ while the other end is free to vibrate under forced ground base excitation. The MATLAB-simulated beam results are presented in table 3.1, using Euler-Bernoulli's equation for forced excitation. Equation 3.6 gives frequencies using discrete values of $n = 1, 2, 3 \dots$ based on the structure dimensions and material properties. The results may or may not match with the actual experimental results due to multiple factors, e.g., equipment or system limitations, surrounding environmental effects, human errors, and extra vector movements.

Equation 3.6 was used to calculate the first five modes of the flexible Kapton (polyimide) cantilever beam having dimensions 5cm x 2cm (length x width). The elastic modulus of Kapton is 2.9 GPa, while the moment of inertia was calculated as $3.4 \times 10^{-15} \text{ m}^4$. The simulation results are shown figure 3.2 and the mode values are shown in table 3.1. The approximate location of the laser sensor is shown in the figure 3.2. The laser sensor is responsible for the feedback from the cantilever beam. In the next section, the materials required to make the polymer solution for the piezoelectric cantilever will be discussed.

Table 3.1: MATLAB simulations of cantilever beam of 5cm x 2cm (lxw) using Euler-Bernoulli's equation.

Frequency	MATLAB Simulation Results (Hz)
f_1	1.96
f_2	12.33
f_3	34.54
f_4	67.69
f_5	111.90
f_6	167.16
f_7	233.47

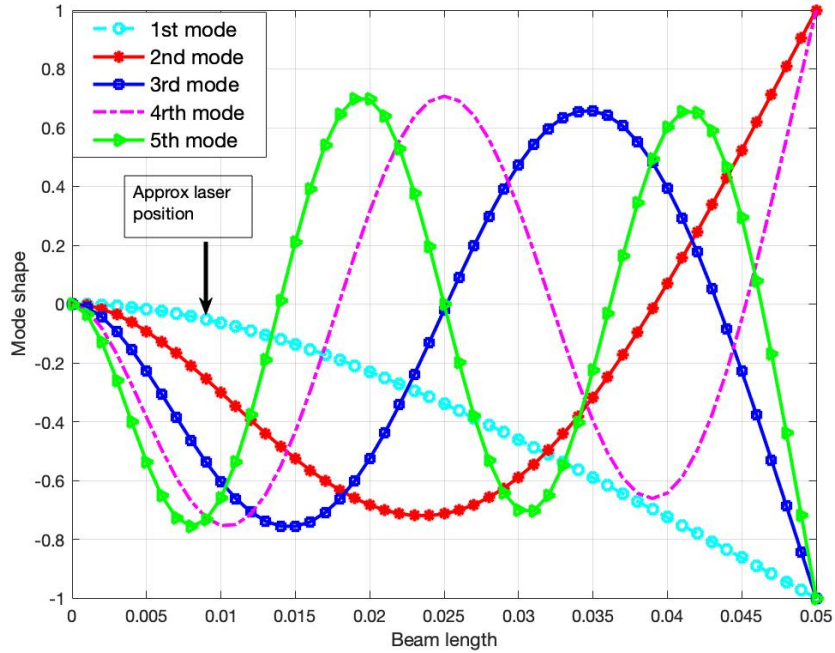


Figure 3.2: First five normalized modes over the length of the flexible beam.

3.2 Materials for Piezoelectric Polymer Solution

The piezoelectric polymer solutions contain a solute, the piezoelectric powder, and the solvent, which dissolves the solute to form a solution. Then, the solution is deposited on host structures using different deposition techniques. There are commercially many solvents available, for example, Dimethylformamide (DMF), Methyl Ethyl

Ketone (MEK), Methyl Isobutyl Ketone (MIBK), and Dimethyl Sulfoxide (DMSO). The chemical properties of the mentioned solvents vary due to their composition and applications. Table 3.2 shows the general chemical properties of the solvents mentioned above and their applications. The solvents mentioned in table 3.2 are mixed

Table 3.2: Chemical properties comparison between solvents and their common uses.

Property/Uses	MIBK (Methyl isobutyl Ke- tone)	MEK (Methyl Ethyl Ketone)	DMF (Dimethyl Formamide)	DMSO (Dimethyl Sulfoxide)
Chemical For- mula	$C_6H_{12}O$	C_4H_8O	C_3H_7NO	C_2H_6OS
Solubility	Immiscible with water	Miscible with many solvents	Miscible with water and other solvents	Miscible with many solvents
Evaporation Rate	Moderate (1.6)	Relatively fast (5.8)	Moderate (con- ditional)	Slow (condi- tional)
Common Uses	Paints, coatings and as solvent	Paints, coatings and as adhesive	Pharmaceuticals and chemical synthesis	Pharmaceutical, cryoprotectant and as a solvent

with piezoelectric powders to make a solution. The solvents are based on mainly chains of hydrogen and carbon along with other elements like sulphur, fluorine, which results in polarity. From the above mentioned solvents, DMF and DMSO solvents are polar solvents, while MIBK and MEK are non-polar solvents. It is necessary understand that for which application the solvent will be used. For example, if the end device is used where the device's interaction with water is not required, the water-soluble solvent will not be used because the solvent in piezoelectric films may leave voids in the film. Also, if the application requires that the piezoelectric material increase in size or swell, then DMF solvent can be used, because DMF solvent penetrates into the polymer matrix causing a change in the overall volume. The other important factor is the evaporation rate at room temperature. From the solvents mentioned above, the evaporation rates show the stability of the solution at room temperature.

From table 3.2, the evaporation rate of MIBK is lower than MEK, which means that the solution containing MIBK as solvent will stay longer at room temperature than the solutions containing MEK as solvent. Similarly, DMF and DMSO evaporation rates are also low, but the rates depend on conditions.

The compatibility of a solvent with the piezoelectric powder also plays an important role. In the present case, generally, the compatibility of PVDF-TrFE with the MEK, DMF, MIBK, and DMSO solvents depends upon many factors, such as concentration of PVDF-TrFE in solvent and duration of exposure at room temperature. As discussed above, the organic solvents differ in their chemical properties, such as evaporation rate, flammable point, and solubility rate. DMF is polar, so it is water-miscible and tends to swell PVDF-TrFE. Using DMF can be advantageous for certain applications where the increased size of PVDF-TrFE is required. In comparison, MEK and MIBK are non-polar solvents, so they do not dissolve in water and do not cause the swelling of PVDF-TrFE. Another important factor is the evaporation rate. MEK has a higher evaporation rate than MIBK, 5.8 and 1.6, respectively, which increases MIBK's stability at room temperature. Depending on the conditions, DMF has a relatively lower evaporation rate than MEK and MIBK, but its chemical resistance is low. DMSO also has a low evaporation rate at room temperature, but the unique property of DMSO is that it also increases the polarity (piezoelectricity). In [41, 42], it was shown that DMSO dissolves the solute quickly due to sulfur's presence and is considered a high dipole moment solvent. When a solute is dissolved in DMSO, due to long chains and better orientation, the crystallinity increases, increasing the piezoelectricity. This was also confirmed experimentally in [43], which showed that the long chains make the solution more stable and the material crystalline compared to the other solvents. This property results in higher output voltage. In [44], it was

discussed that DMSO has low vapor pressure compared to the other compatible solvents, resulting in a slower evaporation rate than for the other solvents investigated in the paper. The FTIR spectra showed that DMSO-based PVDF-TrFE material can have solvent residues after annealing. This was why the final material had long and stable chains and high β presence with TTTT conformation, which increases the piezoelectricity [45]. During the annealing process, any polymer solution's crystallization temperature defines the polymer's phase structure. At low temperatures less than 60 °C, the film growth is slowed due to forming large-size crystal structures, increasing the β presence due to a prolonged evaporation rate. This gives enough time to relax and form the thermodynamic meta-stable β -phase. Above 80 °C, the evaporation rate dramatically increases, giving less time to form long stable chains and decreasing β -phase [45] and reduced piezoelectricity.

In general, the chemical properties of solvents enhance the capabilities of the piezoelectric powder, such as PVDF-TrFE. For example, the unique property of DMSO can be used to create polymer blends with tailored properties. This allows for the modification of the mechanical, electrical, or thermal characteristics of the resulting material. Therefore, DMSO is widely used in sensors, actuators, and biomedical devices. In comparison, MEK and MIBK are often used in coatings and adhesives, while DMF finds applications in chemical synthesis.

In this study, the powdered form of PVDF-TrFE piezoelectric material of molar concentration 75/25 was purchased from PolyK labs. The powder cannot be used directly on any host structure, therefore a solvent is required to make a solution. In this study, MIBK and DMSO were used as solvents.

3.3 Solution Preparation Process

In order to explore the PVDF-TrFE piezoelectric polymer electrically and mechanically, the piezoelectric powder of PVDF-TrFE 75/25 molar concentration was dissolved in MIBK and DMSO solvents. Four solutions were prepared. Solution A was formed using MIBK and DMSO with 0.137 g of PVDF-TrFE powder in 10 ml of solvent, forming a 1.25%*w/v* concentration. The PVDF-TrFE powder completely dissolved after 5 minutes of hand stirring. Solution B, C, and D were formed using MIBK with PVDF-TrFE powder mixed into concentrations of 1.25%*w/v*, 2%*w/v*, and 3%*w/v*, respectively. However, solution mixing was more difficult.

Solution B was formed using MIBK with 0.137 g of PVDF-TrFE powder in 10 ml of solvent, forming a 1.25%*w/v* concentration. The powder did not dissolve using only hand stirring. Magnetic stirring was then used. It was found that at room temperature (23 °C), after 20 minutes of magnetic stirring, the PVDF-TrFE powder did not dissolve. Therefore, the temperature was elevated by putting the beaker with the mixture on a hotplate. The hot plate temperature was increased by 2 °C in steps while stirring the solution for 10 minutes at each step. If the solution was not fully dissolved, then it was further increased another 2 °C for 10 minutes for mixing. When a temperature of 42 °C was reached, the solution dissolved to an obvious solution. Solution A was visibly less viscous than solution B due to sulfur in DMSO. Solutions C and D were also prepared using MIBK but were at higher concentrations. Solution C was at 2 %*w/v* (0.30 g of PVDF-TrFE powder in 15 ml of solvent), and solution D was at 3%*w/v* (0.598 g of PVDF-TrFE powder in 20 ml of solvent). The amount of solvent is higher in C and D solutions because the solvents evaporate during stirring, resulting in low solution volume. The preparations of clear solutions C and D took 1 hour and 2.5 hours at 300 rpm constant magnetic stirring at room temperature.

3.4 Fourier Transform Infrared (FTIR) Spectrum Analysis

As discussed earlier, adding the TrFE chain in PVDF enables the β -phase, which does not require mechanical stretching or high-voltage treatment. Fourier transform Infrared (FTIR) spectrum analysis has been performed to confirm the presence of β - phase presence. FTIR spectrum analysis is a valuable technique in organic synthesis that identifies the compounds/components in a mixture or solution. In principle, when infrared (IR) radiation passes through a solution, a part of the radiation is absorbed by a molecule's covalent bonds of specific wavelengths, which results in a change in the vibrational energy of the bond. The type of induced vibration can be stretching or bending, depending on the atoms in the bond. As a result, we get an absorbance spectrum. Sometimes, the results are also shown in transmittance, which is the reciprocal of absorbance. Different solutions have different solvent molecules with different structures, which gives different spectra. The spectrum is recorded on a graph with wave number [cm^{-1}] recorded on the X-axis, and transmittance or absorbance is recorded on the Y-axis.

In the literature, there are a set standards to identify the FTIR absorption peaks [3] which are listed below:

- a Common peaks
- b Exclusive peaks
- c Dual peaks

Common peaks that appear in all the three α , β and γ phases, exclusive peaks that appear in only one of three α , β and γ phases, while the dual peaks are the results of two different phases. In literature [3], the common range for all three phases are 876-885, 1067-1075, 1171-1182 and 1398-1404 [cm^{-1}]. The exclusive peaks for α , β and

γ phases are mentioned in table 3.3. There are also reports of peaks in the range of 508-512 and 837-841 [cm^{-1}], this depends upon the composition of different samples. It is also reported that the α and β peaks are much stronger than the α phase [3].

Table 3.3: Exclusive and typical peaks for α , β and γ phases [3].

α -phase	β -phase	γ -phase	β -phase (Typical Bands)
410	445	431	431
489	473	482	482
532	1275	811	510
614	-	1234	840
763	-	-	881
795	-	-	1071
854	-	-	1176
975	-	-	1234
1149	-	-	1275
1209	-	-	1401
1383	-	-	-
1423	-	-	-

Fourier transform infrared spectroscopy (FTIR) was used to examine the absorption of infrared energy to determine the molecular vibrational mechanics of a material's crystal structure. The inbound electromagnetic field from the infrared radiation (IR) source interacts with the molecular bonding of the PVDF-TrFE based solution when the electric field component of infrared radiation (IR) and the molecule vibration are perpendicular to one another, resulting in a significant absorption at specific wave numbers. FTIR spectrum analysis for A-E solutions was performed using a Nicolet 6700 FTIR spectrometer. In total, 120 scans were taken for a single sample solution each time. The spectrometer works in a mid-infrared range which is 400-4000 [cm^{-1}] with a resolution of 4 [cm^{-1}] in one minute and the data is analyzed by the software OMNIC 9 (Nicolet 6700) from Thermo Fisher Scientific Inc. After adding three drops of each solution on FTIR's analyzing table, the needle was lowered until it almost touched the drop surface. In FTIR, the needle is a part of the instrument's attenuated total reflectance (ATR) setup. The purpose of this component is to bring

sample into close contact with ATR crystal surface, where the infrared light has maximum interaction with the sample. This improves the signal-to-noise ratio of the measurement. In figure 3.3(a), FTIR spectra for PVDF-TrFE dissolved in DMSO and MIBK and MIBK solutions A-E from 500-1500 $[\text{cm}^{-1}]$ are shown.

Figure 3.3(a) presents the FTIR spectrum of solutions A-E within the range of 500-1500 $[\text{cm}^{-1}]$, highlighting β -phase peaks with dashed lines. A zoomed-in view at 840 $[\text{cm}^{-1}]$ is shown in Figure 3.3(b) for clarity. Table 3.4 summarizes the peak values and absorption amplitudes obtained from the spectrum.

The β -phase peaks of PVDF-TrFE solutions observed in table 3.4 align closely with those reported in the literature [3, 46], even with slight variations due to differences in solution compositions and annealing procedures. Notably, the spectrum in this study was obtained from the solution phase rather than a film, resulting in weaker absorption compared to the annealed films, where peak intensity is higher. For the PVDF-TrFE/MIBK solution, β -phase peaks were identified at 840 $[\text{cm}^{-1}]$, 1278 $[\text{cm}^{-1}]$, and 1290 $[\text{cm}^{-1}]$, corresponding to CF_2 stretching, and strong CH_3 stretching peaks at 1405 $[\text{cm}^{-1}]$ and 1434 $[\text{cm}^{-1}]$. In comparison, the PVDF-TrFE/DMSO+MIBK solution showed dominant β -phase peaks at 1405 $[\text{cm}^{-1}]$ and 1434 $[\text{cm}^{-1}]$, with higher absorption than the MIBK solution alone.

The enhanced absorbance in the DMSO+MIBK solution is attributed to the highly electronegative S=O functional group in DMSO, which has a higher molecular dipole moment than the C=O functional group in MIBK. This higher dipole moment facilitates stronger CH_3 stretching bonds, improving charge transfer at 1405 $[\text{cm}^{-1}]$ and 1434 $[\text{cm}^{-1}]$. Additionally, the long molecular chains in MIBK slow charge transfer, making DMSO more efficient in enhancing piezoelectricity.

In summary, the inclusion of DMSO in the solvent mixture improves the piezo-

electric properties of the solution by increasing charge transfer efficiency, as evidenced by stronger β -phase peaks at key frequencies.

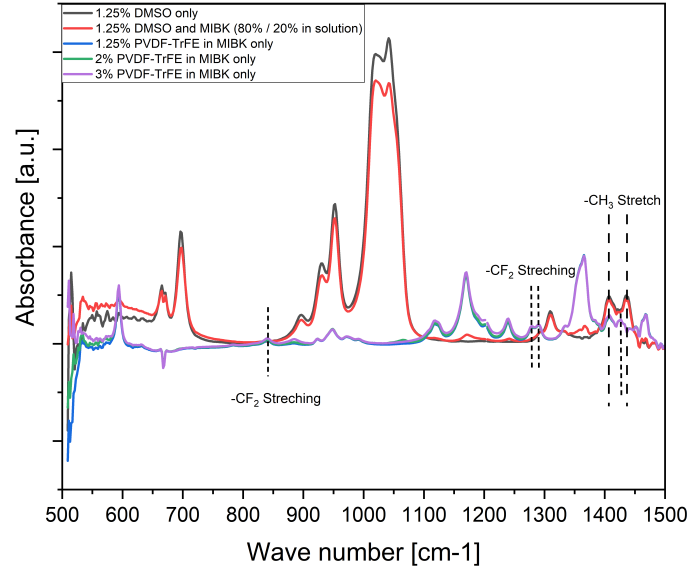
Table 3.4: Absorbance peaks of β -phase for solutions A-E with absorbance amplitude values.

Solution A 1.25% MIBK and DMSO	Solution B 1.25% MIBK Only	Solution C 2% MIBK Only	Solution D MIBK Only 3%	Solution E 1.25% DMSO Only
512 (0.068)	-	-	511 (0.129)	514 (0.146)
-	838 (0.0068)	840 (0.0081)	840 (0.011)	-
-	-	1068 (0.0075)	-	-
-	1280 (0.033)	1278 (0.035)	1278 (0.035)	-
-	1290 (0.038)	1290 (0.039)	1290 (0.039)	-
1405 (0.090)	1405 (0.053)	1405 (0.054)	1405 (0.057)	1405 (0.096)
1434 (0.091)	1425 (0.048)	1427 (0.049)	1425 (0.049)	1434 (0.098)

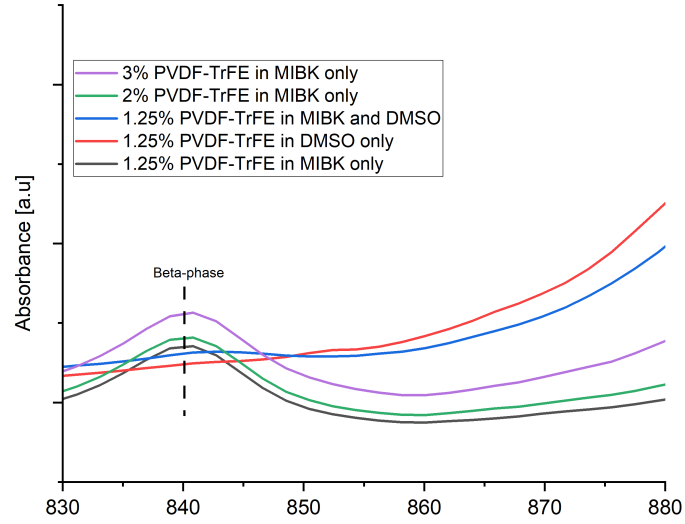
3.5 Solution Deposition Process

The thin film of PVDF-TrFE cannot withstand alone for vibration testing and requires a host structure. Therefore, cantilever structures were explored as substrates for the mechanical and piezoelectric experimental testing of the PVDF-TrFE material. A flexible cantilever consisting of Kapton-HN (Dupont) was used to compare the mechanical performance of the solutions. The thickness of the Kapton cantilever was 127 μm , and 127 μm is the maximum available thickness of the HN family as shown in figure 3.4. For the electrical outputs, a rigid aluminum cantilever with a thickness of 1.54 mm was used as the substrate. The vibration pattern of the stiff aluminum is more consistent, which helps reduce errors compared to the flexible Kapton. Both cantilevers were cut into rectangular shapes, measuring 6 x 2 cm.

Researchers use many piezoelectric solution deposition techniques, such as spin-coating, screen printing, inkjet printing, etc., and sometimes the thick piezoelectric films are glued with metal plates. In the present case, a simple spin-coated technique



(a)



(b)

Figure 3.3: FTIR spectrum of solutions A, B, C, D and E. (b) Zoomed picture at 840 cm^{-1} .

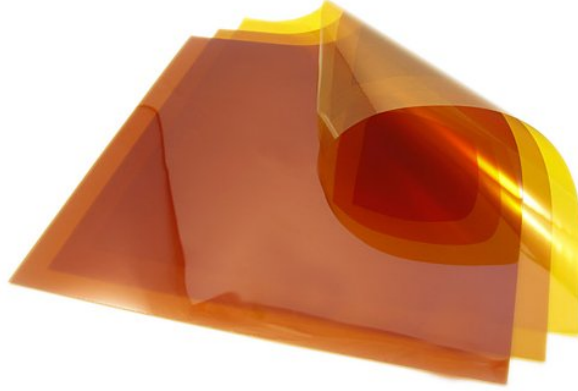


Figure 3.4: Kapton sheet.

was used to deposit the polymer film. The four solutions, A, B, C, and D, were spin-coated on the cantilever at 500 rpm for 200 seconds. For all solutions, a two-step annealing process was used after spin coating. First, for 10 minutes, the sample is annealed in an oven at 50 °C to form a stable crystalline film. This is followed by a 10-minute cooling time at room temperature. Second, the sample is again annealed in the oven at 112 °C for one hour. This two-step process results in the crystallization of the ferroelectric gamma-phase during the first step, and the second step enhances the density of PVDF film [47]. In this way, long-chain formation is possible. The Curie temperature for PVDF-TrFE with a 75/25 molar ratio is 112-121 °C [24]. Therefore, the annealing temperature was kept at 112 °C to avoid changing the material properties. After annealing, the thickness and surface roughness of the polymer films were measured using a KLA Alpha-Step 500 profiler, and the results are shown in table 3.5.

In conclusion, the study explored the mechanical and piezoelectric testing of PVDF-TrFE thin films by depositing them on cantilever substrates to address their inability to withstand vibration testing independently. A flexible Kapton-HN cantilever (127 μm thick) was used for mechanical testing, while a rigid aluminum cantilever

(1.54 mm thick) was employed for electrical measurements, ensuring consistency and reducing errors. The thin films were deposited using a spin-coating technique followed by a two-step annealing process: initial annealing at 50°C for crystallization of the γ -phase, followed by annealing at 112°C for improved film density and long-chain formation. This method preserved the material properties while achieving a stable, crystalline PVDF-TrFE structure. The thickness and surface roughness of the films were measured post-annealing, indicating the effectiveness of the process in optimizing the films for further experimental applications.

Table 3.5: Spin coating results of PVDF-TrFE.

Source	Solvents Used	Annealing Temperature (°C)	RPM	Thickness
Sample A, 1.25%	MIBK and DMSO	10 minutes at 50 °C, followed by 1 hour at 112 °C	500 for 200 seconds	252 nm
Sample B, 1.25%	MIBK	10 minutes at 50 °C, followed by 1 hour at 112 °C	500 for 200 seconds	440 nm
Sample C, 2%	MIBK	10 minutes at 50 °C, followed by 1 hour at 112 °C	500 for 200 seconds	833 nm
Sample D, 3%	MIBK	10 minutes at 50 °C, followed by 1 hour at 112 °C	500 for 200 seconds	953 nm

Chapter 4

Mechanical and Electrical Outputs of Cantilever Based Vibration Sensor

The PVDF-TrFE material was experimentally tested for both mechanical and piezoelectric properties using cantilever structures. To investigate the mechanical characteristics of the PVDF-TrFE solution, a flexible Kapton cantilever with spin-coated PVDF-TrFE polymer was used. For the electrical output rigid substrate testing, a spin-coated aluminum cantilever was used. A ground base shaker was used to drive the vibration on the attached PVDF-TrFE-coated cantilevers at different vibration frequencies and accelerations. Below are the details of the setup used in the experiment.

4.1 Test Setup for Vibration Testing

The testing setup involved a ground base shaker where a cantilever (either made of Kapton or aluminum) was clamped and mounted. A Polytec sensor head with a He-Ne laser of wavelength 633 nm was used to measure the velocity of the vibrating

beam. The laser was focused at a vertical distance of 51.5 cm from the cantilever. The laser spot was placed approximately 1 to 2 cm along the length of the cantilever from its clamp point. The driven vibration characteristics were monitored using a Polytec scanning vibrometer controller and the outputs were analyzed and plotted using an LMS data acquisition center. The shaker system consisted of a U shaped trunnion support base that supported the electrodynamic shaker body. The trunnion allowed the shaker to be configured in different skewed orientations and angles for excitation. Changing the input force was important for exciting structures with vertical and lateral modes that were highly uncoupled. The cantilever (either aluminum or Kapton) had rectangular dimensions of 6 x 2 cm and was mounted using a clamp to the shake platform, which covered 1 cm of the cantilever, leaving a free size of 5 x 2 cm. The system model and test setup are shown in figure 4.1.

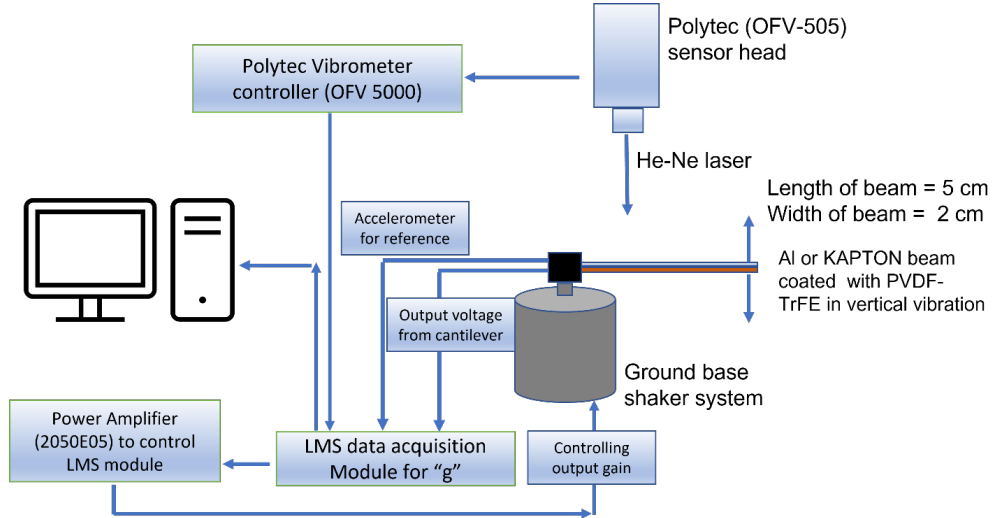


Figure 4.1: The schematic of the test setup used for vibration test.

4.2 Mechanical Results Using Vibration Test

Dynamic response vibration testing is a key method for evaluating the performance of vibration-based sensors by focusing on their response to applied vibrational forces rather than measuring the vibration levels themselves. This technique is particularly useful for identifying resonant modes, where the structure vibrates at its natural frequencies, providing valuable insights into its dynamic properties. In this study, a Kapton cantilever was clamped and mounted on a ground-based shaker (as shown in figure 4.1), which applied controlled vibrational forces at specific gravitational values g . The objective was to understand how the cantilever responds under dynamic conditions, revealing critical vibrational modes and mechanical stability. The testing results help optimize the cantilever's design, ensuring it operates effectively in applications requiring sensitivity to vibrations while minimizing errors due to structural inconsistencies. This approach is crucial for improving the reliability and efficiency of vibration-based sensing devices.

In the vibration testing of flexible structures, the incorporation of a lightweight polymer layer, if characterized by insufficient bending stiffness or that material bends too easily, can worsen resonant vibrational modes due to inadequate structural damping, means that the structure is not effectively dissipating energy during vibrations. As a result, the structure can experience lower amplitude or more pronounced oscillations that deviate from the intended mechanical response. Many groups have studied this issue using analytical modeling based on steady-state forced analysis, transient response, natural vibrations, etc., on piezoelectric flexible structures to understand the vibration problem [48]. However, it is hard to filter the actual data from the noise due to undesired noise. The "noise" here refers to random or unpredictable vibrations or disturbances that interfere with the expected signal, making it harder to accurately

measure or control the system's performance. This noise can cause deviations from the desired response and compromise the system's functionality. The vibration test is analyzed using the frequency response function (FRF) to see the structure's natural response. The FRF analysis determines the resonant frequencies of the vibrating cantilever. A random excitation from 0 Hz to 1500 Hz is employed in vibration testing. A random signal has a continuous spectrum of varying amplitudes. In the output, we get the multiple resonance frequencies, also called spectral density, which includes the noise estimation based on measured data. In practical terms, getting a noise-free estimation response is impossible. In the present case, the data is averaged, with the average number set as 10. Before starting the actual measurements, an important thing which is in the scope of the experiment is that the waveforms of the three devices (a) laser sensor, (b) sensor on test, (c) reference accelerometer should be matched and sinusoidal in nature. If the signals are not matched, then the results are not correct. Testing was first conducted with unit base excitation on Kapton cantilevers coated with solutions A and B, with the results shown in figure 4.3(a). We can see seven frequency modes for the cantilever coated with solution A, ranging from 11.85 Hz to 688.75 Hz. The observation that sample A has two close frequency values, 209.37 Hz and 231.87 Hz, could be due to multiple vibration modes or resonance frequencies being excited simultaneously during the vibration analysis. This may occur because the ground-based shaker could be stimulating the sample in different vector directions, causing the structure to resonate at multiple frequencies. These closely spaced frequencies indicate that the sample is exhibiting a coupled or complex vibrational response, where different modes interact, leading to the appearance of two nearby resonance peaks. For the comparison study, only 209.37 Hz is considered because it has a higher amplitude. For the cantilever coated with solution B, we can see five

frequency modes ranging from 11.91 Hz to 720.50 Hz. The frequencies of cantilevers coated with solutions A and B were closely matched for the first mode but changed at higher modes. A noticeable point is that the measured motion amplitude of the cantilever coated with solution B (MIBK solvent only) is higher than that of the cantilever coated with solution A (MIBK+DMSO solvents). This is due to the different solvent solutions used, which results in the cantilever coated with solution A having reduced amplitude. The cantilever coated with solution B shows more flexibility and greater amplitude up to 224.60 Hz and then drops in amplitude if the frequency is further increased [49]. Another reason that the solution A coated cantilever has less amplitude is that after the annealing, the solution A coated cantilever shows visible bending, as shown in figures 4.2(a) and 4.2(b). It should be mentioned that the cantilever coated with solution B did not exhibit visible bending in its structure.

The same vibration test was repeated with an uncoated Kapton cantilever to

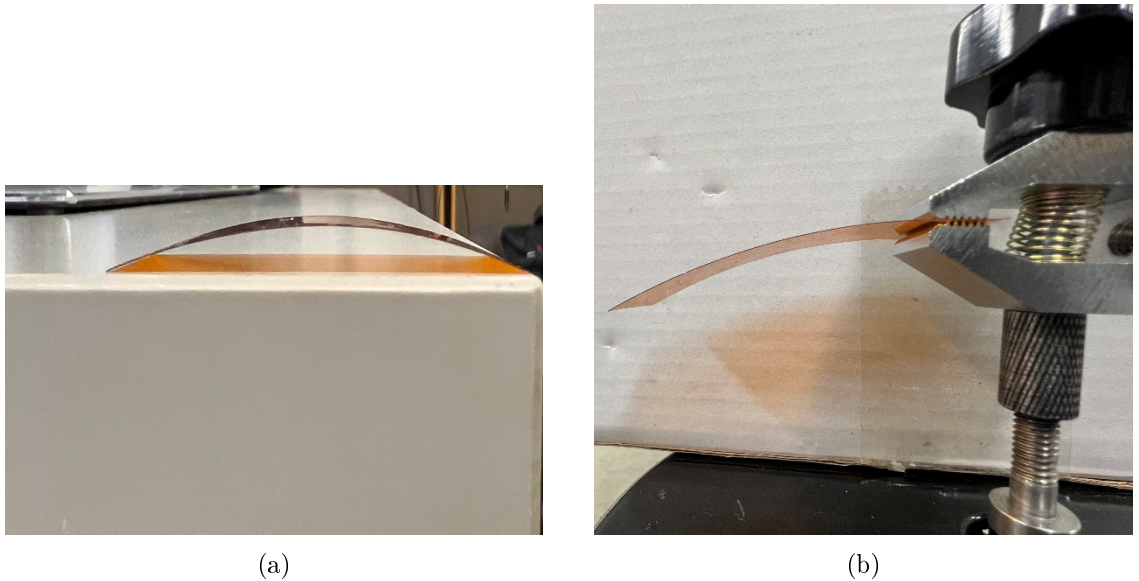


Figure 4.2: (a) Kapton coated with sample A showing bending after the annealing. (b) Bending of Kapton cantilever when clamped.

confirm if these polymer coatings affect the Kapton cantilever's natural frequency

and amplitude. We can see in figure 4.3(a) a higher amplitude for the first mode of the uncoated Kapton cantilever compared to the cantilever coated with solution B. It is more than double that of a cantilever coated with solution A. Figure 4.3(a) shows that the uncoated Kapton cantilever has its highest frequency at 458 Hz with only four modes. This vibration test was also repeated with 2% (sample C) and 3% (sample D) PVDF-TrFE concentrations in MIBK solvent shown in figure 4.3(b). The results are summarized in table 4.1. We can generally see that comparing the MIBK samples B, C, and D, for vibration modes f_3 , f_5 , and f_7 , the frequencies are shifting higher as polymer concentration is increased. Compared with sample A, we see, in general, that this MIBK + DMSO solvent mixture has lower vibration mode frequencies. The experimental frequencies shown in table 4.1 can be compared with the MATLAB simulations shown in table 3.1; we can see that f_1 , f_4 and f_7 from table 3.1 are in a similar range of $f_1 \rightarrow f_3$ of table 4.1 .

In conclusion, the dynamic response vibration testing revealed key differences in

Table 4.1: Natural frequencies of Kapton cantilever at different polymer concentrations randomly excited from 0-1500 Hz at unit base excitation.

Frequency (Hz)	Only Kapton	Sample A MIBK + DMSO with 1.25% Polymer	Sample B MIBK with 1.25% Polymer	Solution C with 2 % Polymer	Solution D with 3 % Polymer
f_1	12.5	11.85	11.91	10	10
f_2	75.78	73.12	77.92	75	80
f_3	230.66	209.37	224.60	227.5	232.5
f_4	—	231.87	—	—	—
f_5	458.0	417.5	432.42	435.0	460.0
f_6	—	570.62	—	—	—
f_7	—	688.75	720.5	767.5	767.5

the vibrational properties of Kapton cantilevers coated with various solutions. Cantilevers coated with solution B (MIBK solvent only) demonstrated greater flexibility and higher amplitude compared to those coated with solution A (MIBK+DMSO

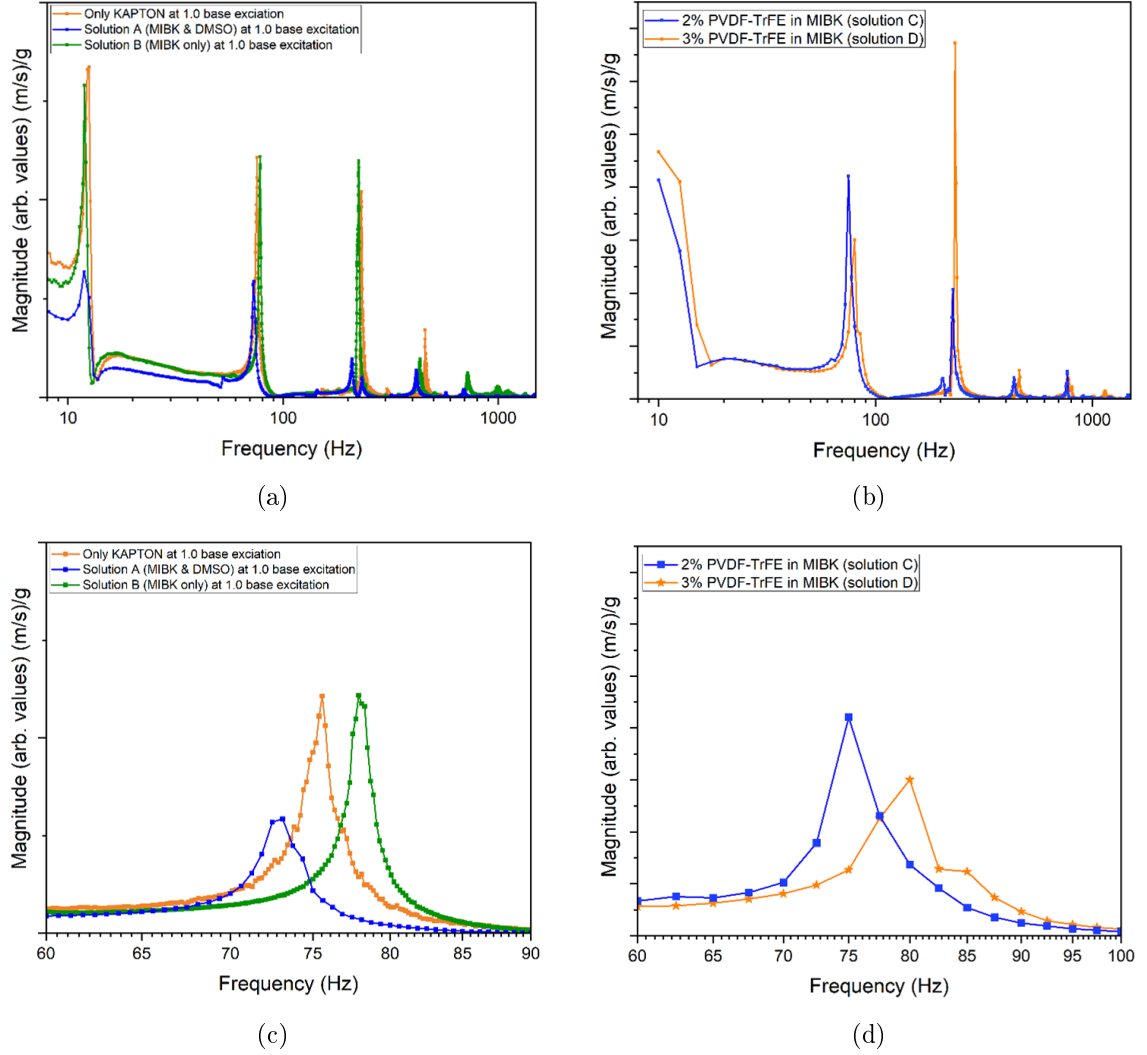


Figure 4.3: Vibration response for Kapton coated cantilevers at 1.0 g base excitation. (a) Response for uncoated Kapton, and Kapton coated with solutions A and B. (b) Response for Kapton coated with solutions C (2%) and D (3%). (c) Zoomed in of (a) for frequencies 60 to 90 Hz. (d) Zoomed in of (b) for frequencies 60 to 100 Hz.

solvent), which showed reduced amplitude due to visible structural bending after annealing. The uncoated Kapton cantilever exhibited the highest amplitudes and fewer vibrational modes, confirming that polymer coatings significantly alter the natural frequency and amplitude of the structure. Increasing PVDF-TrFE concentrations in MIBK (samples C and D) led to higher vibration mode frequencies, indicating that

polymer concentration influences vibrational properties. Comparing experimental results with MATLAB simulations showed good agreement for key modes (f_1 , f_4 and f_7). These findings highlight the impact of solvent composition and polymer concentration on the dynamic behavior of flexible cantilever structures, providing insights for optimizing piezoelectric devices.

4.3 Output Piezoelectric Voltage Results Using Vibration Test

Piezoelectric output measurements were studied using a rigid aluminum cantilever with dimensions 6 x 2 cm because a rigid device would provide more consistent measurements for driven vibration tests. The same setup shown in figure 4.1 was used. The difference is that, now instead of only Kapton based film, there is a whole sensor based on electrodes connected to data acquisition system.

Studies with the 6 x 2 cm rigid cantilever aluminum cantilever required the PVDF-TrFE piezoelectric material to be placed between two electrodes to measure the piezoelectric voltage signal. The aluminum cantilever itself is employed as the bottom electrode. This is then coated with the PVDF-TrFE piezoelectric material. Next, an insulation layer of a photoresist (AZ 1518) is deposited using the spin-coated method to avoid the possible contact of the top electrode with the bottom electrode because one polymer layer deposition may have voids. As per the AZ 1518 datasheet, the thickness will be 1.8 μm at 4000 rpm, but electrodes were still shorted at this thickness. So, next, the spin-coating speed was reduced to 1000 rpm, and the output thickness was approximately 4 μm (as per AZ-1518 datasheet). This thickness solved the electrical shorting of the top and bottom electrodes. Finally, a small patch of silver paint is applied using a brush as a top electrode and allowed to dry at room

temperature. Electrical measurements were performed with rigid aluminum cantilever spin-coated with PVDF-TrFE solutions A, C, and D. The cantilevers were clamped on a ground base shaker where 1 cm was under the clamp, and the rest of 5 cm was suspended in the air.

The four cantilevers were mounted on the ground base shaker and excited at 100 Hz because there are minimum mechanical constraints at low frequencies, and this is also because the calculated resonance frequency of the 6 x 2 cm cantilever is 992.56 Hz. From spin-coating results, we know that the cantilevers have different piezoelectric polymer thicknesses, so, in this case, the output voltages cannot be directly compared until we have the piezoelectric constants (d_{31} and ϵ_{31}). An alternate way to compare is to have the piezoelectric voltage at one frequency and compare the electric fields as $E = V/t$. This is the dividing voltage by the thickness of each structure's polymer film. In this way, the voltage can be normalized because of the thickness effect. The output voltage amplitudes were recorded in the time domain and are shown in table 4.2. Then, the sensitivity (E/g) for the cantilevers can be calculated by the ratio of the electric field and the measured base excitation g of each structure.

Table 4.2: Measured voltages under base excitation at $f = 100$ Hz.

Structure	Voltage (V)	Thickness (t)	Base Excitation (g)	Electrical Field (V/t)	Sensitivity (E/g)
Al cantilever coated with solution A	0.06	252 nm	6.91	2.4×10^5	3.4×10^4
Al cantilever coated with solution C	0.06	833 nm	7.20	7.2×10^4	1.0×10^4
Al cantilever coated with solution D	0.06	953 nm	7.10	6.3×10^4	8.8×10^4

4.4 Piezoelectric Constants Measurement

This experimental investigation aims to measure the piezoelectric constants of PVDF-TrFE film through a detailed measuring procedure. Piezoelectric materials are employed in many applications, such as sensors, transducers, and actuators. To maximize the performance of these devices, it is essential to comprehend and precisely characterize the piezoelectric coefficients S_{11} , E_3 , e_{31} , q_{31} . This study calculated the piezoelectric electrical constants by applying dynamic force to a cantilever. The setup is shown in figure 4.4. The cantilever of area 0.0011 m^2 was clamped on both sides, and a force sensor was attached with the clamp, which is then attached to the base shaker. The direction of the base shaker is set horizontally to produce horizontal directional vibrations to calculate the strain (S_{11}) in one direction. At 100 Hz, the

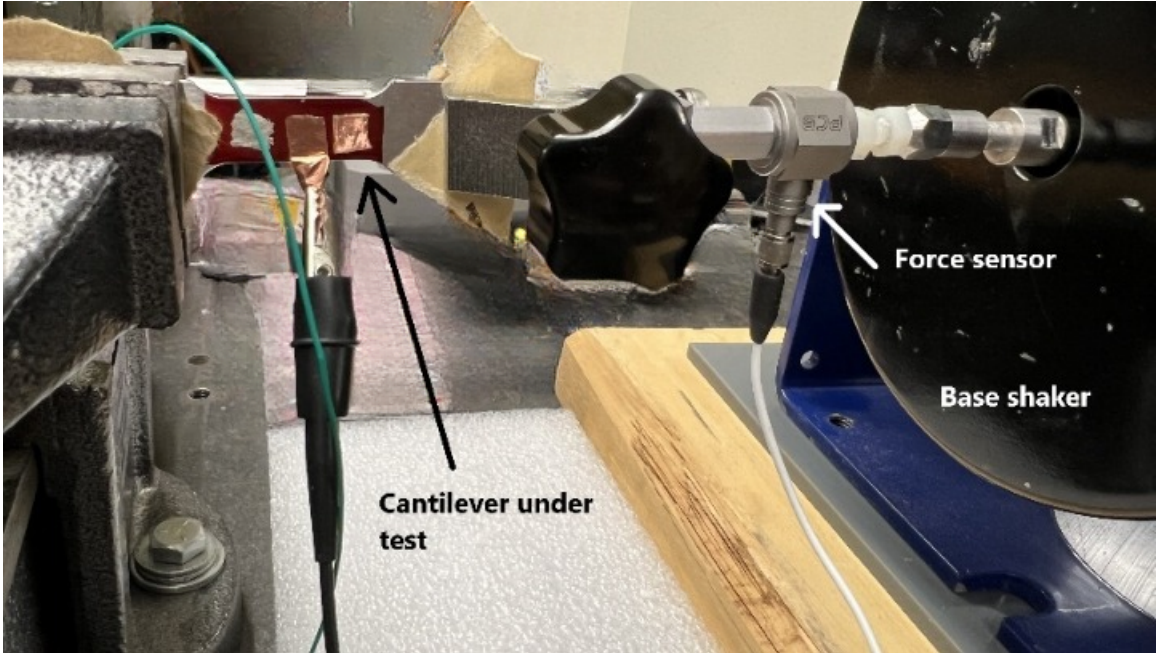


Figure 4.4: The experimental setup for dynamic force test to calculate the force on cantilever.

cantilever beam was excited, and the output piezoelectric voltage (V) and force (F)

were computed. The elastic modulus of the aluminum beam (alloy-5052) was 70.3 GPa. The dynamic force from a force reference was 56 N on a cantilever beam of area 0.0011 m². In equation 4.1, the strain (S_{11}) was determined using the elastic modulus formula. Since the polymer film was formed on a pretty thick piece of aluminum (1.56 mm), there will always be the same strain (S_{11}) for the cantilevers coated with MIBK solution and MIBK+DMSO solution because solutions were deposited on identical aluminum cantilever. Here, S_{11} represents uni-directional strain.

$$S_{11} = \frac{F/A}{E_{Al}} = \frac{56/0.0011}{70.3 \times 10^9} = 7.2 \times 10^{-7} \quad (4.1)$$

After excitation, we get the same output voltage (V_3) of 0.01 V for both structures. We know that the electric field intensity E_3 is the ratio of voltage over thickness (V_3/t), so we get the electric field intensity for the structures coated with DMSO+MIBK solution and only MIBK solution as 3.96×10^4 V/m and 1.05×10^4 V/m respectively. From the piezoelectric constitutive equation, we know the stress-voltage form shown in equation 4.2, where E is the electric field, q is the piezoelectric coupling coefficient from stress-voltage form, D is the applied charge.

$$E = -qS + \epsilon_S^{-1}D \quad (4.2)$$

In the absence of externally applied charge D will be zero, so in terms of the setup configuration the equation 4.2 will become equation 4.3, where E_3 is the electric field in the direction of polar axis and q_{31} is the piezoelectric coupling coefficient from stress-voltage form, where applied stress (1- applied stress) perpendicular to the output voltage (3 - polar axis) and S_{11} is the strain. Equation 4.4 gives the value of

q_{31} .

$$E_3 = -q_{31}S_{11} \quad (4.3)$$

$$q_{31} = -5.5 \times 10^{10} \text{V/m} \quad (4.4)$$

For both cantilevers, the top electrode area was $3.48 \times 10^{-5} \text{m}^2$, and the capacitance was measured to be 0.18 nF. Based on this, the charge density D_3 is $5.17 \times 10^{-8} \text{C/m}^2$, and the total accumulated charge Q is $1.8 \times 10^{-12} \text{C}$. Another piezoelectric constitutive equation is used to determine the piezoelectric coupling coefficient e using equation 4.5 and the stress-charge form. Since no external electric field was applied, $\epsilon_S E = 0$. This allows calculation of e_{31} using equation 4.6.

$$D = eS + \epsilon_S E \quad (4.5)$$

$$e_{31} = \frac{D_3}{S_{11}} = 0.071 \quad (4.6)$$

In summary, table 4.3 shows the measured piezoelectric coefficients using a dynamic force test. We can see a difference in the electric fields of the two devices due to different thicknesses. This results in different values of q_{31} is the piezoelectric coupling coefficient and the dielectric constant (ϵ_r). From these results, we can also confirm that the solution of DMSO and MIBK gives a higher voltage coefficient with fewer dielectric constant values and is more efficient than the MIBK-based solution.

The experimental values in the table 4.3 align well with ranges reported in the literature for similar piezoelectric materials and structures. However exact matching would require comparison with data for materials of the same composition and structure.

For example, the mechanical compliance ($S_{11} = 7.2 \times 10^{-7}$) falls within the ex-

Table 4.3: Measured piezoelectric electrical coefficients excitation at $f = 100$ Hz.

Piezoelectric Coefficient	For 1.25% DMSO+MIBK Based Structure (80% / 20%)	For 3% MIBK Based Structure
S_{11}	7.2×10^{-7}	7.2×10^{-7}
E_3	3.96×10^4	1.05×10^4 V/m
q_{31}	5.5×10^{10}	1.45×10^{10} V/m
e_{31}	0.071	0.071

pected range of polymer-based piezoelectric materials, such as PVDF and its composites, which typically exhibit values between 10^{-7} and 10^{-6} . The electric field output ($E_3 = 3.96 \times 10^4$ and 1.05×10^4 V/m) is also reasonable, as studies on cantilever based PVDF sensors and composite materials have reported electric field strengths in the 10^4 - 10^5 V/m range under similar conditions. The charge coefficient ($q_{31} = 5.5 \times 10^{10}$ and 1.45×10^{10} V/m) is comparable to high performing composite piezoelectric materials, such as ceramic materials $BaTiO_3$, which often shows values between 10^9 and 10^{11} V/m. Similarly, the coupling coefficient ($e_{31} = 0.071$) matches with values observed in PVDF films and composites, which typically range from 0.05 - 0.1. These comparisons suggest that the experimental results are consistent with the values found by other researchers for similar materials and structures.

4.5 Output Piezoelectric Voltage Based on the Change of Frequency

In a separate study, the output of the above structures were also explored at individual frequencies. In a similar manner, the cantilevers were excited at distinct frequencies each time starting from 100 Hz to 2000 Hz using the same experimental setup explained in figure 4.1. This is to see the output voltage response with the change in frequency and to verify that the increase in induced stress in the piezo-

electric film is responsible for the increased output voltage. We can see from table 4.4, that as the frequency increases, the output voltage generated by the piezoelectric material also increases. This behavior is supported by the piezoelectric constitutive equation: $(D = d.\sigma + \epsilon.E)$, where D is the electric displacement, d is the piezoelectric coefficient, σ is the induced stress, ϵ is the permittivity, and E is the electric field. When the electric field (E) is held constant, the electric displacement (D) becomes directly proportional to the induced stress (σ): $D \propto \sigma$. This means that as the induced stress (σ) increases with frequency, the electric displacement (D) also increases, leading to a higher output voltage. The piezoelectric material generates more charge in response to greater mechanical stress, which is why the voltage increases with frequency, assuming other factors (like the electric field) are constant. However, it's important to note that the electric field (E) across the samples is not identical due to the varying thickness of the polymer layers. Since the thickness of the material affects how the stress is distributed, it also influences the electric field generated within the material. A thicker polymer layer may result in a different electric field distribution compared to a thinner one, leading to variations in the generated voltage even if the induced stress is similar. It was observed that at 100 Hz, the voltage outputs of samples A, B and C were nearly identical. This could occur because, at low frequencies like 100 Hz, the cantilever setup across the samples might be near symmetrical and uniform. The excitation at these lower frequencies might not induce a distinct response from each sample, particularly if the samples properties, such as thickness and mechanical characteristics, are similar. At lower frequencies, the vibration modes may be more uniform, resulting in minimal differences in the system's response. However, at higher frequencies, the system's dynamic characteristics become more significant. Differences in the samples properties, such as thickness and electric field distribution,

become more apparent. At these higher frequencies, the system is more likely to engage different resonant modes, and mechanical-electrical coupling is more effectively established. This can lead to variations in the output voltage that are not noticeable at lower frequencies. Therefore, the differences in sample thickness and the resulting variations in electric fields contribute to the observed changes in voltage at higher frequencies.

In table 4.4 for sample A, in which the solution contains DMSO and MIBK solvents, gives the highest voltage of 0.73 V at 2000 Hz, sample C which has only 2% of PVDF-TrFE in MIBK solvent gives highest voltage of 0.28 V while the sample D which has 3% of PVDF-TrFE in MIBK solvent, gives highest voltage at 1500 Hz of 0.75 V while at 2000 Hz, due to system overload the value drops, while all the parameters were kept constant. The output voltages of the cantilevers can not be directly

Table 4.4: Output voltage of the cantilevers at different excited frequencies.

Frequency (Hz)	Sample A	Sample C	Sample D	EF (V/t) for Sample A	EF (V/t) for Sample C	EF (V/t) for Sample D
100	0.06	0.06	0.06	2.38×10^5	7.20×10^4	6.30×10^4
200	0.19	0.14	0.19	7.54×10^5	1.68×10^5	1.99×10^5
300	0.28	0.18	0.30	1.11×10^6	2.16×10^5	3.15×10^5
400	0.36	0.21	0.38	1.43×10^6	2.52×10^5	3.99×10^5
500	0.42	0.23	0.44	1.67×10^6	2.76×10^5	4.62×10^5
600	0.47	0.24	0.50	1.87×10^6	2.88×10^5	5.25×10^5
700	0.50	0.25	0.54	1.98×10^6	3.00×10^5	5.67×10^5
800	0.55	0.25	0.52	2.18×10^6	3.00×10^5	5.46×10^5
900	0.57	0.26	0.61	2.26×10^6	3.12×10^5	6.40×10^5
1000	0.59	0.26	0.63	2.34×10^6	3.12×10^5	6.61×10^5
1500	0.66	0.28	0.75	2.62×10^6	3.36×10^5	7.87×10^5
2000	0.73	0.28	—	2.90×10^6	3.36×10^5	—

compared because all of the cantilevers have different thicknesses. According to the equation 2.23, the open-circuit voltage is directly proportional to the thickness. To solve this problem, a comparison can be made regarding the generated electric field. From table 4.4, we can see that, at 100 Hz, the generated electric field for sample A

is more than three times that the sample C and D, which is because the thickness of the polymer film on sample A is thin as compared to sample C and D and also that the sample A has DMSO solvent which is responsible for increasing the voltage. Similarly, the sensitivity of sample A is higher than samples C and D as shown in table 4.5. The results also show that in the MIBK-based samples, the magnitude of sample D is higher than sample C. After 600 Hz, the increase is of the order of 10. Therefore, we can conclude that increasing the polymer concentration can also increase the piezoelectricity.

The above study examined the output electric field response of piezoelectric can-

Table 4.5: Calculated sensitivities of the cantilevers at different excited frequencies.

Frequency (Hz)	E/g for Sample A	E/g for Sample C	E/g for Sample D
100	3.44×10^4	1.01×10^4	8.92×10^3
200	1.22×10^5	2.67×10^4	3.27×10^4
300	1.97×10^5	3.69×10^4	5.48×10^4
400	2.65×10^5	4.79×10^4	7.33×10^4
500	3.31×10^5	5.56×10^4	9.15×10^4
600	3.82×10^5	5.88×10^4	9.96×10^4
700	4.43×10^5	6.56×10^4	1.31×10^5
800	6.23×10^5	9.06×10^4	1.56×10^5
900	5.32×10^5	7.01×10^4	1.60×10^5
1000	5.92×10^5	9.12×10^4	1.73×10^5

tilevers under varying frequencies, ranging from 100 Hz to 2000 Hz, to analyze the relationship between frequency, induced stress, and voltage generation. The results indicate that higher frequencies lead to increased output voltage, suggesting a direct relationship between frequency and induced stress in the piezoelectric film. Sample A, containing DMSO and MIBK solvents, demonstrated the highest electric field (2.90×10^6 at 2000 Hz), emphasizing the role of DMSO in enhancing voltage output. Sample D, with a 3% PVDF-TrFE concentration in MIBK, achieved its highest voltage (7.87×10^5) at 1500 Hz but experienced a voltage drop at 2000 Hz due to

system overload. Conversely, sample C, with 2% PVDF-TrFE in MIBK, produced a maximum electric field of 3.36×10^5 . Thickness variations among samples influenced the results, as thinner films, like in sample A, produced higher electric fields. The data also shows that sample D exhibited better performance than sample C due to higher polymer concentration, resulting in enhanced piezoelectric properties. Overall, increasing polymer concentration and the inclusion of DMSO as a solvent were shown to improve piezoelectric output, with frequency playing a critical role in optimizing voltage generation.

4.6 In Contrast of PVDF-TrFE Material with PZT and Commercial Sensor

The aluminum cantilever is also explored as a base for the PZT and LDT0-028K vibration sensors. Both were attached to two cantilevers and excited similarly to what was described earlier. The output voltage and sensitivity of the devices made with solutions A and D were also compared with the existing sensors. One was based on PZT material (known for its high piezoelectric output), and the second was a commercially available flexible vibration sensor.

The PZT material was purchased from APC International Ltd and was a rectangular strip measured 22.7 mm long and 0.5 mm thick (figure 4.5(a)), formed from PZT material with metal electrodes on both sides. The flexible commercial sensor was purchased from TE Connectivity (Model # LDT0-028K) and is made of a 0.125 mm polyester substrate, coated with a 28 μm thick piezoelectric PVDF polymer film with screen-printed Ag-ink electrodes (figure 4.5(b)). The properties of the PZT material and the LDT0-028K sensor are mentioned in table 4.6. As the dimensions of the PZT device and the LDT0-028K vibration sensor are not comparable with the laboratory-

made devices, the outputs were compared as a whole structure. The PZT strip and the LDT0-028K sensor were glued with the help of copper conductive epoxy onto identical rigid aluminum cantilevers of dimensions 6 x 2 cm as shown in figure 4.6(a) and 4.6(b), while the PVDF-TrFE film was deposited by spin-coated on aluminum beam. The vibration measurements were done by mounting the aluminum cantilever

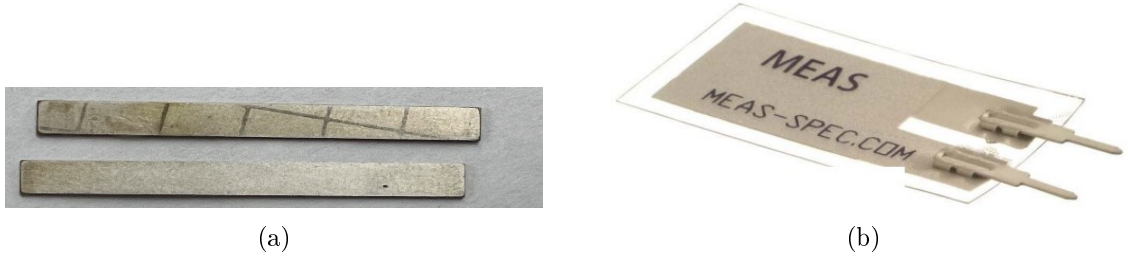


Figure 4.5: (a) PZT material. (b) LDT0-028K vibration sensor.

Table 4.6: Dimensions of commercially available sensor and the PZT material.

LDT0-028K vibration sensor	Thickness of Piezoelectric Material	28 μm
	Total width of sensor	10.2 mm
	Total length of sensor	23.5 mm
PZT device	Thickness of piezoelectric material	0.5 mm
	Total width of sensor	3.75 mm
	Total length of sensor	22.7 mm



Figure 4.6: (a) PZT strip, glued with conductive copper on aluminum cantilever. (b) LDT0-028K vibration sensor mounted on aluminum cantilever.

Table 4.7: Measured voltages under base excitation at $f = 100$ Hz.

Structure	Voltage (V)	Base Excitation (g)	Sensitivity (V/g)
Al cantilever coated with solution A	0.06	6.91	0.0086
Al cantilever coated with solution D	0.06	7.10	0.0084
LDT0-028K vibration sensor attached on Al cantilever	0.06	7.70	0.0078
PZT strip attached on Al cantilever	0.27	7.40	0.0365

onto the ground base shaker and excited at 100 Hz, as discussed in table 4.2. The voltage amplitudes in table 4.7 compare the cantilevers coated with solutions A and D, the attached PZT device, and the attached commercial LDT0-028K vibration sensor. The output voltage comparison is based only on the whole structure response, not on the material and their thickness, provided all the experimental parameters are constant. In conclusion, our experimental devices have output voltage and sensitivity that is similar to the commercial vibration sensor when excited at 100 Hz. Similarly, the cantilevers that had PZT and LDKT0-028K vibration sensors glued on were also excited at a range of frequencies from 100 Hz to 2000 Hz. Table 4.8 shows both devices output voltages. It is evident that the PZT structure generates higher voltages compared to the structure with the LDT0-028K vibration sensor attached. This is because PZT is a ceramic material, while the LDT0-028K sensor uses PVDF material.

The similarity in the output voltage at 100 Hz across different samples can be attributed to the cantilever's low sensitivity or identical baseline response under these test conditions, while the higher voltage output 0.73 V of PZT based cantilever arises due to better strain transfer, higher piezoelectric coefficients. The primary objective of this test was to assess the output voltage differences of the cantilevers within this

Table 4.8: Output voltage of the cantilevers at different excited frequencies.

Frequency (Hz)	Output Voltage (V) of PZT Device Attached on Al	Output Voltage (V) LDT0-028K Sensor Attached on Al
100	0.06	0.06
200	0.19	0.14
300	0.28	0.18
400	0.36	0.21
500	0.42	0.23
600	0.47	0.24
700	0.50	0.25
800	0.55	0.25
900	0.57	0.26
1000	0.59	0.26
1500	0.66	0.28
2000	0.73	0.28

frequency range (100 Hz - 2000 Hz). Figure 4.7 shows the measured variation in base excitation g with the change in frequency. The graph compares the base excitation (g) versus frequency (Hz) for various solutions and materials applied to aluminum beam cantilevers. The solutions (A, C, D) and piezoelectric materials (PZT and LDTM-028K) exhibit distinct excitation behaviors across the frequency spectrum. All solutions show a decrease in base excitation as frequency increases, with some variance in their specific response patterns. PZT demonstrates higher excitation at certain frequencies, particularly at lower ranges, indicating better performance in vibration sensitivity compared to the other solutions. Peaks and dips may suggest resonance and damping effects unique to each material or solution. At 800 Hz, the dip may be due to anti-resonance effect or higher damping effect which reduces the base excitation.

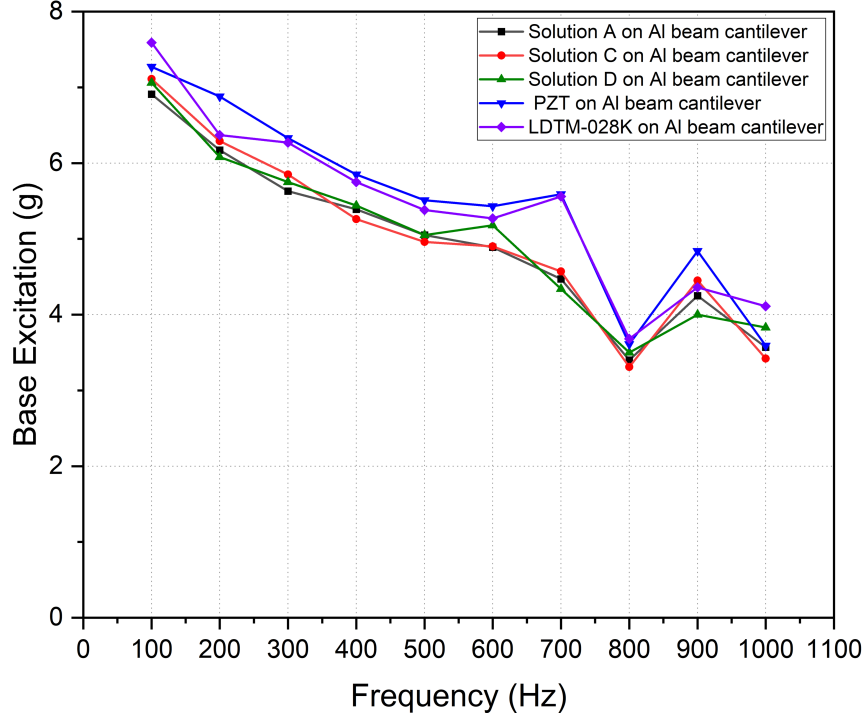


Figure 4.7: Variation in base excitation of different samples with the change of frequency.

4.7 Output Voltage of Flexible Kapton Sensor

The 6 x 2 cm flexible Kapton cantilever also explored the output voltage response. Silver was first sputtered on the Kapton cantilever to fabricate the device, which acts as the bottom electrode. Next, the polymer solution (solution A) was spin-coated. In the first study, silver was again sputtered at 150 W for 15 minutes for the top electrode. This damaged the polymer film due to the high temperature inside the sputtering chamber and the film's thickness of 252 nm. The sputtering of the Ag top electrode on the polymer should be done at a lower temperature to ensure that it does not melt or damage the polymer film and to be below the Curie temperature of PVDF-TrFE which is 112-121 °C [24], to not affect the electrical characteristics [50]. In the following study, the thicker 3% polymer concentration solution D was used,

the sputtering power was lowered to 100 W, and the sputtering time was 2 minutes. As a result, the polymer film survived the process. Sputtering parameters for both experiments are shown in table 4.9. Figure 4.8(a) shows the Ag sputtered line on top of the PVDF-TrFE layer, which acts as a top electrode. To obtain the electrical signal in the vibration tests, the bottom and the top silver electrodes were connected with connection cables using copper tape as shown in figure 4.8(b), and the part up to the connections was clamped on a ground base shaker. Table 4.10 shows the output voltages of each excited frequency, and the results show that the output voltage is in the range of 0.20 V-0.26 V. These results are similar to the sample C cantilever and approximately three times less than the sample A and D. This is because Kapton is a flexible material. The surrounding factors can impact the aluminum rigid cantilevers more than the aluminum rigid cantilevers.

Table 4.9: RF Sputtering parameters.

Parameters	Values for Sample Coated with Solution A	Values for Sample Coated with Solution D
Pressure background	3.5 μ T	3.5 μ T
Pressure work	17 mT	17 mT
Argon gas flow	100 sccm	100 sccm
Power	150 W	100 W
Time	15 minutes	2 minutes
Thickness	—	$\approx$ 50 nm

4.7.1 Mechanical Response of Flexible Kapton Sensor

The frequencies obtained from the Kapton flexible sensor using vibration testing are natural frequencies, as they represent the resonant modes of the structure. The mechanical response of the flexible Kapton sensor coated with solution D and the sputtered electrodes is also explored with the change in frequency. The device was clamped on the ground base shaker and randomly excited similarly as described in

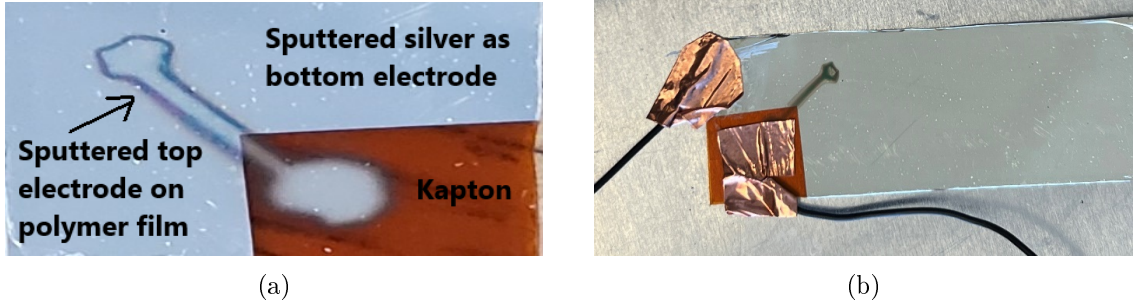


Figure 4.8: (a) Zoomed top sputtered electrode silver on PVDF-TrFE film. (b) Full device with connections.

Table 4.10: Output voltage of the Output voltage (V) of flexible Kapton sensor at different excited frequencies.

Frequency (Hz)	Output Voltage (V)
100	0.04
200	0.13
300	0.18
400	0.22
500	0.19
600	0.25
700	0.26
800	0.26
900	0.22
1000	0.21
1500	0.25
2000	0.24

section 4.2. The result was compared to the previous Kapton cantilevers coated with solutions A, B, C, and D (without sputtered silver electrodes) studied in figure 4.3. The device was randomly excited from 0 Hz to 1500 Hz at unit base excitation, and the mechanical FRF response was obtained as shown in figure 4.9. We can see that the natural frequency of this device is noticeably different from the devices in Figure 2, which had no sputtered silver electrodes on them. This shows that the addition of silver electrodes affects mechanical performance. Table 4.11 shows the output natural frequencies measured.

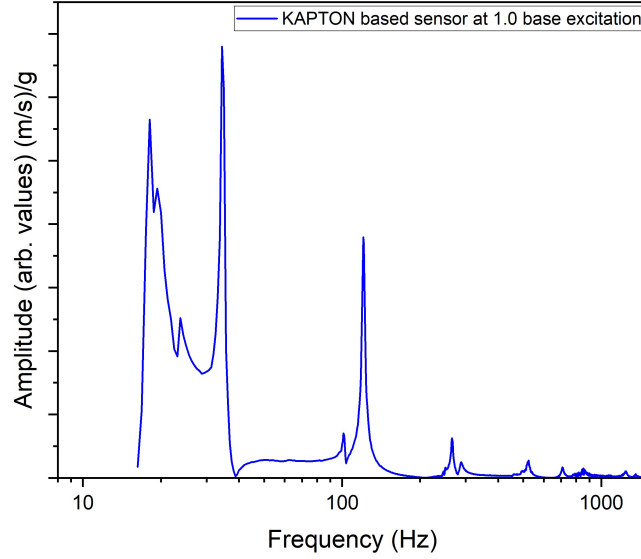


Figure 4.9: Mechanical response of Kapton based sensor at unit base excitation.

Table 4.11: Natural frequencies of Kapton cantilever vibration sensor coated with solution D, randomly excited from 0-1500 Hz at unit base excitation.

Frequency (Hz)	Test results
f_1	18.12
f_2	34.37
f_3	120.62
f_4	266.25
f_5	524.37
f_6	715

4.8 Conclusion

The study investigated the mechanical and electrical responses of spin-coated PVDF-TrFE films on flexible Kapton cantilevers using different solvent compositions (MIBK and MIBK+DMSO) and polymer concentrations (1.25%, 2%, and 3% w/v). The results showed that the choice of solvent had a significant impact on the material properties. The combination of MIBK+DMSO solvents resulted in reduced vibration amplitude and higher piezoelectric voltage coefficients (q_{31}) compared to cantilevers

coated with only MIBK solvent. This improvement is attributed to the polar nature of DMSO, which enhances film crystallization and piezoelectric performance. For example, at 100 Hz, the sensitivity (E/g) of the cantilever coated with the MIBK+DMSO solution was more than twice that of cantilevers coated with MIBK alone.

When compared with a commercially available LDT0-028 K vibration sensor, the lab-configured devices demonstrated similar output voltage but significantly higher sensitivity by 90.6 % between lab made sensor and commercial sensor. This indicates the effectiveness of the fabricated PVDF materials, particularly in the context of flexible sensors. The study also highlighted the impact of silver sputtered electrodes, showing that their addition altered the mechanical response, particularly the natural frequencies of the flexible sensors. The introduction of electrodes needs for precise design of minimally effect mechanical performance.

In comparison to published results (explained above), this study reinforces the importance of solvent choice and process conditions. Prior research has often utilized MIBK solvents alone; however, the combination of MIBK+DMSO provides a novel approach that enhances the piezoelectric properties. For example, other studies have reported lower sensitivities in piezoelectric sensors using simpler solvent systems, underscoring the novelty and effectiveness of this approach. The findings contribute to the advancement of flexible piezoelectric devices, enabling their application in areas such as precision vibration sensing, wearable technology, and energy harvesting.

Chapter 5

Flexible PCB with PVDF-TrFE

Polymer as Acoustic Sensor

The intent of this work is to develop and evaluate a cantilever-structured acoustic sensor fabricated on a flexible PCB substrate using PVDF-TrFE polymer, a piezoelectric material. The sensor is designed to detect variations in acoustic sound frequencies without requiring additional poling or polar solvents, simplifying the fabrication process. To achieve this, a multi-layered structure is created, where a copper base layer (electroplated on the PCB) serves as the bottom electrode, followed by a spin-coated PVDF-TrFE polymer layer, and a sputtered silver top electrode completing the structure. The sensor is precisely laser-cut into a cantilever shape (5 x 2 mm) to enhance its sensitivity to vibrations. The performance of the sensor is tested under sinusoidal acoustic signals ranging from 600-1200 Hz to assess its frequency responsiveness. The findings highlight that the piezoelectric properties of PVDF-TrFE are effectively utilized without additional poling or polar solvents, demonstrating its potential for flexible, low-cost, and efficient acoustic sensing applications.

5.1 Literature Review

The polymer solution can be deposited in many ways, such as spin coating, inkjet printing, screen printing, and electro-spinning, with spin coating and electro-spinning being common. In [51] S. Khan et al. used MEK as a solvent to make a PVDF-TrFE solution and then to further increase the piezoelectric properties, MWCNTs were used. The screen printing technique produced a thick layer of PVDF-TrFE/MWCNT film in between the silver electrodes made using stencils. The sensor was later used as a pressure sensor. The sensor was tested under polarized and un-polarized conditions to observe the performance in terms of voltage by applying the force. In [58], Mingran et al. fabricated pressure sensors using DMF as a solvent and electro-spun PVDF-TrFE and PVDF-TrFE/ZnO polymer solutions. They were fabricated on flexible copper electrodes, with a similar second copper electrode attached to the piezoelectric films. The device was checked by auto-clicking test, and later, the ZnO was added to increase the piezoelectric performance. In [59], Fazle et al. used MEK as a solvent and PVDF-TrFE solution to make a vibration sensor. An electro-spinning process on aluminum deposited the PVDF-TrFE, and a second copper electrode was clamped. Then, the vibration sensor was tested in the acoustic region from 30 Hz to 15 kHz, and the output voltages were recorded. In [60], Sandeep et al. used DMSO to form a polymer solution spin-coated on a polyethylene terephthalate (PET) plastic substrate. The first electrode was molybdenum metal sputtered on the PET, and the second electrode was thermally evaporated aluminum. The device was aimed for an energy harvester, but the sensor was also tested for frequencies below 100 Hz using a vibration test to get the output piezoelectric voltage. In [61], Qingkai et al. fabricated an acoustic sensor using a PVDF-TrFE membrane. The PVDF-TrFE was dissolved in DMF solvent and deposited on a quartz substrate using a flow-stream method.

Later, the film was removed, and platinum electrodes were deposited on both sides by magnetic sputtering. The sensor was tested over a 2-3kHz range. In [?], Yi Lu et al. fabricated a wearable heart sound sensor to observe the difference between normal and abnormal readings. DMF and acetone were used as solvents to prepare a PVDF-TrFE solution. Then, they fabricated a PVDFTrFE/ZnO/graphene composite film using an electro-spinning technique. The film was sandwiched with silver paste and copper foils and then encapsulated using silica gel. The sensor response was measured from 0 to 2 kHz at 65 dB sound pressure. In [?], X. He et al. designed and fabricated a PVDF-TrFE based flexible acoustic wide-band RF filter. The polymer film was obtained by dissolving PVDF-TrFE powder into a DMF solvent and then using a spin-coating technique. Later, the film was also polarized to increase the piezoelectricity. The proposed response of a flexible PCB-based filter was achieved with a high bandwidth of 13 MHz and an insertion loss of 2.87 dB. The flexible filter was also explored under different strains.

In all of the above examples, PVDF-TrFE was deposited by screen printing, electro-spinning, or spin coating method on rigid or plastic flexible surfaces. In the case of the electro-spinning deposition [59] of PVDF-TrFE, voltage is applied to the metal base to enable the adhesion between the polymer and the metal. By doing this, the applied voltage increased piezoelectricity. Similarly, in [60], a large amount (15%) of PVDF-TrFE was dissolved in a polar solvent (DMSO), which is known for increasing the piezoelectricity. In summary, in all of the above cases, the performance of PVDF-TrFE was enhanced by applying voltage, using a large amount of polymer, or using a polar solvent. The polar solvents such as DMSO and DMF have high dipole moments. In contrast, DMSO tends to increase the crystallinity of film by creating stable and long chains, which increases the piezoelectricity [45].

In this chapter, a simple fabrication process is presented to construct a flexible acoustic sensor. A flex-PCB material is used as the sensor substrate, which is subsequently patterned into the desired acoustic sensor shape using a laser cutting process. The PVDF-TrFE material was dissolved in MIBK solvent and spin-coated onto the flex-PCB substrate since it provides suitable adhesion property [24]. In contrast, other methods like screen printing and electro-spinning have poor adhesion. The piezoelectric response was sufficient not to require additional methods to enhance the piezoelectricity. The sensor was tested for its vibratory reaction, followed by testing its ability to measure acoustic signals ranging from 300 Hz to 1200 Hz frequency.

5.2 3% PVDF-TrFE Solution Preparation

A 75/25 molar concentration of piezoelectric PVDF-TrFE polymer powder was acquired from PolyK Laboratories. A polymer solution was prepared using a combination of methyl isobutyl ketone (MIBK) solvent and PVDF-TrFE powder. Solution concentrations from 1.25% - 3% were explored to determine which have high β -phase to give a more significant piezoelectric response and to explore the film thickness vs. concentration, as the film thickness is a factor in piezoelectric response. For the 1.25% w/v polymer solution, 10 ml MIBK solvent and 0.137 g of PVDF-TrFE powder were combined, and 30 minutes of stirring at 300 rpm at room temperature were needed to fully dissolve the powder. For the 2% w/v polymer solution, 0.30 g was combined with 15 ml of MIBK solvent, and 1 hour of stirring was required. For the 3% w/v polymer solution, 0.598 g of PVDF-TrFE powder was mixed with 20 ml of MIBK solvent, and 2.5 hours of stirring was needed.

5.3 Fourier Transform Spectroscopy (FTIR) Results for 3% PVDF-TrFE Solution

The FTIR technique was used for the above solutions to verify the amplitude of β -phase to identify which formulation may offer greater piezoelectric output voltage. In FTIR spectroscopy, the vibrational mechanics of molecular structure is observed. At certain wave numbers, the molecular structure shows significant absorbance. A few drops of each solution were poured on the FT-IR (Nicolet 6700) analyzing table, and the needle was lowered close to the solution surface. The scan was done from 500 $[\text{cm}^{-1}]$ to 1500 $[\text{cm}^{-1}]$ and the figure 5.1(a) and 5.1(b) shows the zoomed data in the vicinity of 840 $[\text{cm}^{-1}]$ and at 1405 $[\text{cm}^{-1}]$, which are known β -phases. The β -phase absorbance data for all three concentrations is shown in Table 5.1. It can be seen that the 3% polymer solution has higher β -phase absorbance, and so the 3% solution was used for the fabrication of the acoustic sensor.

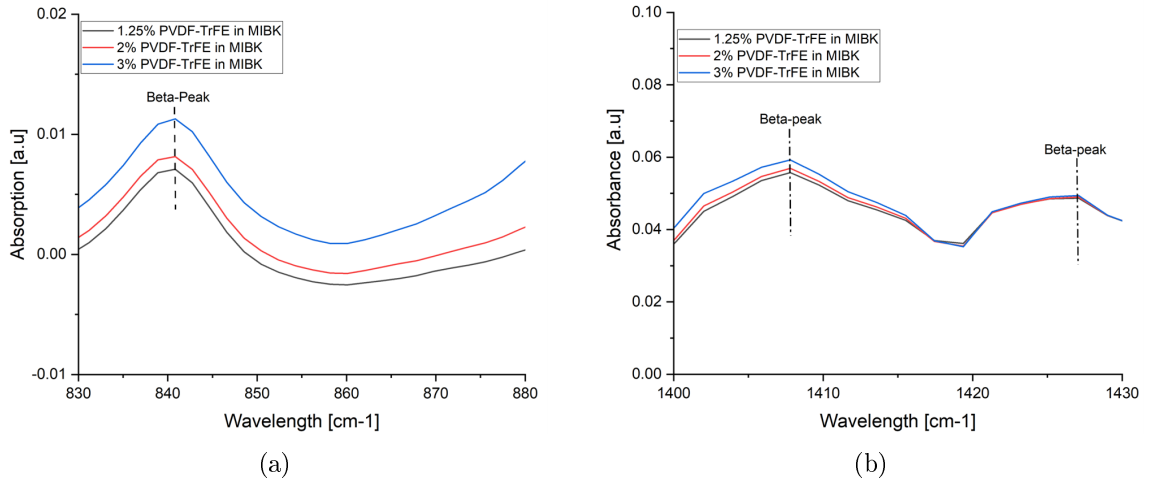


Figure 5.1: FTIR spectrum of solutions 1.25% - 3%. (a) Zoomed picture at 840 $[\text{cm}^{-1}]$. (b) Zoomed picture at 1407 $[\text{cm}^{-1}]$ and 1427 $[\text{cm}^{-1}]$.

Table 5.1: Absorbance peaks of β -phase for solutions 1.25% - 3% with absorbance amplitude values.

Solution with 1.25% MIBK Solvent	Solution with 2% MIBK Solvent	Solution with 3% MIBK Only
838 (0.0068)	840 (0.0081)	840 (0.011)
1405 (0.053)	1405 (0.054)	1405 (0.057)
1425 (0.048)	1427 (0.049)	1425 (0.049)

5.4 Device Fabrication

A flexible polyimide circuit board (PCB) material was purchased from PCB-Way.com and used for the cantilever structure. The thickness of PCB polyimide is 25 μm , and an electroplated copper of thickness of 18 μm serves as the piezoelectric device's bottom electrode. An array of 16 square metal electrodes of dimensions 5x5 mm was designed as shown in figure 5.2 and the cantilever acoustic sensor is later fabricated by laser cutting within a square electrode.

Before the PVDF-TrFE polymer deposition, the flexible PCB was cleaned using

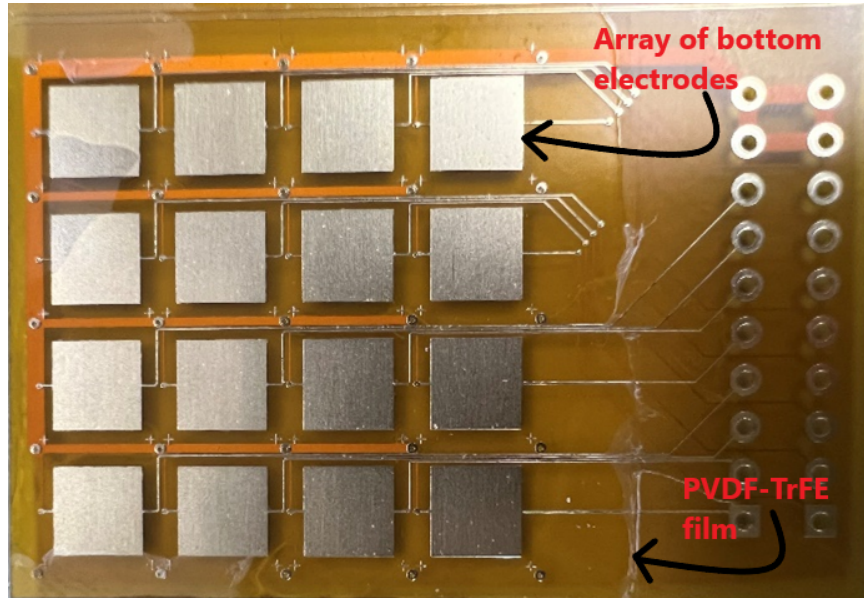


Figure 5.2: Array of electroplated copper pad on flexible PCB.

IPA and dried with nitrogen gas. Since PCB is a flexible substrate, it was taped onto a microscope slide and then fixed onto the spin-coater mount for spin coating. The PVDF-TrFE solution was poured on the flexible PCB substrate and spin-coated at 500 rpm for 200 seconds. Then, the substrate was initially annealed in a convection oven for 10 minutes at 50 °C. The solution was removed from the oven, left at room temperature for 10 minutes, and again annealed at 112 °C for 1 hour. This temperature is below the Curie point of PVDF-TrFE with a 75/25 molar ratio, which is 112-121 °C [24]. In the first part of this two-step annealing process, the ferroelectric gamma-phase crystallizes to form a stable crystallized film, and in the second step, the density of PVDF film is increased [47]. This allows for the creation of lengthy chains. The transparent PVDF-TrFE film is visible in figure 5.2. The schematic of the fabrication process is shown in figure 5.3. After the spin coating and annealing, the film thickness and surface roughness were measured using a KLA Alpha-step 500 profiler. The film measurement is shown in table 5.2.

The RF-sputtering technique was used for the top electrode because the sputter-

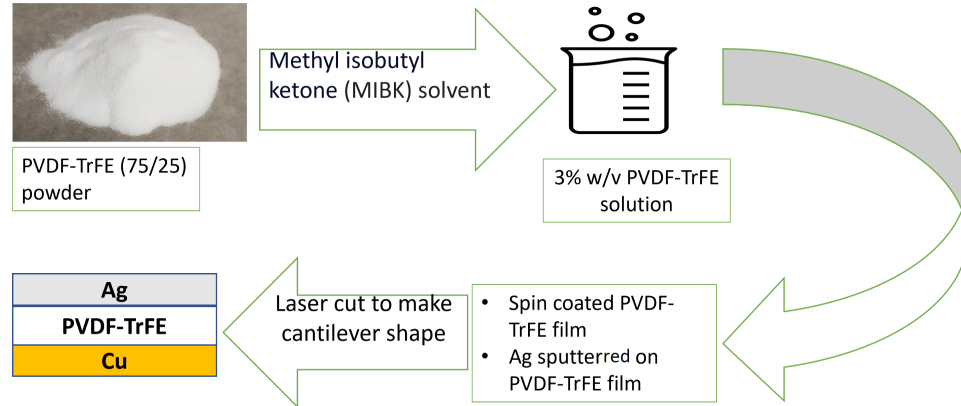


Figure 5.3: The schematic for the fabrication of PVDF-TrFE based cantilever.

ing process will provide a layer of uniform thickness. The sputtered silver film seems to have lower or equivalent stress, because the structure did not bend. Sputtering

Table 5.2: Spin coated film measurements.

Polymer solution contents	Annealing temperature (°C)	RPM	Thickness
3% PVDF-TrFE powder, MIBK solvent	10 minutes at 50 °C, followed by 1 hour at 112 °C	500 for 200 seconds	953 nm

on sub-micron polymer film is difficult because the high energy silver particles and the chambers inside temperature can easily damage the thin polymer film. For this purpose, the power was kept at 100 W, and the sputtering time was restricted to only 3 minutes because the purpose of the silver layer was only to complete the circuit as a top electrode. A pre-made stencil mask was used to restrict silver at the designated area. The RF-sputtering parameters are mentioned in table 5.3. The sputtered silver electrode is shown in figure 5.4.

Laser micromachining was used to cut out the cantilever shape from the square

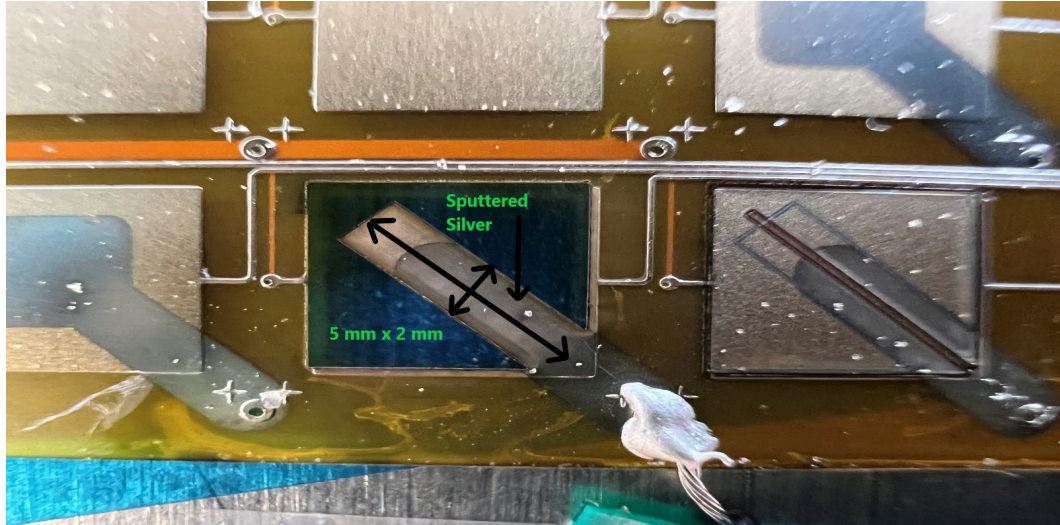


Figure 5.4: The silver sputtered line on top of spin coated PVDF-TrFE film.

pads, using an ultraviolet (355 nm) diode-pumped solid-state picosecond laser (A-355ps Laser Micromachining system) from Oxford Lasers Ltd. The important parameters such as laser power, cutting speed, and number of passes are shown in table

Table 5.3: RF sputtering parameters of silver on PVDF-TrFE film.

Base Pressure	5 μT
Argon sputtering pressure	17 mT
Argon gas flow	100 sccm
Power	100 W
Time	3 minutes
Thickness of Silver	$\approx$ 50 - 100 nm

5.4. After the laser cut, the device was tested with a multimeter (circuit specialist Model# MS8264) to verify that there was no electrical short-circuit between the bottom and top electrodes. Flexible wires were soldered to the connection points as compared to epoxy bonding, because in epoxy bonding an extra annealing of the substrate is required which may alter the material properties. Figure 5.4 shows the laser cut cantilever along with soldered wire for external connections.

Table 5.4: Laser cutting parameters and machine settings.

Laser machine setting	Values
laser wavelength	355 nm
Cutting pass speed	1 mm/sec
Number of passes	35
laser power w.r.t max. power	30% of 0.036 Watt
Maximum pulse energy	0.12 mJ
Attenuation	0.6 %
Milling pulse energy	0.72 μ J
Pulse duration	6 ps
Pulse frequency	400 Hz

5.5 Observation of Change in Acoustic Frequency

To induce acoustic vibrations, a piezoelectric vibration sensor and a speaker were positioned 5 cm apart, with a 400 Hz signal serving as a reference. Initial testing at 400 Hz revealed that the output signal was obscured by noise, rendering it unreadable. This noise was attributed to low-frequency interference from electrical equipment. To mitigate this issue, a filter circuit was designed to suppress the noise.

Figure 5.5 illustrates the experimental setup. As depicted, a cantilever was positioned 5 cm in front of a speaker (MidiLand Model # MLI-699) and connected to a circuit incorporating a trans-impedance amplifier. The amplifier was designed to regulate voltage and reduce noise through the inclusion of a feedback capacitor. To further minimize signal noise, sequential high-pass filters, up to fourth order (4 filters), were employed. The filtered signal was subsequently amplified by a voltage amplifier circuit. Finally, the output waveform was visualized using an oscilloscope (Tektronix, Model No. TBS1052B-EDU). Due to significant noise in output signals below 600 Hz, a cutoff frequency of 600 Hz was established for input excitations.

To determine the natural frequency using COMSOL, a cantilever structure with dimensions 5 mm x 2 mm was modeled, consisting of four layers: a flexible polyimide base, a copper bottom electrode, a PVDF-TrFE polymer film, and a silver top electrode. An eigenfrequency analysis was conducted to calculate the natural frequencies. The first eigenfrequency was calculated to be 650 Hz.

Figure 5.6 presents the output wave forms obtained from acoustic testing within the 600-1200 Hz frequency range. The baseline waveform, representing the absence of an acoustic input, is shown at the bottom of the figure 5.6. As the acoustic signal frequency was increased to 600 Hz, the output waveform transitioned towards a sinusoidal form with reduced distortion. Due to the high-pass filter's cutoff frequency of 600 Hz, acoustic testing was not performed below this frequency. The test circuitry exhibited a gain of 0.5 at 600 Hz and a gain of 1 at 1200 Hz. The gain was calculated based on the capacitor and resistor values at which it started giving readable waveform at 600 Hz. As the high-pass filters allow high frequencies, attenuating lower ones, with the 600Hz cutoff crucial. At 600Hz, a gain of 0.5 shows partial attenuation, typical for real-world filters, suggesting a complex design beyond a simple first-order. At

1200Hz, well above the cutoff, a gain of 1 indicates minimal attenuation, confirming proper pass-band function. These gain values reflect the filter's expected behavior: attenuation at the cutoff and unaltered signal in the pass-band.

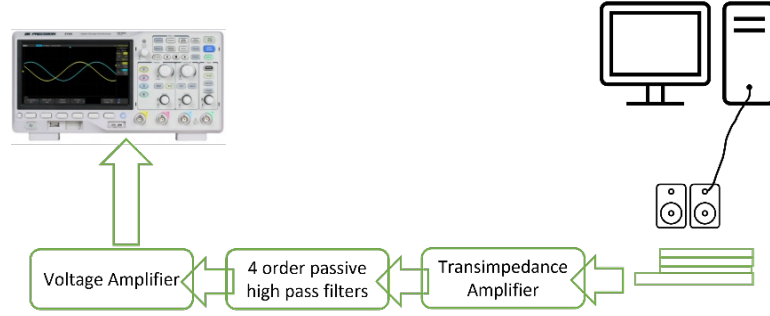


Figure 5.5: The schematic of acoustic test setup.

5.6 Conclusion

The described work presents a novel approach to fabricating a flexible acoustic sensor utilizing a PVDF-TrFE polymer layer sandwiched between metal electrodes on a flexible PCB substrate, configured in a cantilever structure. This sensor design is significant due to its ability to detect sinusoidal acoustic frequencies in the range of 600-1200 Hz without requiring poling or the use of polar solvents during the fabrication process.

The innovation lies in the integration of a flexible PCB substrate with a cantilever-based sensor structure, combined with the straightforward spin-coating of the piezoelectric polymer and the use of a sputtered silver top electrode. While PVDF-TrFE is a widely studied piezoelectric material for sensor applications, the specific methodology described, which omits conventional poling and employs a flexible PCB as the base, has not been reported in the literature.

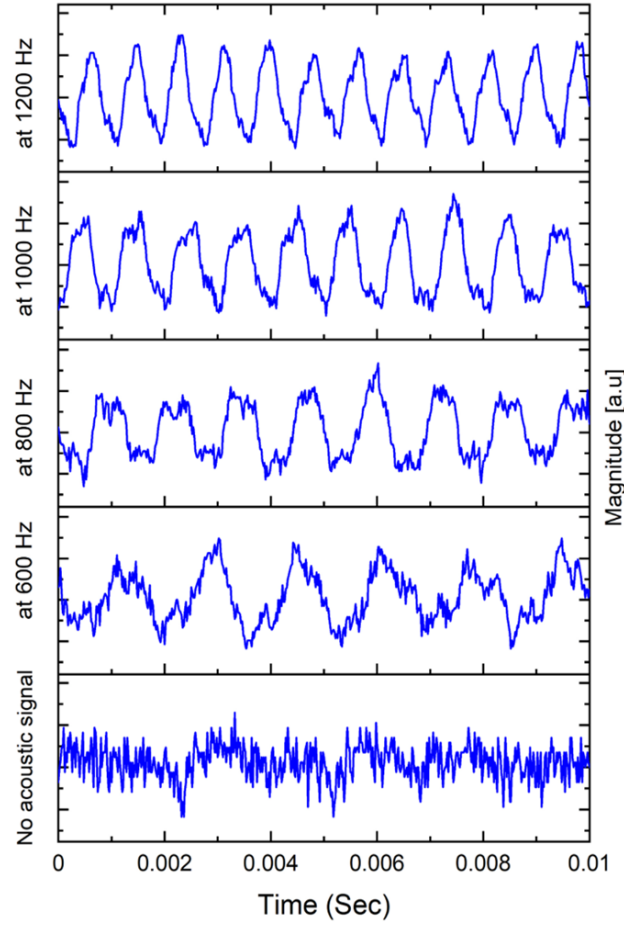


Figure 5.6: The resultant sound signals when excited from 600 Hz-1200 Hz.

Comparative analysis with existing studies highlights the uniqueness of this approach. For instance, prior research on high-performance acoustic wave sensors leveraging PVDF-TrFE membranes typically focuses on combining piezoelectric and optical effects, such as the Fabry-Perot effect, but does not use flexible PCB substrates or cantilever structures. Similarly, studies on flexible film bulk acoustic wave filters have primarily targeted radio-frequency applications and do not employ the fabrication techniques or structural configuration outlined in this work.

In conclusion, this methodology represents a novel and impactful contribution to

the domain of flexible acoustic sensors. It offers potential advantages in terms of ease of fabrication, reduced material processing steps, and the elimination of the need for poling, thereby making it a valuable innovation for future sensor technologies.

Chapter 6

Flexible PCB Magnetic Field Sensor based on PVDF-TrFE Piezoelectric Polymer

PVDF-TrFE is being explored in magnetic field sensing applications, but involved with the use of filler materials. This study, however, takes a novel approach by investigating the potential of PVDF-TrFE in developing a magnetic field sensor without the need for filler enhancements. The fabrication process involved using a commercial PCB process to create a flexible sensor. A thin coating of PVDF-TrFE solution was applied via spin-coating onto copper electrodes, with a top electrode created through silver sputtering. The experimental investigation included measuring the actuation response and the output voltage near a 0.10 T permanent magnet. The actuation displacement of 13 μm was observed at 0.10 A, resulting in a Lorentz force of 2.2×10^{-4} N and a spring constant of 17 N/m. In contrast, when operating as a magnetic field sensor with 70 mA current at 79 Hz resonance, the PVDF-TrFE voltage response was 0.0253 V, corresponding to a sensitivity of 0.13 V/T.

The above characteristics are indicative of the sensor's capability to operate under low-force conditions, which can be beneficial in sensitive actuation systems requiring minimal energy input. The fabrication approach could be particularly useful in flexible electronics, wearable sensors, or environments requiring lightweight and adaptable sensor solutions. Applications such as health monitoring, portable magnetic field measurement devices, or small-scale robotics could benefit from this technology due to its combination of flexibility, ease of fabrication, and adequate sensitivity for low-field applications.

6.1 Literature Review

Piezoelectric polymer materials have shown their performance as they are effective for many applications, including sensors, actuators, and energy harvesting devices. These are alternatives to ceramic materials that can offer biocompatibility. They also have an uncomplicated preparation process and are cost-effective, and the research is expanding to increase efficiency by making hybrid solutions. To take advantage of the ferroelectric nature, different materials are integrated into PVDF to enhance its polar properties. These materials include metal oxide, like $\text{Pb}(\text{ZrTi})_3$, BaTiO_3 , ZnO , etc., called piezoelectric fillers [?]. Non-piezoelectric materials are also being used to enhance the performance of PVDF, such as RGO (reduced graphene oxide) [?]. This shows a broad range of options for materials integration into PVDF. There are many applications in which researchers have explored the properties of PVDF and its composites. For example, pressure sensors [?], [53], [58], gas sensors [?], [?], acoustic sensors [55], [61], and also magnetic performance [?], [?]. Researchers use magnetic composites like ferrites [?], [?] to facilitate its magnetic response for specifically magnetic applications. However, if the addition is multiferroic, it will enhance

the magnetic response and piezoelectric properties [?].

In [?], Liliana et al. used multifunctional magneto electric material ([Bmim][FeCl₄]) along with PVDF-TrFE to use for magnetic sensing and actuation device development. The designed sensor features frequency-dependent sensitivity and operates in an AC magnetic field. With a maximum sensitivity (s) of 76 mV.Oe⁻¹, the materials exhibit voltage responses in the mV range, making them appropriate for creating magnetic field sensors. The magnetoionic (MI) interaction and the composite's shape account for the strong ME responsiveness (highest ME voltage coefficient of 15 V.cm⁻¹.Oe⁻¹) and magnetic bending actuation displacement (2.1 mm). In [?] Zhenji. Z et al. worked to increase the beta-phase of PVDF-TrFE by the addition of CFO@PDA, which is a magnetic nanofiller. The resultant sensor was tested by bending and pushing scenarios. The magnetic field-oriented film yielded the highest output voltages in a non-contact magnetic field-driven experiment, measuring 17.4 mV at 4 Hz and 12 mV at a drive amplitude of 19 Vpp, respectively, compared to the values of 7.1 mV and 7 mV for the film without magnetic field orientation. In contrast, a flexible sensor [?] was fabricated by gluing the polymer-based magneto-electric laminate composed of Metglas on both sides of commercially poled PVDF film. The sensor's sensitivity and resolution values are 30 mV.Oe⁻¹ and 8 μOe for the DC magnetic field sensor and 992 mV.Oe⁻¹ and 0.3 μOe when used as AC magnetic field sensor. The examples mentioned above focus on enhancing the magnetic response of PVDF and its composites by adding magnetic materials.

In this work, piezoelectric film based on 3% PVDF-TrFE solution was used as the sensing material in a magnetic field sensor without adding filler magnetic materials. The PVDF-TrFE material was analyzed using the Fourier transform (FTIR) to verify the material formulation's presence of β-phase in its molecular structure. Spin coat-

ing was applied to the sensor without the use of extra piezo materials or non-piezo filler during the solution-making process. The tested sensor structure is a U-shaped conductor fabricated on a flexible PCB, which employs Lorentz force coupling in a magnetic field to enable deflection. The U-shape design enhances sensitivity, making it suitable for weak magnetic fields. The sensor is first tested as an actuator to determine its mechanical performance. It is then tested in the presence of a permanent magnet to explore the ability of the piezoelectric material to detect the conductor motion due to magnetic force deflection.

6.2 Experimental Results

6.2.1 Design and Fabrication of Piezoelectric Magnetic Sensor

Piezoelectric materials typically generate charge in response to the applied mechanical stress. A U-shaped actuator structure was employed as the sensor. The sensor employs the Lorentz coupling effect in the magnetic field to create mechanical bending stress, and the PVDF-TrFE is used as a sensing material. The U-shaped structure has 12 mm x 2 mm side arms, and a central crossbar is 22 mm x 2 mm. For the experimental sensor testing, the crossbar is oriented perpendicular to the external magnetic field, and the side arms are oriented parallel to the field so that the resulting Lorentz force will be zero on the side arms. The design was provided to PCBway to fabricate the copper metal layer of thickness 18 μm on both sides of a flexible polyimide substrate of thickness 25 μm . Figure 6.1(a) and 6.1(b) shows the initial fabrication from PCBway before the actuator was cut out. In Figure 6.1(a), the copper conductor on the lower side of the flexible PCB is used to provide current, while in Figure 6.1(b), the copper electrode will act as the sensor's bottom electrode.

The electric field produced by the current flow in the lower copper conductor will interact with the nearby permanent magnet, causing deflection in the sensor. Figure 6.1(c) shows the schematic of electrode positions on the polyimide substrate. A spin coating technique was performed to deposit the PVDF-TrFE polymer solution on the copper electrode shown in Figure 6.1(b). The structure was attached using tape on a microscope slide because polyimide is a flexible substrate. The polymer solution was poured and spun at 500 rpm for 200 seconds. The structure was baked in a convection oven at 50 °C for 10 minutes to form a solid polymer film and then at 112 °C for 1 hour per the standard two-process baking process [47].

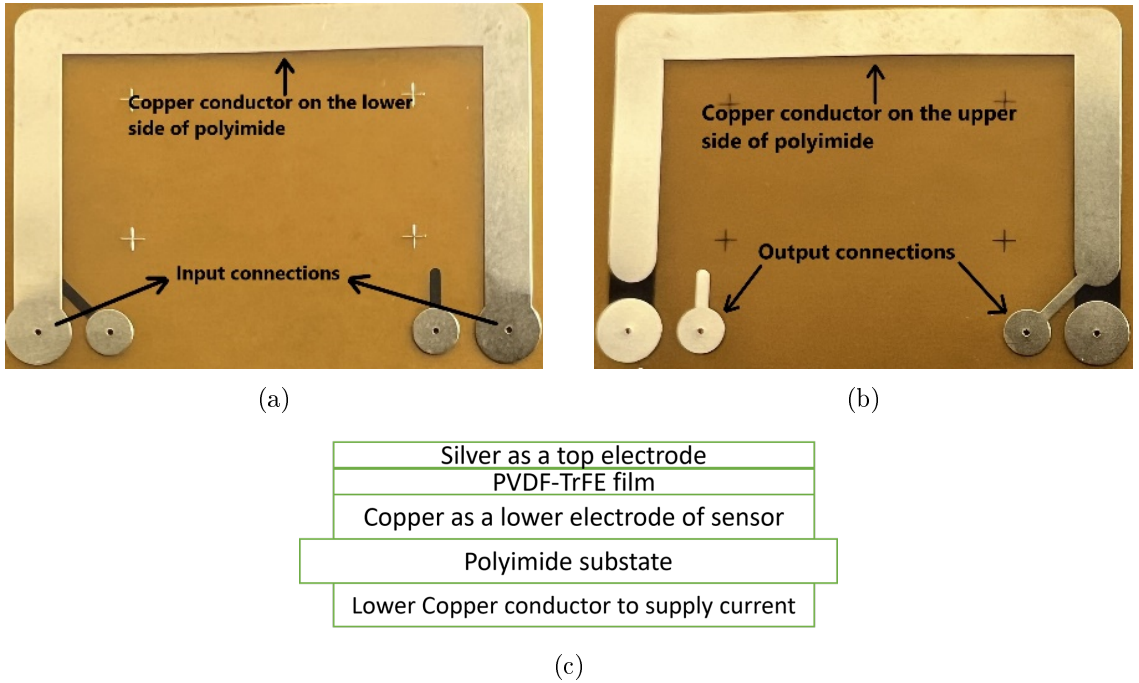


Figure 6.1: U shaped sensor is presented. (a) Bottom side of polyimide substrate copper electrode to connect with current source. (b) Upper side of polyimide substrate copper electrode as a bottom electrode for sensor. (c) Schematic of electrode positions on polyimide substrate.

The film thickness was measured using the KLA-500 Alpha step profiler. The spin coating parameters and the film thickness are mentioned in table 6.1; this is a similar

process discussed in [16]. To complete the fabrication, silver as a top electrode was RF - sputtered on top of polymer film, and the sputtering parameters are mentioned in table 6.2. Then, the inside area was cut using a sharp knife to form a U shape. The wires were connected with the output points on the structure for output connections, as shown in Figure 6.1(b). Figure 6.2 shows the U-shaped outcome after the sputtered silver and cutting with a knife.

Table 6.1: Spin-coating deposition parameters.

Polymer Concentration	Solvent Used	Annealing Temperature (°C)	RPM	Thickness
3% w/v PVDF-TrFE	MIBK	10 minutes at 50 °C, followed by 1 hour at 112 °C	500 for 200 seconds	≈950 nm

Table 6.2: RF sputtering parameters of silver on PVDF-TrFE film.

Base pressure	5 μ T
Argon sputtering pressure	17 mT
Argon gas flow	100 sccm
Power	100 W
Time	3 minutes
Thickness of Silver	≈375 Å

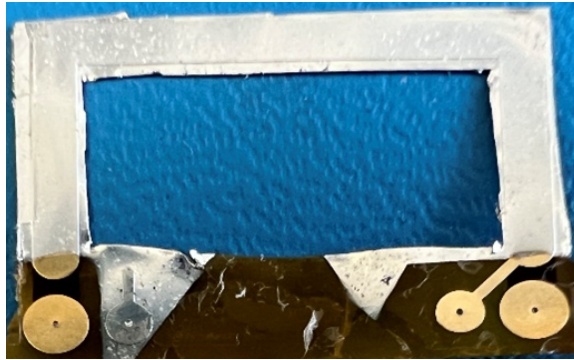


Figure 6.2: U shaped sensor after silver sputtering.

6.3 Actuation Displacement in a Magnetic Field

The experimental sensor's actuation is due to force coupling between the current flowing in the crossbar and the incident magnetic field, as determined by the Lorentz relationship. The setup schematic is shown in Figure 6.3, which shows that the direction of magnetic field lines is perpendicular to the crossbar.

The U-shaped sensor was measured to have a resistance of $0.065\ \Omega$. A series

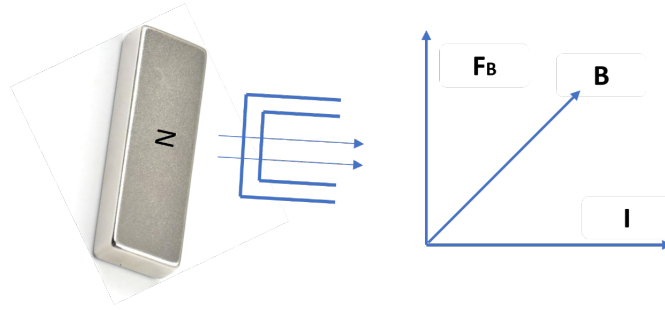


Figure 6.3: The schematic of piezoelectric sensor in the permanent magnetic field.

resistance of $4.7\ \Omega$ was used to limit the current in the sensor. In Figure 6.4, the polyimide's copper conductor on the lower side (input connections) is soldered with wires.

A permanent magnet is placed close to the sensor at a distance of 10 mm to provide the magnetic field. The magnetic strength of the permanent magnet, 0.10 T (1040.3 Gauss), was measured by the Alpha lab model GM 2 Gauss meter. The system was placed and fixed on an Olympus microscope (model # BX-RLA2) stage, as shown in figure 6.4.

It was observed that there was no vertical displacement in the sensor when the current flowed through it without a permanent magnet. On the other hand, actuation is the process of starting a movement. In this instance, a permanent magnet was the cause of the movement. A magnetic field surrounds the cross bar as a result of the

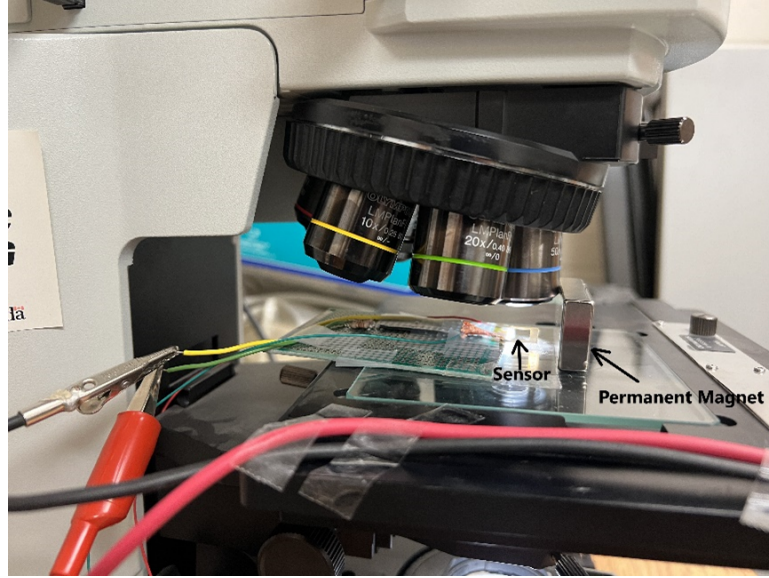


Figure 6.4: The experimental setup for measuring the actuation.

current flowing through it. The vertical displacement is the result of its interaction with the field of a nearby permanent magnet. The displacement of the sensor in the magnetic field is measured by re-focusing the microscope on the sensor as it moves due to displacement. The measurement accuracy with the employed 50x objective is approximately $\pm 1 \mu\text{m}$.

6.4 Lorentz Force and Spring Constant

The force per unit length on the current-carrying conductor can be calculated using the Lorentz force equation 6.1, which describes the magnetic force F experienced by a current-carrying conductor in a magnetic field.

$$F = ILB\sin\theta \quad (6.1)$$

where F is force experienced by the sensor, I is the current flow, L is the length of the conductor (22 mm) and θ is the angle between I and the magnetic field B . The

angle between the direction of the current I and the direction of the magnetic field B is $\theta = 90^\circ$ to experience maximum force.

To calculate the sensor's spring constant, a current of 0.10 A was applied in the magnetic field's presence. A vertical displacement of d of 13 μm was observed. Using equation 6.1, the Lorentz force solves to 2.2×10^{-4} N. The sensor's spring constant can be calculated from Hook's law $F = kd$, as this relation is only valid in linear regime until the structure is not over stressed. The spring's constant at 0.1 A is 17 N/m.

6.5 Output Voltage in the Presence of Magnetic Field

The U-shaped structure is now explored as a piezoelectric sensor for measuring the deflection caused by the Lorentz force from an incident magnetic field. For this purpose, instead of giving DC voltage as input, a sinusoidal voltage from the function generator is used.

A multi-layered structure was designed on COMSOL to find the resonance frequency. The structure consists of polyimide as a base, copper, PVDF-TrFE, and silver, as shown in Figure 6.5. The designed structure on COMSOL has the exact dimensions of the fabricated sensor. The material properties for copper and polyimide are taken from the COMSOL library. For PVDF-TrFE, the value of the elastic modulus of PVDF-TrFE was used as 2.9 GPa.

In COMSOL, a physics-controlled meshing sequence is selected for meshing. Stationary Multiphysics is used to determine the Eigen frequencies. The simulations have shown that the first Eigen resonance frequency of the U-shaped structure occurs at 80.7 Hz and the second resonance frequency at 207.9 Hz. The first COMSOL Eigen resonance frequency is shown figure 6.6.

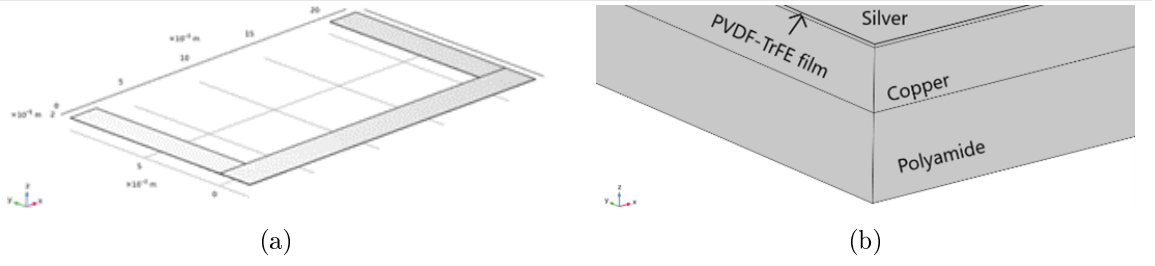


Figure 6.5: (a) The schematic of U-shaped sensor from COMSOL. (b) Zoomed picture of the structure indicating the layers.

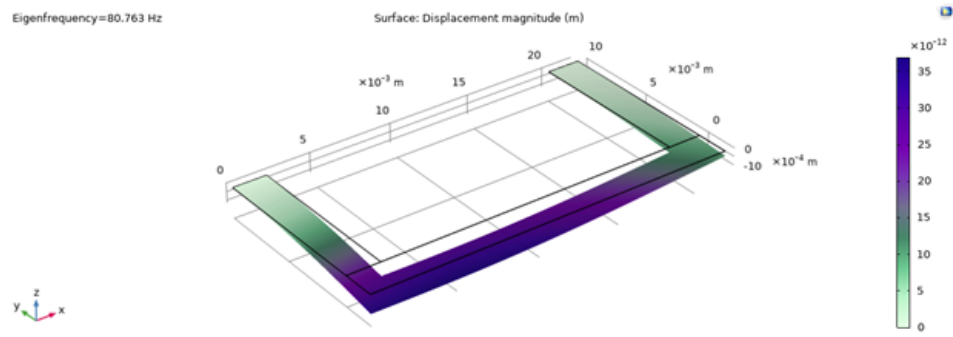


Figure 6.6: The first Eigen frequency of the U-shaped magnetic sensor using COMSOL.

The input electrodes shown in figure 6.1(a) were connected to the function generator (Standard Research systems Model # DS335) from where the sinusoidal voltage is provided, and the output electrodes were connected to the oscilloscope (Tektronix, Model # TBS1052B-EDU) from where the output voltage is observed, which has an input impedance value of $10 \text{ M}\Omega$. A permanent magnet is placed with the orientation shown in figure 6.3 at a distance of 10 mm to the sensor, because the poles are at the surface. The magnetic field was measured by the GM 2 gauss meter, which was 0.10 T. The test setup is shown in figure 6.7 with input and output connections.

As the first resonance frequency from COMSOL is 80.7 Hz, the initial frequency for the experimental test was done at 50 Hz to see the response below the resonance frequency. The measured output voltage response on the PVDF-TrFE for a 70 mA

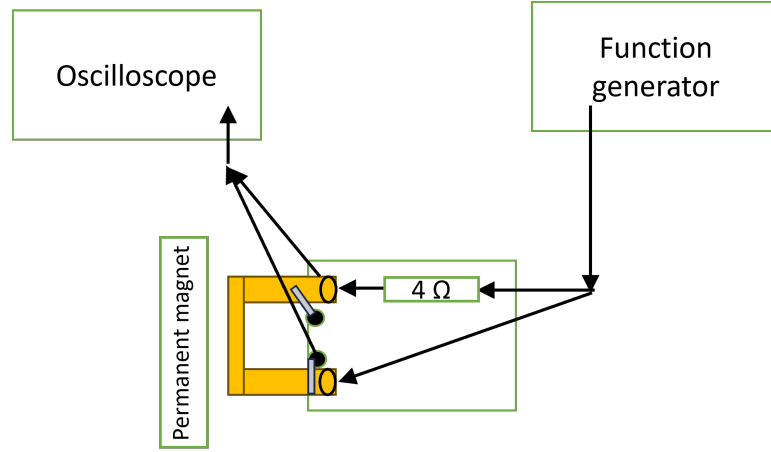


Figure 6.7: The test setup for magnetic field sensor.

current with 330 mV are shown in figure 6.8, with the shown output voltage response of the PVDF-TrFE shown as the average of five maximum amplitudes. We can see a reduced response at 50 Hz and 60 Hz, due to a possible charge leakage cross the PVDF-TrFE material. The subsequent measurements were taken from 66-85 Hz at 1 Hz increments. A constant voltage of 0.021 V is observed from 66-69 Hz. Peaks were observed at 70 Hz and at 79 Hz, but the amplitude of peak at 79 Hz is higher than peak at 70 Hz making this an apparent resonance peak, which is close to the COMSOL simulated value of 80.7 Hz. Voltage drop between 70 Hz and 76 Hz was also observed. This may be due to damping effects, anti-resonance effects or non-linear interactions introduced by the magnetic field and the sinusoidal excitation. A peak of 0.0254 V is observed at 79 Hz. The sensitivity of the device is 0.13 V/T at 79 Hz. After 79 Hz, the voltage again dropped, and showed similar behavior as in 70-76 Hz. Thus, we can say that 79 Hz is the structure's resonance, similar to the first harmonic found in COMSOL simulations.

The bias current I_{bias} influenced the output voltage behavior, as the force is the product of current and magnetic field. The proximity of the DC magnetic field to the

sensor still played a significant role in determining the sensor's response. The magnetic field could interact with the sinusoidal voltage, causing modulations in the sensor output voltage. The decision not to use an A/D converter or pre-amplifier in the experiment was aimed at directly observing the sensor's raw output voltage response to the applied sinusoidal voltage and DC magnetic field. However, introducing an A/D converter or pre-amplifier might have helped mitigate signal distortions. Additionally, the output voltage levels in the range of 0.017-0.026 V may not be sufficiently high for direct measurement without amplification or conversion, as quantization effects in the data suggest limitations in the oscilloscope's ability to resolve low signal levels accurately.

A simple U-shaped piezoelectric Lorentz force based magnetic field sensor is

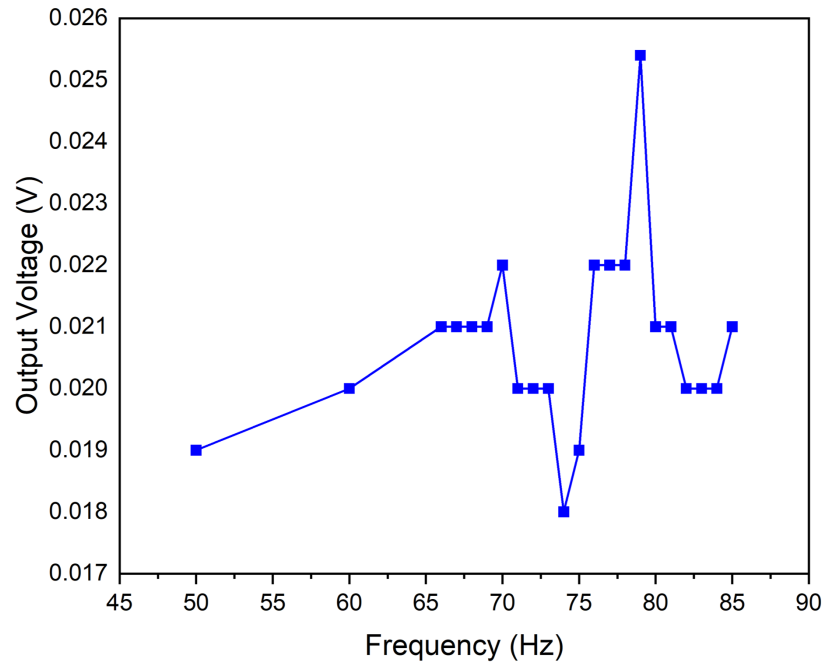


Figure 6.8: Output voltage of sensor with an input of 70 mA, in the presence of a 0.10 T magnetic field.

fabricated on a flexible polyimide substrate with a few deposition steps. The sen-

sor consists of copper and silver as a bottom and top electrode while a spin-coated PVDF-TrFE film between them. The device is tested both as an actuator and as a sensor output in the presence of the magnetic field. In actuation mode, the U-shaped device showed a linear vertical displacement with the applied current. A displacement $13\text{ }\mu\text{m}$ was observed when 0.10 A current was applied. When employed as a magnetic field sensor in the presence of 0.10 T magnetic field and with a sinusoidal current of 70 mA at 79 Hz mechanical resonance, an output voltage sensitivity of 0.13 V/T was measured on the PVDF-TrFE material, due to deflection of the sensor structure.

Chapter 7

Expolration of PVDF-TrFE as a Bearing Sensor

An additional use of PVDF-TrFE-based applications is being explored in mechanical parts due to their ability to be deposited on any surface and adhere well. 3% PVDF-TrFE solution was deposited onto a bearing outer conductive surface as a sensing layer and silver patch was made to get the output signal. Then, the Bently motor rod was passed through the bearing and the motor was spun at different speeds. In the experiment the bearing was not moving but the vibrations produced by the rotating motor rod produced signals which were recorded at the LMS data acquisition software (owned by Siemens).

7.1 Fabrication of Sensor on Bearing Surface

The 3% PVDF-TrFE-based solution was used for the polymer film deposition and the solution preparation procedure has been explained in chapter 3. The deposition of PVDF-TRFE solution on flat surfaces is quite simple, as described in chapter 3.

However, the spin-coating of 3D objects is not possible using a conventional method because, in spin-coating, the centrifugal force pushes the solution outwards to form a homogeneous layer. In the case of the ball bearing, the solution will not cover the whole surface during spin coating because it is in a 3D shape. One possible solution is that the spin-coater can move in both inward and outward directions alternatively, but there is a possibility that the entire surface may not be covered. The other easy method of polymer deposition is to use a paintbrush if the layer thickness is not a critical factor. A brush method deposits a polymer film on the bearing conductive surface. For this purpose, the bearing was placed in a standing position because the film deposition on the whole bearing surface was not required. A few drops were put on the top surface using a cotton stick as shown in the schematic figure 7.1(a) and then annealed using a standard procedure explained in chapter 3. To avoid a short circuit, a dielectric layer of photoresist (AZ1518) was also deposited using a similar method of PVDF-TrFE deposition. After the annealing process, a patch of silver paint was put on the photoresist layer using a paintbrush to form a top electrode, and it was let dry for a day to make it fully conductive. After the drying, the silver was also conductive and served as the top electrode, while the bearing was the bottom electrode. Figure 7.1(b) shows the bearing with the silver as the top electrode.

7.2 Test Setup

A copper tape was used on the bearing surface as a bottom electrode for the output connections, and a copper tape was used on a silver patch for a top electrode. In figure 7.2(a), there is a bottom holding space for the ball bearing, and figure 7.2(b) shows the upper holding space. The bearing was placed between the two the holding spaces. Then the holders were screwed as shown in figure 7.3, and then the whole

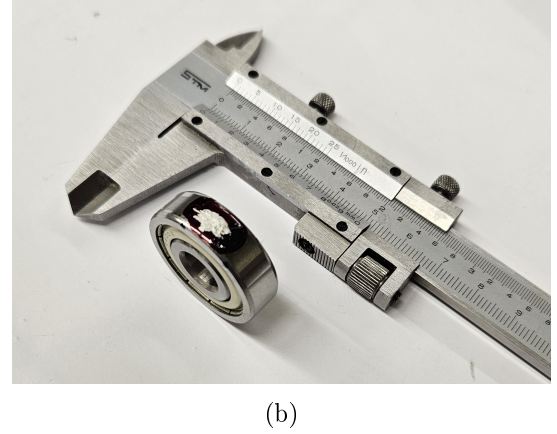
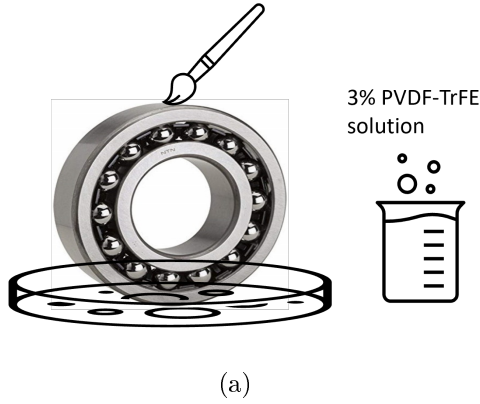


Figure 7.1: (a) The schematic of employing the polymer film. (b) The bearing with PVDF-TrFE layer and the silver patch.

holder was mounted and screwed on the rigid base aligned with the motor height. A motor from Bently Nevada Corp. (Serial # P500945) and a rod of diameter 10 mm were used for rotation. A Bently Nevada motor speed controller controlled the rotation speed. A rod was clamped in the motor using an insulator coupler to avoid the connection between the rod, the motor, and the bearing sensor. Then, the rod was passed through the bearing, as shown in figure 7.3. The copper tape was connected to an oscilloscope, and the motor was rotated at different speeds to get the output data from the LMS data acquisition system. Figure 7.3 depicts the test setup for detecting the vibrations in the rotating rod.

7.3 Results and Discussion

The experiment can be explored in two scenarios; in the first case, the sensor can be used as an unloaded sensor. This means that there is no pressure on the sensor surface, and the position of the sensor will be in the empty area as shown in figure 7.2(a) and figure 7.2(b). In the second case, the sensor can be placed in a way that the inner surface of the holder is pressing the sensor, which refers to a loaded sensor.

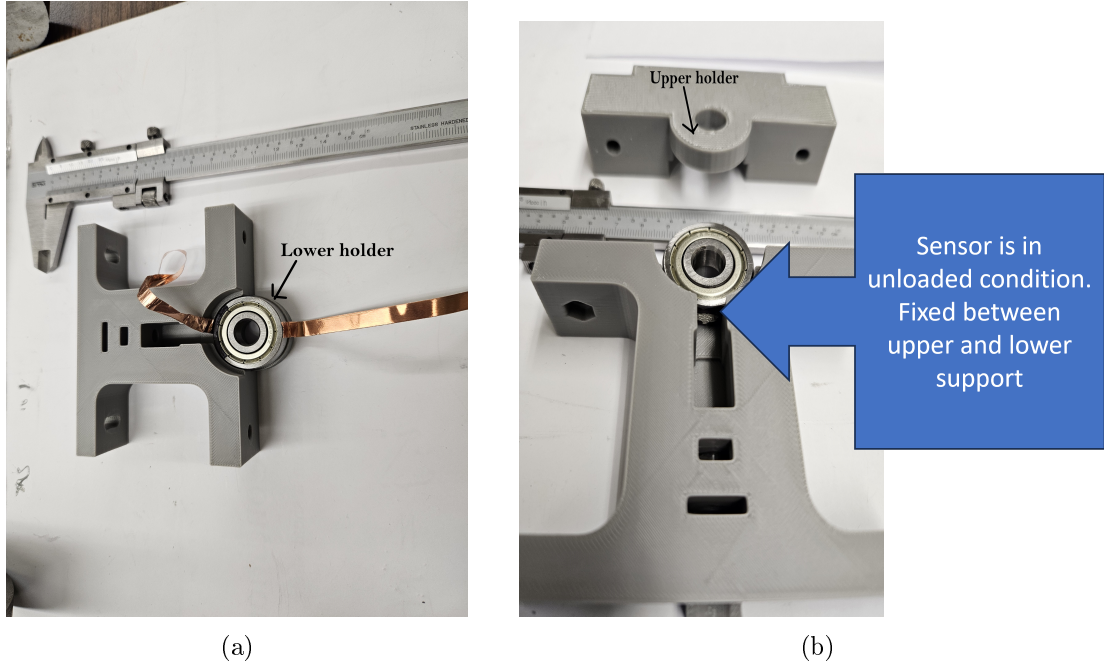


Figure 7.2: The two place holders with same height as the rode. (a) Lower support is screwed on. (b) Upper holder.

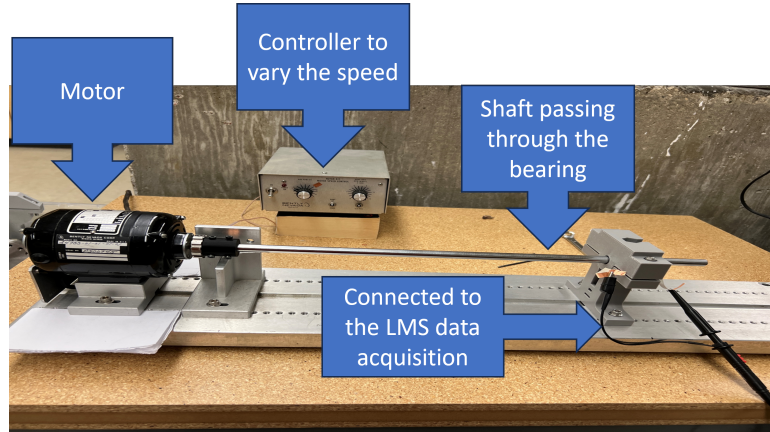


Figure 7.3: The test setup for detecting vibrations in rotating rod.

The unloaded sensor scenario is discussed below.

The rod was rotated at different speeds with the help of motor controller. Then, the output voltage was recorded using the LMS data acquisition software. In order to record the measurement, the rotation speed was set on the controller, then frequency

(in Hz) was measured by the cellular (iPhone 13 Pro) phone camera using video tachometer software (downloaded from Apple applications store). And the RPM was divided by 60 to get the frequency. Figure 7.4(a) and 7.4(b) illustrates the relationship between the rotational speed of the bearing system and the voltage output of the piezoelectric sensor. At higher speeds (3037.2 rpm or 50.62 Hz), the output voltage amplitude is greater than the lower speeds (2193.6 rpm or 36.56 Hz), indicating that increasing the speed results in increased stress or pressure on the piezoelectric layer. This is due to the relative motion of the inner and outer races of the bearing: the inner race moves in the opposite direction to the ball bearings, while the outer race moves in the same direction. The differing angular velocities create higher stress on the piezoelectric material at higher speeds, leading to higher voltage output. Table 7.1 shows the output results at different RPMs. Maximum voltage was achieved at 3037.2 rpm and plotted in figure 7.5.

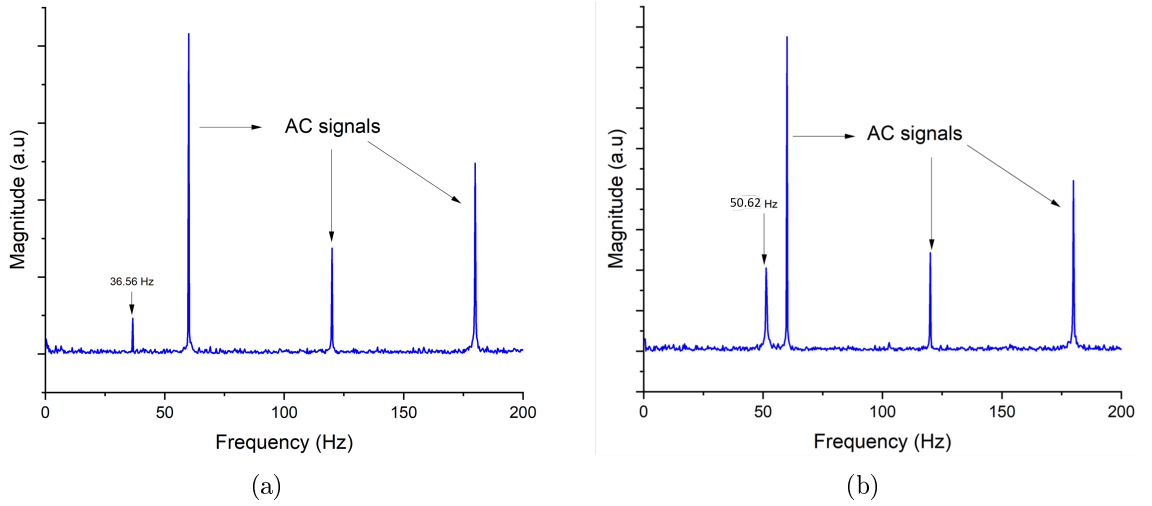


Figure 7.4: (a) Output voltage at 2193.6 rpm or 36.56 Hz. (b) Output voltage at 3037.2 rpm or 50.62 Hz.

Table 7.1: Output voltage at different RPMs.

RPM	Frequency (Hz)	Output Voltage (V)
993.6	16.56	2.54×10^{-5}
993.6	16.56	2.21×10^{-5}
993.6	16.56	2.15×10^{-5}
1012.2	16.87	3.23×10^{-5}
2193.6	36.56	4.64×10^{-5}
3037.2	50.62	1.146×10^{-4}
3075	51.25	7.71×10^{-5}
3093.6	51.56	1.74×10^{-5}

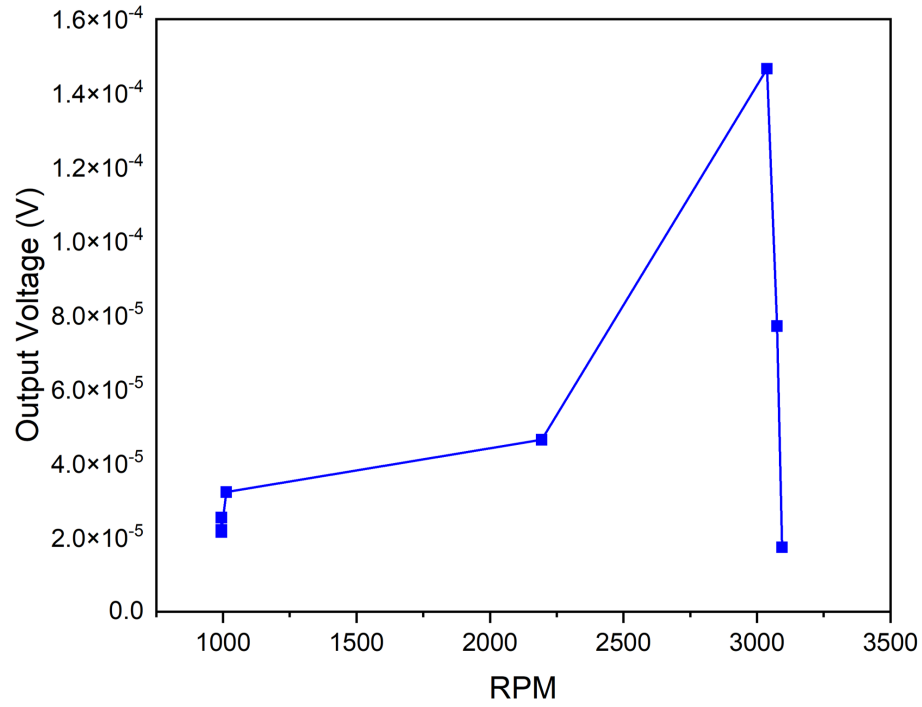


Figure 7.5: The output voltage of bearing sensor at different rotations.

The PVDF-TrFE was also explored in a ball bearing to be used as vibration sensor. In initial tests, PVDF-TrEF was deposited on the surface of bearing and a revolving shaft was passed through the ball bearing, which was fixed in supports. Different speeds were applied to the motor, and the voltage output signal was recorded.

Chapter 8

Conclusion and Future Work

The work presented in this thesis is mainly focused on PVDF-TrFE polymer to find the electrical properties and the mechanical properties. There are several co-polymer combinations and molar concentrations of the piezoelectric polymers. Their molar concentration and co-polymer combinations determine the piezoelectric output. The piezoelectric polymers go through at least five phases. The phases are ϵ , γ , δ , α , and β . Among these phases, the β -phase is a crucial one that produces piezoelectric output. These days, scientists are investigating methods to raise the β -phase in order to improve the piezoelectric performance of piezoelectric polymers. These methods often comprises on stretching, mixing, and polarization with various oxides. When co-polymer TrFE is introduced to PVDF, the piezoelectricity increases without the need for stretching or polling in order to enable the β -phase.

The mechanical and electrical performance of the PVDF-TrFE powder was examined when it was combined with MIBK (Methyl Isobutyl Ketone) solvent at various PVDF-TrFE concentrations to create a piezoelectric solution. Dimethyl sulfoxide (DMSO), is another solvent that is employed. Because of the sulfur content, DMSO dissolves the solute quickly, but because it evaporates more quickly than MIBK, the

solution is more stable at ambient temperature. The development of lengthy chains in film formation, which improves the piezoelectric performance, is another significant DMSO characteristic.

During the initial phase of the study, flexible Kapton cantilever was coated with piezoelectric solutions based on MIBK and DMSO combination, which were then annealed in a convection oven to produce a thin film. Vibration testing was done on PVDF-TrFE using the Kapton cantilever to investigate its mechanical characteristics. Comparing films made using the mixture of MIBK and DMSO, it was discovered that films made with MIBK solvent had higher vibrational voltage amplitudes. Comparing higher concentrations of PVDF-TrFE to lesser quantities, the vibrational amplitude was larger. Mechanical comparison results show that while the MIBK-based solution generates larger vibrational amplitudes, DMSO shows change in the mechanical characteristics of the film. The experiment's second section was centered on the electrical reaction. To do this, the solutions were spin coated once more on an aluminum cantilever with Kapton-sized proportions. Because of its uniform vibration pattern, aluminum's structure is more stiff than Kapton's, which lowers error. The findings indicate that an increase in PVDF-TrFE concentration leads to a corresponding rise in piezoelectric voltage. Additionally, the 1.25 % MIBK + DMSO based polymer solution yields an equivalent sensitivity of 3% polymer solution having only MIBK. This is likely due to the polar nature of DMSO, which forms long chains during the baking process. Along with that the piezoelectric coefficients S_{11} , E_3 , e_{31} , q_{31} of the laboratory made sensors were also compared. It was observed that E_3 and q_{31} of 1.25 % MIBK + DMSO based polymer solution was higher than 3% polymer solution having only MIBK. The experiments in the third section compare only the output voltage, regardless of the thickness of commercial vibration sensor, the laboratory

based vibration sensors and the available ceramic-based device. It was discovered that the explored PVDF-TrFE materials can generate greater and comparable piezoelectric voltage as a commercial polymer vibration sensor.

In terms of applications, a 5 x 2 mm cantilever was fabricated on a flex-PCB using a laser-cut procedure, and it was evaluated in the 600 Hz-1200 Hz range of acoustic frequencies. It was found that applying sound signals at various frequencies caused the PVDF-TrFE coated cantilever to respond.

Another U-shaped piezoelectric Lorentz force based magnetic field sensor is fabricated on a flexible polyimide substrate with a few deposition steps. The sensor consists of copper and silver as a bottom and top electrode while a spin-coated PVDF-TrFE film between them. The device is tested both as an actuator and as a sensor output in the presence of the magnetic field.

To sum up as a potential application, a ball bearing was also used to make the vibration sensor. In initial tests, a revolving shaft was inserted into the ball bearing. Different speeds were applied to the motor, and the voltage output signal was recorded.

In conclusion, the mechanical and electrical characteristics of the device are impacted by variations in the concentrations of polymers and the composition of the solution. Another benefit of polymer-based solutions over ceramic piezoelectric materials is the ease with which the films may be applied to surfaces. Because of the polymer's stronger adhesion to host structures, there is no longer a requirement for glue.

8.1 Future Work

As explained regarding the properties of the PVDF-TrFE polymer, it exhibits excellent piezoelectric properties even without adding any metal oxides. Also, no high voltage or stretching was used to increase the piezoelectric properties. Being a solution, the deposition process varies depending upon the application. The polymer solution was deposited on the circular surface of a ball bearing using a brush because spin coating is not possible, to have the better sensor optimizations and better outputs, the following suggestions can be applied.

1. On the circular surface, direct spin-coating is not possible. There should be an option for the machine to reverse the rotating direction. This is to get a uniform thickness on circular surfaces.
2. After additional optimization of the polymer solution and thickening it, it is now possible to use the solution on a circular surface because the flow can be restricted. The optimization process involves adjusting the polymer concentration. Because during the initial tests, the amplitude of the results was not high, and the output was unstable at certain rotations. However, increasing the thickness of the polymer or using a higher concentration may stabilize the output results.
3. Using a bearing device for active repair detection may not be suitable due to limitations in thickness and instability in output results. Instead, sudden changes in stress values can indicate the presence of a discontinuity in the results, which can be used for active repair detection. Polymer films are found to be more sensitive than ceramic materials in this regard.

4. Further optimizations are required to enhance output quality and eliminate undesired signals before performing the loaded test by applying extra pressure.

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