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affiliée à l'Université de Montréal

**3D Printing of Polyvinylidene Fluoride-Barium Titanate based Flexible
Piezoelectric Sensors for Continuous Blood Pressure Monitoring**

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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Ce mémoire intitulé :

**3D Printing of Polyvinylidene Fluoride-Barium Titanate based Flexible
Piezoelectric Sensors for Continuous Blood Pressure Monitoring**

présenté par **Arijit MANDAL**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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DEDICATION

*This work is dedicated to
all the people who helped me to reach where I am now...*

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I would like to express my deepest gratitude to the members of my advisory committee who guided me during this master's project. A heartfelt thank you goes to my supervisor, Sampada Bodkhe, assistant professor in the Department of Mechanical Engineering at Polytechnique Montréal and director of the Laboratory of Intelligent Structures. Without her guidance, this project would never have seen the light of day. Her trust, support, and introduction to the field of 3D printing of sensors have been invaluable during these past two years.

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RÉSUMÉ

La fabrication additive, souvent désignée sous le nom d'impression 3D, a révolutionné la manière de produire en permettant une production plus rapide, en réduisant les déchets et en offrant une personnalisation inégalée. Un des secteurs qui a particulièrement bénéficié de cette avancée est le domaine biomédical. Cette étude s'aventure dans l'univers des dispositifs médicaux spécifiques au patient, en explorant spécifiquement le potentiel des capteurs piézoélectriques imprimés en 3D pour la surveillance en temps réel de la pression artérielle et du rythme cardiaque. Notre attention s'est concentrée sur la création de capteurs à partir d'un matériau intelligent: le fluorure de polyvinylidène (PVDF). Doté de propriétés piézoélectriques, il est particulièrement adapté à la fabrication de capteurs de pression. Le PVDF est reconnu pour sa biocompatibilité, sa flexibilité et sa capacité intrinsèque à transformer le stress mécanique en tension électrique. Malgré des coefficients piézoélectriques inférieurs à ceux des alternatives céramiques, l'adoption de stratégies comme l'ajout de nanoparticules de BaTiO_3 a considérablement amélioré ses performances. Les capteurs ont été fabriqués en utilisant la méthode d'impression 3D Direct-ink write (DIW), qui a augmenté la sensibilité du PVDF en l'étirant pendant le processus de fabrication. Des paramètres d'impression clés comme la taille de la buse et la pression ont été ajustés pour obtenir une phase β optimale de 70% et une cristallinité totale de 48,3%. La polarisation thermique a encore augmenté la sensibilité du capteur à une valeur d_{33} de 12 pC N^{-1} . Les capteurs résultants ont été soigneusement caractérisés sous des pressions dynamiques, démontrant une excellente linéarité ($R^2 = 0,99$) et une durabilité sur 1 heure (3600 cycles). Leur sensibilité à la pression de $0,024 \text{ V kPa}^{-1}$ démontre encore l'efficacité de ces capteurs. Le potentiel de ces capteurs a été testé à travers des mesures continues de pression artérielle et de rythme cardiaque sur un sujet humain. Le capteur a montré des performances dans les marges d'erreur permises avec un écart type de 3,87 mmHg, 0,63 mmHg et 2,4 battements par minute pour la pression artérielle systolique, la pression artérielle diastolique et le rythme cardiaque respectivement, comparé à un appareil standard de surveillance de la pression artérielle. Cette étude met en lumière le potentiel prometteur de la création de capteurs portables grâce à l'impression 3D, ouvrant de nouvelles perspectives pour les applications médicales spécifiques aux patients. Cette recherche marque une avancée essentielle dans la surveillance de la pression artérielle, offrant une alternative robuste, écologique et conviviale aux dispositifs de surveillance traditionnels et encombrants.

ABSTRACT

Additive manufacturing, often referred to as 3D printing, has revolutionized the way products are made by enabling quicker production, minimizing waste, and allowing for unmatched customization. One domain witnessing notable strides from this development is the biomedical sector. This study ventures into the realm of patient-specific medical devices, specifically exploring the potential of 3D printed piezoelectric sensors for real-time blood pressure and heart rate monitoring. Our focus centred on crafting sensors from a smart material - polyvinylidene fluoride (PVDF), imbued with piezoelectric properties, makes it an apt choice for fabricating pressure sensors. PVDF is recognized for its biocompatibility, flexibility, and inherent ability to convert mechanical stress into electrical voltage. Despite its lower piezoelectric coefficients compared to ceramic alternatives, the adoption of strategies such as the inclusion of BaTiO₃ nanoparticles significantly boosted its performance. The sensors were fabricated using the Direct-ink write (DIW) 3D printing method, which enhanced the sensitivity of PVDF through stretching during the fabrication process. Key printing parameters such as nozzle size and pressure were fine-tuned to achieve an optimal β -phase of 70% and an overall crystallinity of 48.3%. Thermal contact poling further increased the sensor's sensitivity to a d_{33} value of 12 pC N⁻¹. The resulting sensors were meticulously characterized under dynamic pressures, demonstrating excellent linearity ($R^2 = 0.99$) and durability across 1 hour (3600 cycles). Their pressure sensitivity of 0.024 V kPa⁻¹ further signifies the efficiency of the sensors. The potential of these sensors was tested through continuous blood pressure and heart rate measurements on a human subject. The sensor exhibited performance within permissible error margins with a standard deviation of 3.87 mmHg, 0.63 mmHg and 2.4 beats per minute for systolic blood pressure, diastolic blood pressure and heart rate respectively when compared with a standard blood pressure monitoring device. This study illuminates the promising potential of creating wearable sensors using 3D printing, further expanding the horizons for patient-specific medical applications. This research signifies a crucial advancement in blood pressure monitoring, offering a robust, eco-friendly, and user-friendly alternative to traditional, bulky monitoring devices.

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LIST OF SYMBOLS AND ABBREVIATIONS

3D	Three dimensional
AM	Additive manufacturing
A_α	Absorption fraction of α -phase
A_β	Absorption fraction of β -phase
BaTiO ₃	Barium titanate
BP	Blood pressure
CAD	Computer aided design
CNTs	Carbon nanotubes
CPR	Cardiopulmonary resuscitation
d	Direct piezoelectric coefficient
DBP	Diastolic blood pressure
DIW	Direct-ink write
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
FDM	Fused Deposition Modelling
FTIR	Fourier transform infrared spectroscopy
F_β	B-phase fraction
PDMS	Polydimethylsiloxane
PLA	Polylactic Acid

PLLA	Poly(L-lactic acid)
PPG	Photoplethysmography
PPW	Pulse pressure wave
PTT	Pulse transit time
PVDF	Polyvinylidene fluoride
PVDF-HFP	Polyvinylidene fluoride-co-hexafluoropropylene
PVDF-TrFE	Polyvinylidene fluoride-co-trifluoroethylene
PZT	Lead zirconium titanate
SBP	Systolic blood pressure
ZnO	Zinc oxide
α	Alpha
β	Beta
γ	Gamma
χ_c	Total crystallinity
d'	Converse piezoelectric coefficient
ε	Dielectric permittivity
ε_0	Dielectric permittivity of a vacuum ($8.854 \times 10^{-12} \text{ F m}^{-1}$)

CHAPTER 1 INTRODUCTION

1.1 Background

Additive manufacturing often referred to as 3D (three-dimensional) printing, is a rapidly emerging technology with the potential for a revolutionary shift within the manufacturing industry. Its benefits are abundant, including accelerated production speeds, customization, reduced material waste, and simple fabrication processes.[1] These compelling advantages have led to its rising popularity across several sectors, such as aerospace, automotive, biomedical, and robotics.[1-3] A crucial factor in its widespread adoption is the reduced cost and accelerated production timelines that it offers.[2, 3]

The unique capability of this technology to produce patient-specific devices lends itself particularly well to the biomedical field.[4] The simple fabrication process paves the way for ramping up the production of critical medical devices during emergencies, such as global pandemics during supply-chain disruptions.[5] Consequently, there's a driving motivation to further harness and expand the capabilities of AM, particularly for crafting medical devices adept at remote and continuous health monitoring.

One promising avenue involves enhancing AM capabilities to fabricate smart materials, like polyvinylidene fluoride (PVDF). PVDF is a semi-crystalline polymer noted for its piezoelectric properties.[6] Piezoelectricity, the conversion of mechanical stress into electrical voltage (and vice versa), makes PVDF an ideal material for pressure or force sensors. Since PVDF generates voltage from its inherent properties, it does not need external power, making it perfect for long-term medical applications without the complications of carrying, recharging and replacing bulky batteries.[7, 8] PVDF's biocompatibility, flexibility, chemical resistance, and low wear and tear resistance contribute to its attractiveness for creating comfortable and environmentally friendly sensors, that can be used over extended periods. [7, 9, 10]

However, as a polymeric piezoelectric material, PVDF does present one drawback—it has lower piezoelectric coefficients than its ceramic counterparts.[4] Nevertheless, various techniques can enhance these coefficients. For instance, the addition of BaTiO₃ nanoparticles,[6, 8-10] mechanical stretching,[11, 12] polar solvents,[8, 10, 12] and electrical poling[13-15] are found to improve PVDF's piezoelectric performance. Notably, the direct-ink-write 3D printing process also contributes to this enhancement by inducing stretching during

fabrication and assisting in the alignment of polymer chains, thus increasing the piezoelectric coefficient.[8, 10, 12, 13]

Given their biocompatibility, flexibility, dynamic pressure sensing ability, and excellent frequency response, 3D printed PVDF sensors offer great potential for real-time, continuous monitoring of vital health parameters like blood pressure and pulse rate.[5] Traditional methods of blood pressure measurement, often relying on bulky and uncomfortable cuffs, are unable to provide continuous readings.[16] In the event of medical emergencies such as cardiopulmonary resuscitation (CPR), continuous monitoring of blood pressure can significantly enhance the effectiveness of the treatment. There are some advances in continuous non-invasive BP measurement using piezoelectric sensors but they either are not environmentally friendly (use lead based material) or necessitate complex fabrication processes, like electrospinning.[17-19]

In our work, we delved into the potential of 3D printed piezoelectric sensors for real-time blood pressure monitoring. We fabricated the sensors using the direct ink write 3D printing method, characterized their potential for dynamic pressure detection, and tested their performance on a subject. For testing on subjects, the sensors were placed on the skin near radial artery, secured with a strap and the data was collected for 600 seconds. Simultaneously a standard BP device (UA-767FAM) was used to collect data and these data were compared against each other. The results confirmed the ability of these sensors to serve as continuous blood pressure monitoring devices, suggesting a promising direction for future technology.

This project is a collaboration with IMPACK CPR, a Montreal-based start-up developing a computerized CPR system. They aim to create an automated device that paramedics can use to perform CPR. To obtain feedback from each compression and monitor changes in blood pressure, they propose using a flexible pressure sensor patch. This patch would be placed on the patient near the radial artery, providing continuous blood pressure readings during each compression. The data from these sensors would then be used to control the pressure of the computerized CPR device, allowing for more precise and effective treatment.

1.2 Thesis organization

The thesis is divided into six different chapters. The first chapter provides an introduction and outlines the structure of the work. The second chapter presents a comprehensive literature review covering topics of piezoelectricity, the role of PVDF in piezoelectric sensors, the fabrication of PVDF-based piezoelectric sensors, the principles and techniques of 3D printing

and the application of 3D printing in the fabrication of PVDF-based piezoelectric sensors. It also covers blood pressure monitoring, including the traditional methods and the emerging field of continuous monitoring using flexible and piezoelectric sensors. The third chapter identifies the research problem and outlines the specific research objectives of the study. The fourth chapter is a research article on the development and evaluation of 3D printed flexible PVDF-BaTiO₃ based piezoelectric sensors for continuous blood pressure monitoring, including the methodology, results and discussion of the study as submitted to the *Advanced Engineering Materials* journal. The fifth chapter provides a general discussion of all the results. The sixth chapter concludes the thesis by summarizing the findings, drawing conclusions and making recommendations for future research in this field.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction to piezoelectricity

The property of piezoelectricity—a term that encapsulates two distinct effects—was first identified in inorganic crystals by Jacques and Pierre Curie in the 1880s.[20] When we refer to piezoelectricity, we allude to a feature that allows non-centrosymmetric crystals to generate an electric polarization or charge when stress is applied, and vice versa. In the first case, the process is called the direct piezoelectric effect.[4] It empowers these materials to sense dynamic changes in pressure and force. The second case, known as the indirect piezoelectric effect, finds extensive use in actuation.

Piezoelectric materials can detect dynamic forces with frequencies ranging from a few Hz to several MHz and enable precise measurements of forces up to several kiloNewtons (kNs).[21] These materials can operate under harsh conditions, severe shock, or a variety of chemicals. The piezoelectric property naturally occurs in some materials such as quartz or Rochelle salt.[21] This property can also be induced in some ceramic and polymeric materials. The choice of materials always depends on the special requirements of applications.

The first non-ceramic materials that showed piezoelectricity were biomaterials like bone, wood, and DNA.[22] However, the piezoelectric constants were 1/20th of quartz which is around 2.3-4 pC/N. The discovery of piezoelectricity in polyvinylidene fluoride (PVDF) in 1969 by Heiji Kawai is considered a milestone because the piezoelectric constants in PVDF were larger than those previously discovered in polymers.[23] This resulted in significant research on PVDF in the following years. Today, piezoelectric polymers are at the center of research, from biomedical applications to energy harvesting.

2.1.1 Theory of piezoelectricity

Piezoelectricity is caused by non-centrosymmetry in the crystal structure of an element.[4] When the crystal structure is deformed, this asymmetry creates a net positive and negative charge on two sides of the crystal's center and hence a dipole is created as shown in the figure 2.1.

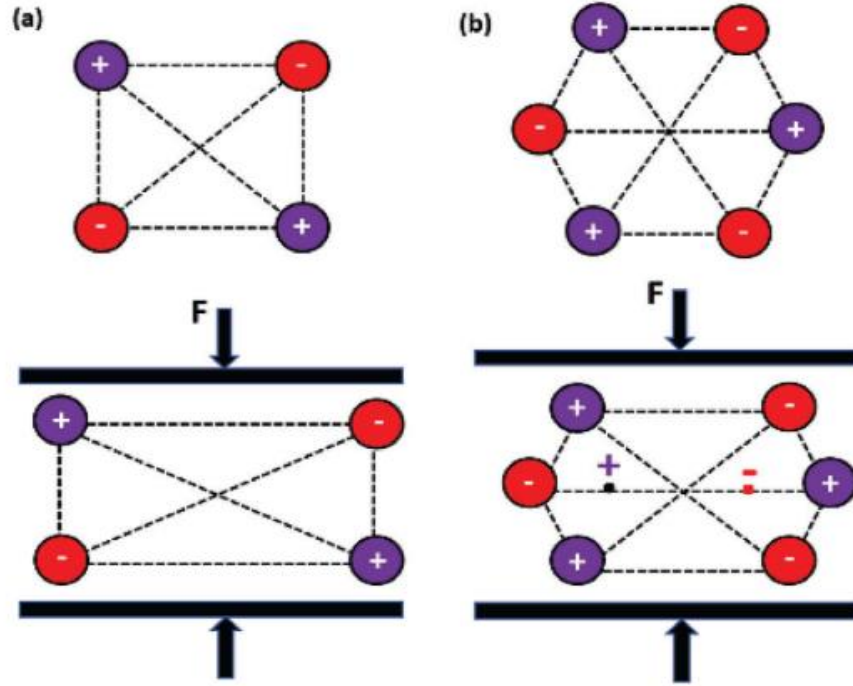


Figure 2.1 Schematic of 2D crystals (a) Non Piezoelectric square (b) Piezoelectric hexagon [4]

The piezoelectric relations based on IEEE constitutive equations are described below. [22, 24] The equation for direct piezoelectric effect where the material produces voltage under applied stress and the indirect piezoelectric effect where the material produces strain in presence of electric field is given by:

Direct Effect:

$$D_k = d_{jk}T_j + \varepsilon_{km}^T E_m \quad (2.1)$$

which can be also written in tensor form as below:

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} \varepsilon_{11}^T & \varepsilon_{12}^T & \varepsilon_{13}^T \\ \varepsilon_{21}^T & \varepsilon_{22}^T & \varepsilon_{23}^T \\ \varepsilon_{31}^T & \varepsilon_{32}^T & \varepsilon_{33}^T \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \quad (2.2)$$

Indirect Effect:

$$S_i = s_{ij}^E T_j + d_{im}' E_m \quad (2.3)$$

The variables T , S , E , and D correspond to stress, strain, electric field, and electric displacement, respectively, in the context of a piezoelectric material. The piezoelectric constant is denoted as ' d ' which is defined as the charge produced per unit of applied stress. The material's mechanical compliance when an electric field E is constant is shown as ' s^E ', whereas ' ϵ^T ' stands for the material's permittivity when the stress T is constant. The subscripts ' i ', ' j ', and ' k ' indicate different directions within the material's coordinate system, similar to x , y , and z in Cartesian coordinates, and can take values between 1 and 3. Rotational movement around these three axes is marked by the subscript ' m ', which can have values from 4 to 6.

Piezoelectric energy harvesting devices primarily function in two modes. In mode 33, stress applied runs in the same direction as polarization, which is the thickness direction ("3"). In contrast, mode 31 sees stress applied at a right angle to the polarization direction.

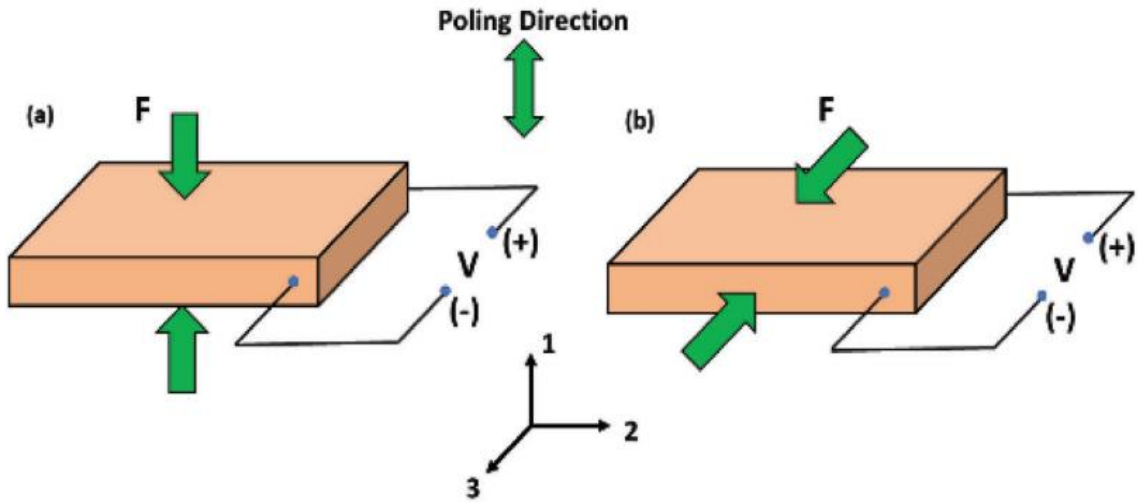


Figure 2.2 Operating modes of piezoelectric material a) 33 mode b) 31 mode [4]

The relationship between the direct and indirect piezoelectric coefficients can be given as:

$$d = \epsilon_r \epsilon_0 d' \quad (2.4)$$

where ϵ_r and ϵ_0 (8.854×10^{-12} F/m) are the relative dielectric permittivity of the piezoelectric material and the dielectric permittivity of the vacuum, respectively.

2.1.2 Types of piezoelectric materials

The piezoelectric materials can be broadly classified into following categories[21]:

Crystals: These are naturally occurring materials, such as quartz and Rochelle salt, which exhibit the piezoelectric effect.

Ceramics: These are piezoelectric materials that possess a polycrystalline structure that is; they are made up of many crystals or grains which can vary in size and orientation. Some examples of piezoceramic materials include barium titanate, lead zirconate titanate, and zinc oxide.

Polymers: These are flexible materials that exhibit piezoelectricity. Examples include polyvinylidene fluoride (PVDF) and its copolymers, nylon, and poly-L-lactic acid.

Composites: These are combinations materials that demonstrate piezoelectric activity. Some examples are PVDF-BaTiO₃ composites, PVDF-PZT composites, and PDMS-PZT composites.

Table 2.1 Types of piezoelectric materials [21]

Category	Piezoelectric Material	Piezoelectric constant (d_{31} , pC/N)	Young's Modulus (N/m ²)
Crystal	Quartz	2.3-4.6	90×10^9
Ceramic	PZT	110	60×10^9
Ceramic	BaTiO ₃	78	59×10^9
Polymer	PVDF	23	2×10^9
Composite	1-3 PZT/epoxy	170-230	$13-33 \times 10^9$

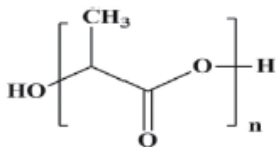
2.1.3 Flexible Piezoelectric materials

The flexible piezoelectric sensors are generally made of polymers. They can undergo higher strains and hence are good candidates for applications in biomedical fields to be used as wearable devices, electronic skins and soft actuators which require higher bending or twisting

(PVDF's young's modulus is 30 times less as compared to PZT as shown in table 2.1).[22] They tend to have less piezoelectric constant and lower melting point than piezoceramics but they are very useful for applications which require flexibility and can be easily integrated into gloves for robotics applications or as a sensor patch.[24]

Table 2.2 Some commonly used flexible piezoelectric materials and their properties are listed below [22, 24]

Materials	Structure	Piezoelectric Coefficient (d_{ij}) pC/N
PVDF	$\left[\begin{array}{cc} \text{H} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{F} \end{array} \right]_n$	$d_{33} \approx 23-30$
PVDF-TrFE	$\left[\begin{array}{cc} \text{F} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{H} \end{array} \right]_a \left[\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{H} \end{array} \right]_b$	$d_{33} \approx 25-40$
PVDF-HFP	$\left[\begin{array}{cc} \text{F} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{H} \end{array} \right]_a \left[\begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{CF}_3 \end{array} \right]_b$	$d_{33} \approx 24$
PLLA	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{O} - \text{C} - \text{C} \\ \quad \\ \text{H} \quad \text{O} \end{array} \right]_n$	$d_{14} \approx 10$
Nylon	$\left[\begin{array}{c} \text{H} \\ \\ -\text{N} - (\text{CH}_2)_{2m+1} - \text{C} \\ \quad \quad \quad \\ \quad \quad \quad \text{O} \end{array} \right]_n$	$d_{31} \approx 3$

PLA	 $\text{HO} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---} \text{C} \text{---} \text{C}(=\text{O}) \text{---} \text{O} \end{array} \right]_n \text{H}$	$d_{33} \approx 1.5$
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2.2 PVDF in piezoelectric sensing

The piezoelectric property of polyvinylidene fluoride (PVDF) was discovered by Kawai in 1969.[7] PVDF is a semi-crystalline polymer and exists in five known phases: α , β , γ , δ , and ϵ . [4, 7] The properties of PVDF depend on its phase. The α and β phases are the most common, with some amount of the γ phase, which is a transition state between the two. The α - phase is non-polar, whereas the β - phase is the most polar due to its structure (shown in figure 2.3) and shows the highest dipole moment (8×10^{-30} C m). In the α - phase, the PVDF chain forms a trans-gauche conformation (TGTG'), and in the β - phase, it forms an all-trans conformation (TTTT).[4, 7] The γ - phase, which is an intermediate phase between α and β , exhibits a low dipole moment and has a mixture of trans and gauche conformations as shown in Figure 2.3.

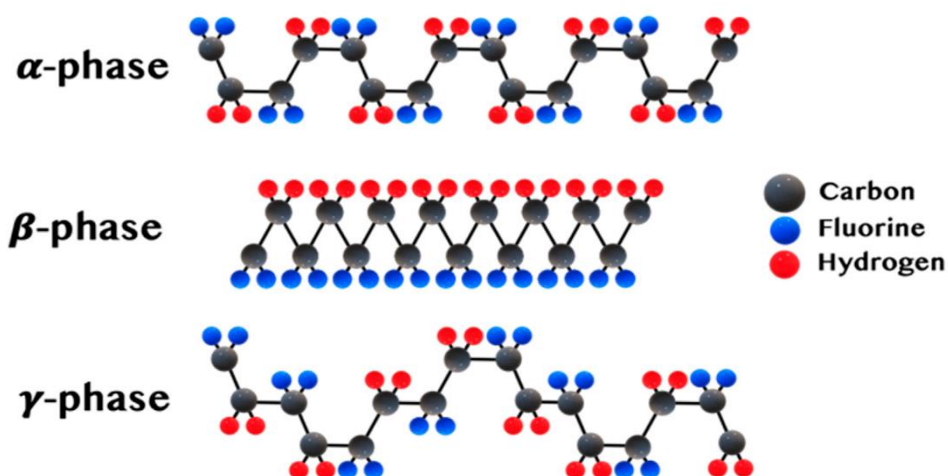


Figure 2.3 Molecular orientation in α , β , and γ - phases of PVDF [7]

Increasing the β -phase content in PVDF:

The piezoelectric output in PVDF can be increased by enhancing the β -phase content.[8, 12, 22] The β -phase is influenced by both the fabrication and post-processing procedures. Fabrication processes involving the use of polar solvents can affect the β -phase content after crystallization.[8, 10, 12] These polar solvents assist in the alignment of chains by interacting

with the fluorine atoms in the PVDF molecular chains.[12] A suitable combination of solvents for the fabrication of PVDF can lead to a high β -phase. The β -phase will also depend on the solvent evaporation rate and fabrication temperature.[25-28]

Another method for improving the β -phase in PVDF is the addition of fillers.[12, 29-32] Various fillers like PZT, BaTiO₃, CNTs, ZnO, etc., are added to enhance the β - phase and piezoelectric output of PVDF. Among these, BaTiO₃ and ZnO are biocompatible and hence suitable fillers for medical applications.[24, 29, 31]

In post-processing, the β -phase can be increased by annealing, [22, 25, 33] mechanical stretching,[11, 12, 31] and electrical poling.[12-15] Various authors report conflicting results regarding the effect of annealing on the β -phase of PVDF.[25, 33, 34] Mechanical stretching in the ratio of five is found to be optimum for maximum β - phase.[11]

Electrical poling involves applying a high electrical field across the PVDF to align all the dipoles in the same direction and also increase the β - phase content.[11] There are two types of poling processes: corona Poling and contact Poling.

In corona poling, a high voltage is applied with the help of a needle which causes a breakdown of air or corona discharge that aligns the dipoles in the polymer.[13] In contact poling, the voltage is applied directly to the polymer using electrodes which leads to the alignment of dipoles.[15] The polymer is usually heated during the process to allow the polymer chains to move more freely during the poling process.

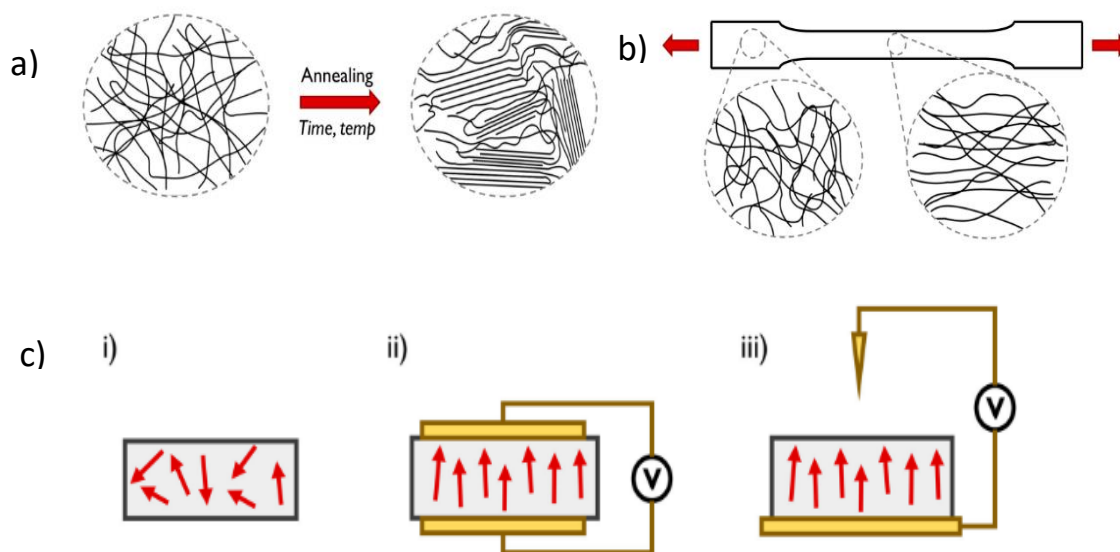


Figure 2.4 Ways of increasing β - phase post fabrication process a) annealing b) stretching c) Poling i) unpoled sample, ii) Contact poling process, iii) Corona poling process [22]

2.3 Fabrication methods of PVDF based piezoelectric sensors

The most commonly used methods for fabricating PVDF and PVDF-based polymer composites include solution casting, spin coating, electrospinning, hot pressing, among others.

2.3.1 Solution casting:

Solution casting is a simple technique for fabricating PVDF films. In this method, a solution of PVDF is prepared by dissolving it in suitable solvents such as acetone or N,N-dimethylformamide (DMF) using heat and agitation. The solution is then spread onto a flat surface, and the solvents are allowed to evaporate, leaving behind a PVDF film.[28]

2.3.2 Spin coating:

Spin coating is another manufacturing method that produces thin and uniform PVDF films. In this approach, the PVDF solution is poured onto a glass substrate rotating at a specific RPM. The rotation spreads the solution across the glass, and as the solvent evaporates, a film forms. The thickness of this film is controlled by the rotational speed and can range from several nanometres to a few micrometres.[35]

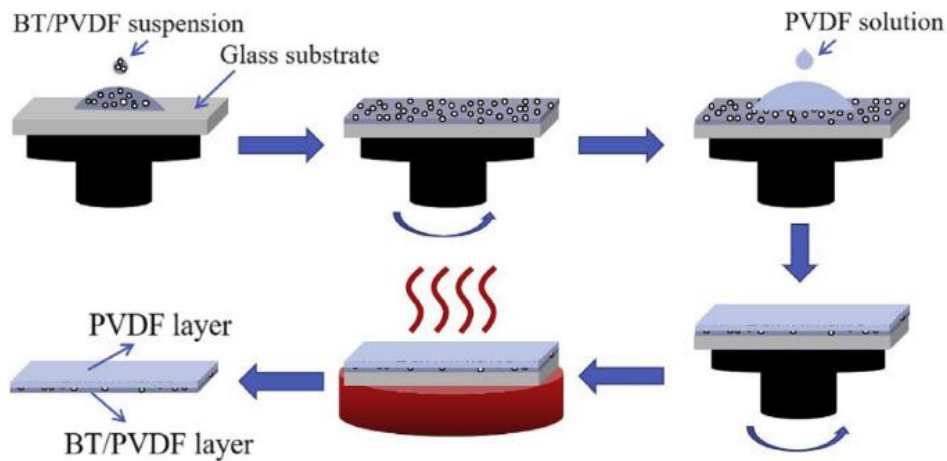


Figure 2.5 Spin Coating process [36]

2.3.3 Electrospinning:

Electrospinning involves creating nanoscale (diameter) piezoelectric fibers using high voltage electric fields. Here, the PVDF solution is injected through a syringe nozzle under high voltage. This leads to the formation of a Taylor cone at the syringe tip when the electrostatic force exceeds the surface tension, producing thin fibers after solvent evaporation. These fibers are collected on a grounded collector in the form of thin films. Factors such as solution concentration, voltage, tip-to-collector distance, and flow rate can be optimized to control properties like fiber diameter and the β -phase. [7, 27, 36, 37]

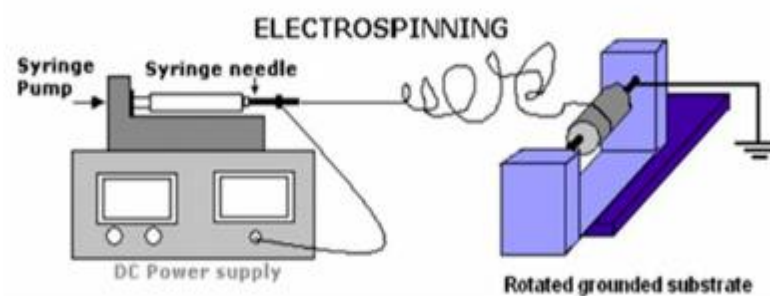


Figure 2.6 Electrospinning process [7]

2.3.4 Hot pressing:

Hot pressing is a technique used to create PVDF sheets. In this method, PVDF powder is melted between two metal plates, and pressure is applied to form thin sheets from the melted PVDF. After cooling, thin PVDF films are obtained. PVDF produced in this way generally has a low β -phase and requires stretching to transform the α -phase into the β -phase.[38]

2.3.5 Other methods:

Apart from the methods mentioned above, the other methods include electrospraying,[39] ultrasonic spraying,[40] cold pressing,[36] blade casting,[41] melt blending,[42] and 3D printing.[11, 12, 31, 43] The 3D printing of PVDF-based piezoelectric sensors allows for the prototyping of complex three-dimensional structures, offering a cost-effective and efficient approach. Furthermore, it eliminates the need for subsequent steps like cutting and mold creation. The fabrication of PVDF-based piezoelectric sensors by 3D printing is discussed in more detail in the following sections.

2.4 3D printing: principles and techniques

Additive manufacturing, commonly known as 3D printing, is a process of manufacturing a three-dimensional object by depositing materials layer by layer. This technology was invented in the 1980s by Charles Hull.[44]

2.4.1 Overview of 3D printing process:

The process for 3D printing an object generally involves the following steps:[1, 3]

3D Modelling: In this step, the desired 3D model of an object is prepared using a Computer-Aided Design (CAD) software package. After the model is prepared, it is saved in .STL file format for the slicer software.

Slicing: After the model of the object is prepared, it is cut into thin horizontal layers so that the printer can print the object layer by layer. This process is called slicing and is executed using a slicing software. After slicing the model, the slicing software generates a G-code file for the printer.

3D Printing: The G-code data is transferred to the printer using a USB or SD card, and the print is launched. Depending on the printing process and print material, suitable printing

parameters such as printing speed, temperature, and resolution can be selected to optimize the print.

Post-Processing: This process involves removing the extra supports if any, curing, or heat treatment to improve the properties of the printed part.

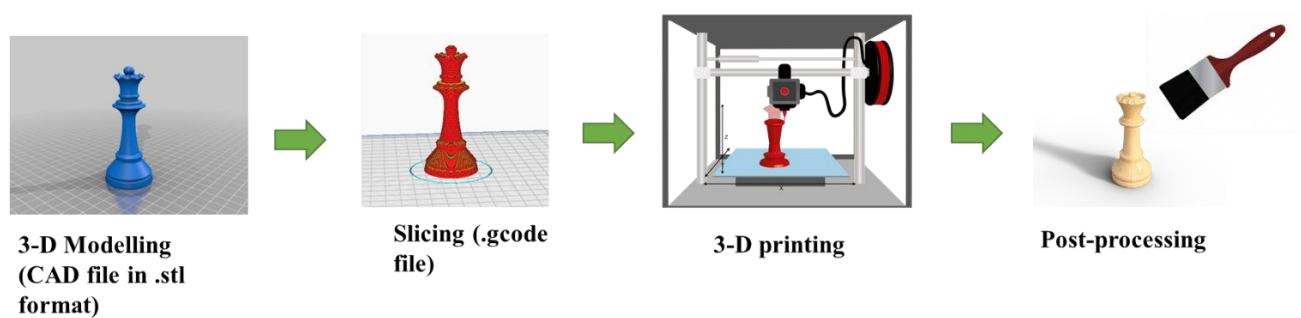


Figure 2.7 3D printing steps

2.4.2 Printing materials:

The printing materials generally depend on the printing process but can be categorized as polymers, metals, ceramics, and composites.[1] Polymers are most commonly used for 3D printing as they have a low melting point and are inexpensive.[45] Recently, printing of metal parts is also gaining popularity due to less material wastage and faster production.[46] A significant part of research in 3D printing is being done with composite materials due to their exceptional strength to weight ratio.[47]

2.4.3 Types of 3D printing:

The selection of the printing process depends on various factors such as cost, material, printing quality, and printing speed.[1] The most commonly used printing process is Fused Deposition Modelling (FDM). [11] In this method, a thermoplastic polymer or polymer composite filament is passed through a heated nozzle above its melting temperature and the object is formed layer by layer. This process is comparatively inexpensive and fast but generally results in a poor surface finish. Stereolithography (SLA) is another method which can produce high-quality surface finish products and high accuracy.[48] In SLA, UV light is used to cure a photopolymer resin and form the object layer by layer. This process is comparatively slow and has a limited choice of materials.[48]

If one wishes to print a material without supports, selected laser sintering (SLS) can be a good option.[49] In this method, a powder-based material is heated below its melting point and sintered to create 3D objects. This process can also be used to print metals.[50]

However, if the print involves a thermoset-based polymer composite or needs to be at room temperature, then Direct Ink Write (DIW) is a convenient choice.[8] The DIW is a method where the polymer or polymer composite solution is extruded at room temperature on the printing bed. The polymer can cure in various ways, such as through solvent evaporation, high-temperature curing, or UV rays, to produce the 3D printed part.[51]

Table 2.3 Types of 3D printing processes, their applications, resolutions and cost [2, 45]

3D Printing Method	Materials Used	Applications	Printing Resolution	Cost
Fused Deposition Modeling (FDM)	Thermoplastics (e.g., ABS, PLA)	Prototyping, consumer products, tooling, engineering parts, architectural models	100-300 microns	Low to moderate
Stereolithography (SLA)	Photopolymer resins	Prototyping, jewellery, dental models, intricate models, concept modelling	25-100 microns	Moderate to high
Selective Laser Sintering (SLS)	Nylon, polyamide, metal powders	Functional prototypes, end-use parts, tooling, aerospace components	100-200 microns	High

Digital Light Processing (DLP)	Photopolymer resins	Dental models, jewelry, industrial prototypes, custom parts	25-100 microns	Moderate to high
Binder Jetting	Sand, metal powders, ceramics	Sand casting molds, metal parts, architectural models, artistic sculptures	100-300 microns	Moderate to high
Direct Metal Laser Sintering (DMLS)	Metal powders (e.g., titanium, stainless steel)	Aerospace components, medical implants, complex metal parts	20-100 microns	High
Electron Beam Melting (EBM)	Metal powders	Orthopedic implants, aerospace components, dental applications	50-200 microns	High
PolyJet	Photopolymer resins	Prototyping, medical models, product design, consumer goods	16-32 microns	Moderate to high
Direct Ink Write (DIW)	Hydrogels, biopolymers, colloidal suspensions	Tissue engineering, soft robotics, biomedical applications, flexible electronics, sensors, organs	Variable (depends on ink/material)	Variable (depends on ink/material)

2.5 3D printing of PVDF-based piezoelectric sensors

The 3D printing of PVDF based sensors allows manufacturing of intricate designs and adjustable physical properties particularly suited for the manufacturing wearable sensors.[45] When 3D printed, the PVDF is stretched during the 3D printing process, which causes chain alignment in the polymer and hence increases the electroactive β - phase.[8, 12] However, electrical poling is required as an additional step to align high sensitivity.[15] Several authors have tried to do simultaneous poling with 3D printing, but the sensitivity reported is much lower when compared to a sensor that is poled after fabrication.[13] 3D printing PVDF offers the advantage of fast and customized production of sensors.[2] Also, the sensors produced can be easily integrated or embedded in 3D printed parts, which can transform normal objects into smart objects with the capability to sense the environment.[10] The flexibility and ease of the manufacturing process can help to scale up production during a pandemic-like situation.

Table 2.4 PVDF-based sensors fabricated by 3D printing[2]

Fabrication method	Materials	Piezoelectric coefficient [pC N⁻¹]	Output voltage [V]	Output current [nA]
FDM	PVDF	$d_{31} = 0.048$	NA	0.106
FDM	PVDF	$d_{33} = 0.007$	NA	0.0039
FDM	PVDF	$d_{33} = 0.01$	NA	0.0065
FDM	15 wt% BaTiO ₃ -PVDF	$d_{33} = 0.1$	NA	0.0442
FDM	9 wt% BaTiO ₃ -PVDF	$d_{31} = 0.0029$	NA	0.05
FDM	9 wt% BaTiO ₃ -PVDF	$d_{31} = 0.021$	NA	0.15
FDM	PVDF	x	NA	1.6

DIW	10 wt% BaTiO ₃ -PVDF	$d_{31} = 18$	2.8	NA
DIW	93 wt% BaTiO ₃ -PVDF	$d_{33} = 420$	NA	NA
DIW	71 wt% BaTiO ₃ -PVDF	$d_{33} = 200$	NA	NA
DIW	10 wt% BaTiO ₃ -PVDF	$d_{31} = 18$	NA	NA
SLS	PVDF-pBT- 4Ag	$d_{33} = 9$	10	142

2.6 Direct ink-write 3D printing of PVDF-BaTiO₃:

Direct Ink Writing (DIW) 3D printing involves extruding Polyvinylidene Fluoride (PVDF) or PVDF-based composites through a nozzle at high pressure and room temperature.[8, 10, 52] This method was utilized by Bodkhe et al. to print PVDF and Barium Titanate (BaTiO₃) nanocomposite-based piezoelectric ink, which displayed a piezoelectric coefficient d_{31} value of 18 pC N⁻¹. Several methods of mixing BaTiO₃ to prepare the ink were compared, such as ball milling, extrusion, and sonication. Ball milling for 20 minutes was found to be the ideal process for mixing and preparing the nanocomposite-based ink.[8] Longer milling times led to heat generation, which facilitated the formation of a more thermodynamically stable α -phase. In contrast, milling for less than 20 minutes did not cause the necessary agglomeration of BaTiO₃ particles for the nucleation of the β -phase.[8] The addition of BaTiO₃ nanoparticles was evaluated at different percentages, and 10% by weight was found to be optimal, increasing the β -phase by 16% compared to solely 3D printed PVDF films. These printed films generated approximately 2 volts with simple finger taps.[8, 10]

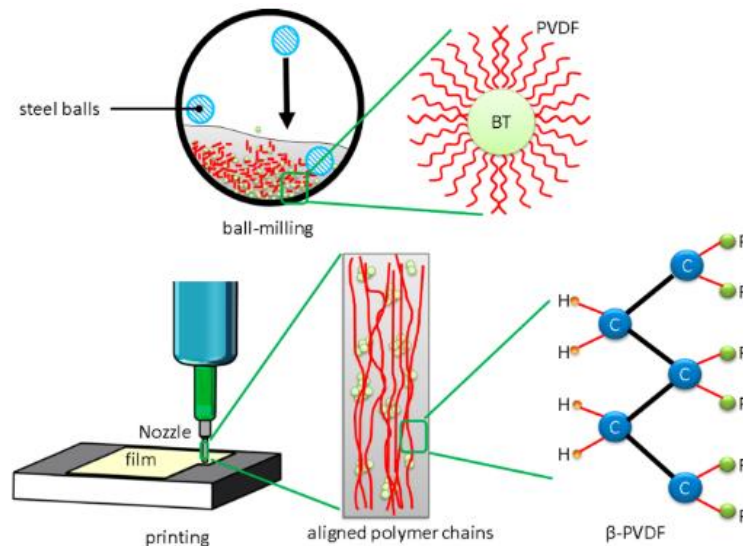


Figure 2.8 Direct ink write 3D printing of PVDF nanocomposite based sensors[8]

2.7 Blood pressure monitoring

Blood pressure is a critical indicator of overall health. It refers to the pressure exerted by blood on the artery walls during circulation.[16] Systolic blood pressure measures the pressure on the artery walls when the heart contracts and pumps blood, whereas diastolic blood pressure refers to the pressure when the heart relaxes and expands. The range of normal systolic and diastolic blood pressure for a healthy adult are 90-140 mmHg and 60-90 mmHg, respectively. [53]

Hypertension is a condition characterized by systolic and diastolic pressure exceeding 140 mm Hg and 90 mmHg, respectively. It is a leading cause of cardiovascular diseases and can result in strokes or heart attacks. [53]

On the other hand, hypotension occurs when the systolic pressure and diastolic pressure drop below 90 mmHg and 60 mmHg, respectively. This condition might lead to symptoms like dizziness, fatigue, and nausea, as the blood may not circulate throughout the body efficiently.[53]

Stephen Hales made the first instance of blood pressure measurement in 1711.[54] Hales measured the blood pressure of a horse by connecting a glass tube to the animal's artery and observing the rise and fall of blood within the tube. Regrettably, the horse did not survive the process, making it evident that this method was not suitable for humans. Fortunately, we now possess far more humane and effective techniques for measuring blood pressure.[16]

2.7.1 Traditional blood pressure monitoring

Non-invasive blood pressure measurement:

Auscultatory: The auscultatory method is the traditional technique for measuring blood pressure and is often considered the gold standard, particularly in clinical environments. This method involves the use of a stethoscope and a sphygmomanometer, which uses an inflatable cuff placed around the arm. The pressure in the cuff is increased until the artery is completely blocked and blood flow is halted. The cuff is then gradually deflated. A clinician uses the stethoscope to listen for Korotkoff sounds, which are the sounds of blood starting to flow again through the artery.[55] The pressure at which the first sound is heard is known as the systolic pressure. The cuff is further deflated until no sound is heard, and the pressure at this point is known as the diastolic pressure.[55]

This method requires a skilled medical professional for accurate blood pressure measurement and does not provide continuous readings.[16]

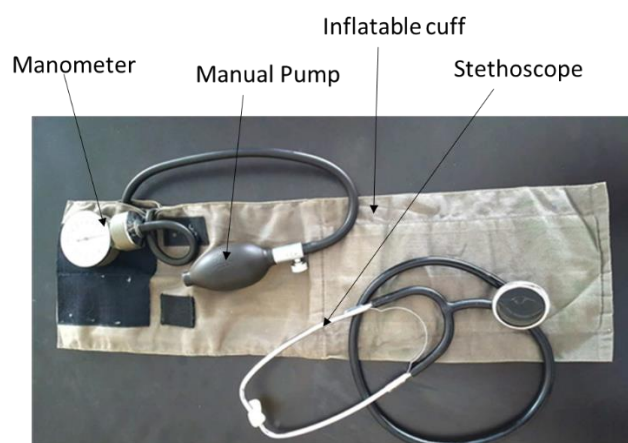


Figure 2.9 Equipment for auscultatory technique: blood pressure cuff with stethoscope[55]

Oscillometric: The oscillometric method is commonly employed in electronic or automatic blood pressure devices. It consists of an inflatable cuff and a pressure sensor that measures vibrations in the arterial wall due to the pulsatile flow of blood. The cuff is inflated to a value higher than the blood pressure and then deflated. The pulsatile vibrations or oscillations are recorded by the pressure sensor. The point where the amplitude of oscillation is highest is considered the mean arterial pressure. Using this value, the systolic and diastolic pressures are calculated using a mathematical relation.[16, 55] This method is less operator-dependent but

might be less accurate for patients with irregular heart rhythms or arrhythmia. It can overestimate systolic blood pressure and underestimate diastolic blood pressure.[16] Also, it provides an average value over a period of time, not a beat-to-beat blood pressure value.



Figure 2.10 Oscillometric BP monitoring device[55]

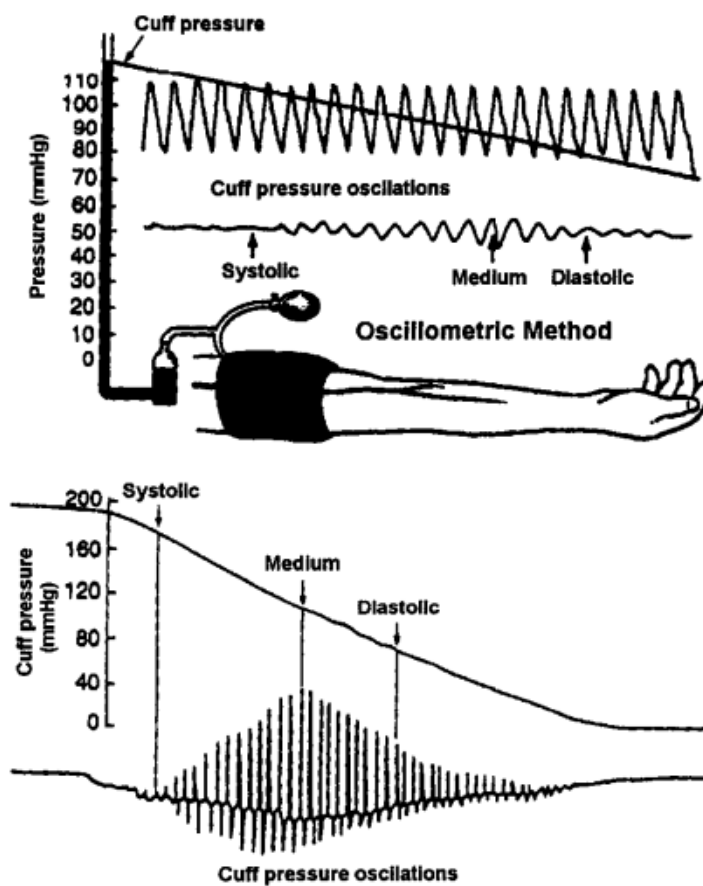


Figure 2.11 Process of measuring BP using oscillometric method[56]

The process of BP estimation by oscillometric method is shown in the figure 2.11. The medium or mean arterial pressure (MAP) is the pressure in the cuff for which the amplitude of oscillation

is maximum. The device then uses an algorithm (proprietary) to calculate the SBP and DBP from the MAP based on ratios (depends on the manufacturer). The SBP and DBP is related to MAP empirically by the following equation[56]:

$$\text{MAP} = \frac{1}{3} \text{SBP} + \frac{2}{3} \text{DBP} \quad 2.5$$

Invasive blood pressure measurement:

Arterial catheter: This is a direct method for measuring blood pressure. Due to its accuracy, it is generally used in critical care settings. In this method, a catheter is inserted into an artery, and the pressure is measured using an electronic system. This method measures continuous and real-time systolic, diastolic, and mean arterial pressure.[57] Though this method provides continuous and real-time beat-to-beat blood pressure values, its invasive nature carries risks such as infection, bleeding, and thrombosis.[57]

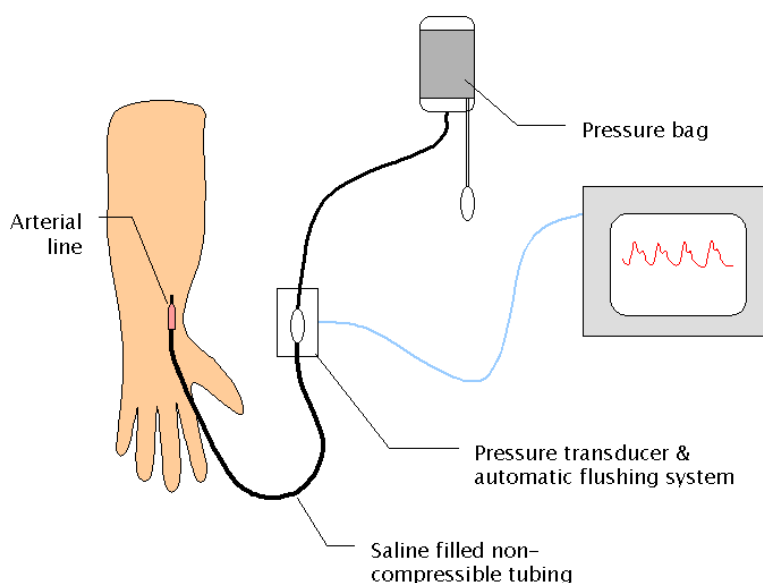


Figure 2.12 BP measurement using an arterial catheter[58]

2.7.2 Arterial blood pressure waveform

The arterial pulse waveform is the graphical representation of blood pressure with time for each cycle of the heartbeat.[16] It has two parts, systole and diastole, as shown in the figure. During systole, the pressure rises to the highest point, and the peak value gives the systolic pressure for

that beat. Then, the pressure begins to fall, and a second peak appears due to the closure of the aortic valve to prevent the backflow of blood through the arteries during expansion. This small peak is known as the dicrotic notch. Then, the pressure falls to the lowest point, which gives the value of diastolic pressure before it rises again for the next cycle.[5]

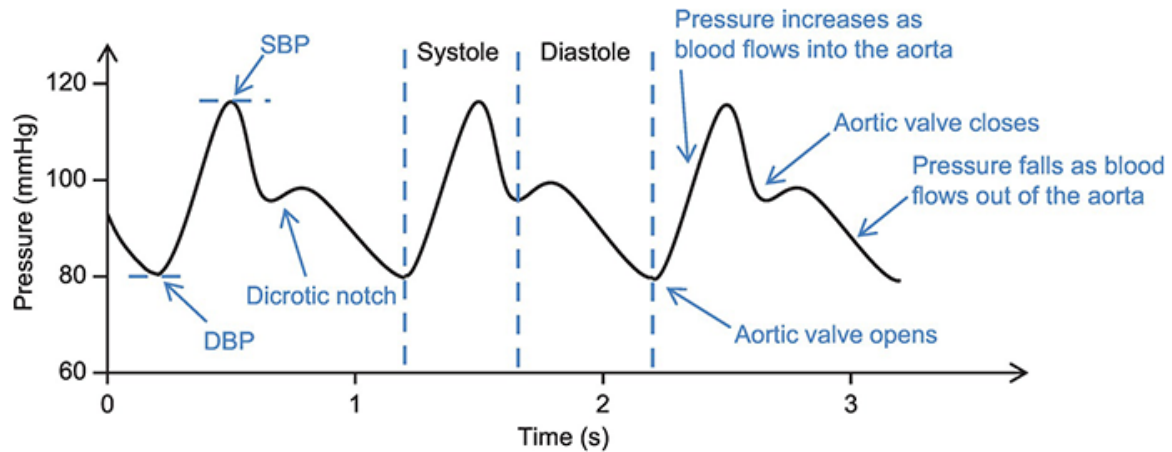


Figure 2.13 Arterial blood pressure waveform [59]

2.7.3 Continuous non-invasive BP monitoring techniques

Applanation tonometry: This method involves using a pressure sensor to flatten (applanate) an artery. As the artery is flattened, the pressure is transferred to the pressure sensor, which reads the blood pressure value continuously. The accuracy of measurement can be affected by sensor placement and movement. It can be uncomfortable for patients and is not suitable for long-term blood pressure monitoring.[60]

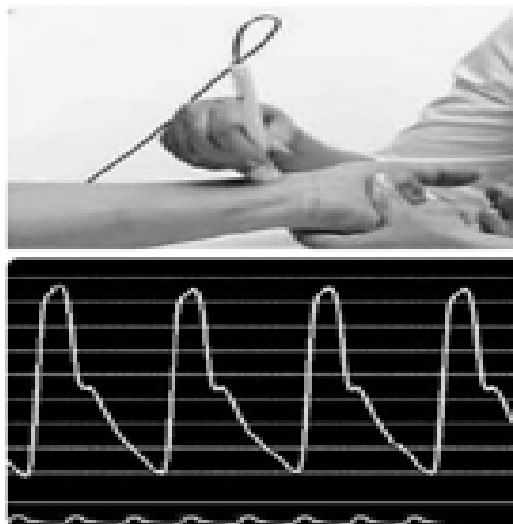


Figure 2.14 BP measurement using applanation tonometry[60]

Photoplethysmography (PPG): This method uses optical sensors to measure changes in blood volume in the artery. A light source illuminates the skin, and a photodetector measures the amount of light reflected or transmitted. The amount of light absorbed changes with the volume of blood in the artery, which is used to estimate changes in blood pressure.[61] The measurement can be affected by ambient light, skin colour or pigmentation, contact with the skin, and movement.[62]



Figure 2.15 BP measurement using PPG sensor[63]

Pulse transit time (PTT): In this method, two sensors are used to capture blood pressure at different points in the artery. The time difference between the peaks gives the value of pulse transit time, which can be used to calculate blood pressure.[64] It requires the use of multiple sensors and is affected by factors such as heart rate, arterial stiffness, and body temperature.[65]

$$DBP(t) = DBP_{(cuff,initial)} + \Delta mmHg_a + \Delta mmHg_b + \Delta mmHg_c \dots \quad 2.9$$

where, SBP(t) and DBP(t) are systolic BP and diastolic BP at time t and $\Delta mmHg$ is the pressure change between two consecutive peaks or valleys as measured by the sensor as shown in figure 2.17.

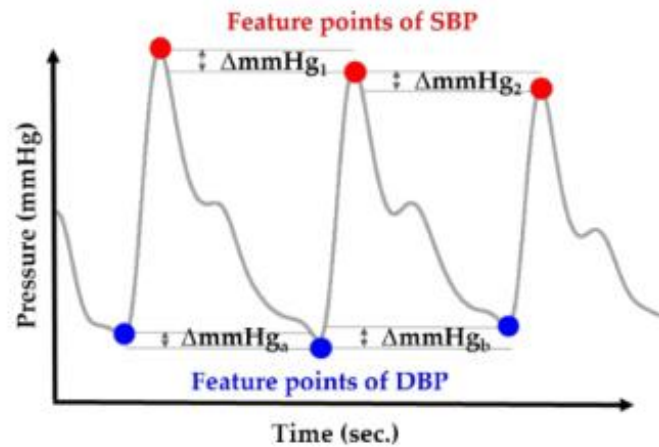


Figure 2.17 Process of measuring beat to beat BP from pulse pressure wave using piezoelectric sensor[68]

However, the sensors used were not flexible and hence were not attached well, which might not give very accurate readings. If flexible sensors are used, these limitations can be overcome. Also, the amplitude of the waveform will depend on the hand orientation and the depth of tissue between the skin and artery, which might affect the results. These factors were not taken into account in their work, which might impact the results. It is important to consider these factors while calculating blood pressure from the sensors.

2.7.4 Recent developments in non- invasive continuous BP monitoring

Recent research has focused on developing soft, wearable sensors for continuous blood pressure monitoring using various technologies. These include capacitive, liquid metal, resistive, and bioimpedance-based systems, among others. Figure 2.16 illustrates soft wearable sensors based on these technologies. However, the fabrication process for these sensors involves numerous steps, making it a cumbersome and costly endeavour. Table 2.5 outlines the challenges of the recent research on soft wearable sensors.

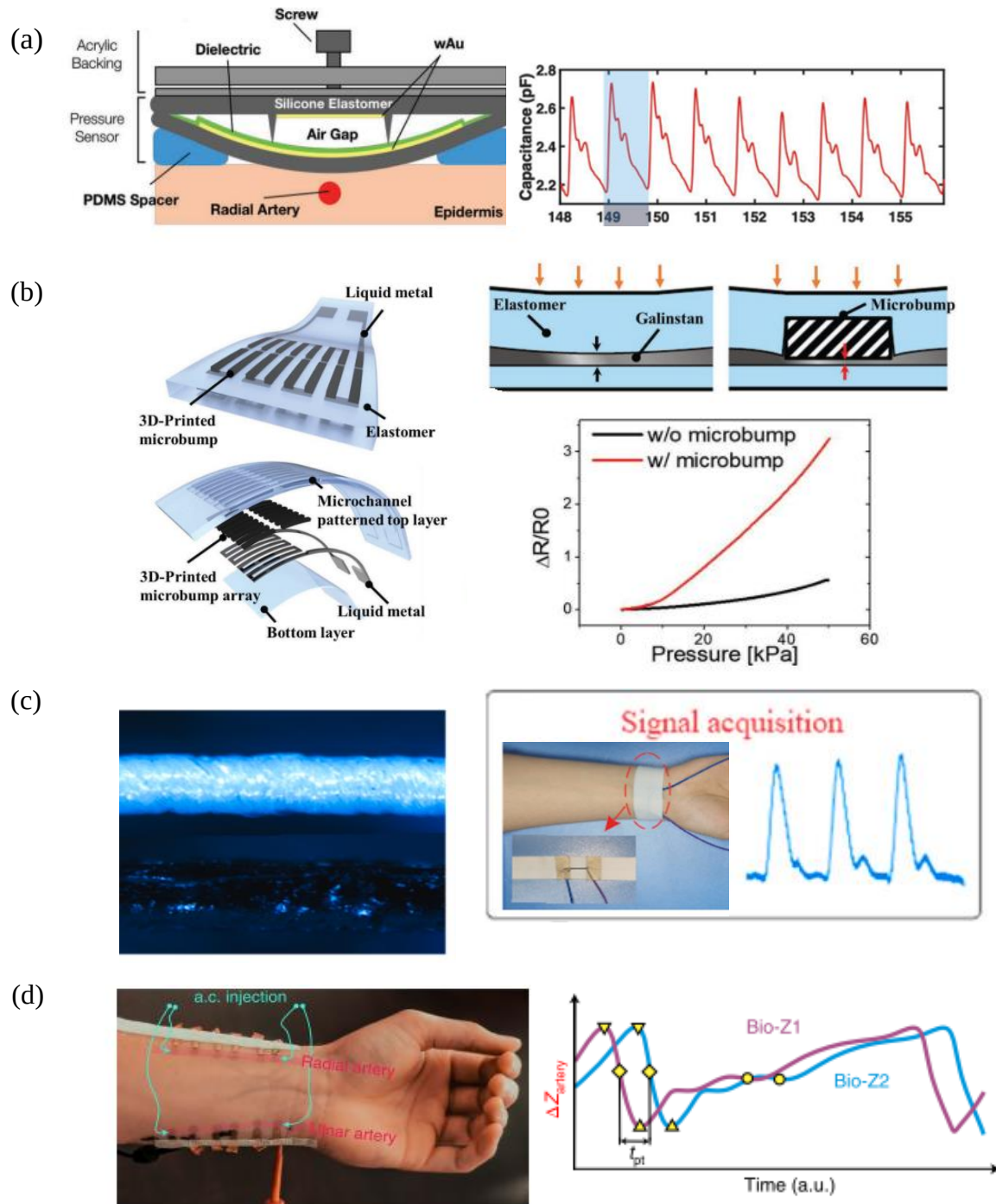


Figure 2.18 Recent developments in non-invasive Continuous BP monitoring using a) soft capacitive sensor [69] b) liquid metal-based pressure sensor (3DBlips) [71] c) MWCNTs based resistive sensor [67] d) graphene based bioimpedance tattoos [72]

Table 2.5 Recent developments in non-invasive Continuous BP monitoring [18, 67-69, 71-74]

Author	Development	Sensor Type	Fabrication Process/Limitations	Self Powered sensors ?	3D printed ?
Joshua Kim et al.	Developed soft wearable capacitive pressure sensors with a sensitivity of 0.148 Kpa-1	Capacitive Pressure Sensor	Fabrication involved complex and expensive clean-room processes like sputtering and etching.	No	No
Yang et al.	Highly sensitive flexible capacitive pressure sensor was created, utilizing BaTiO ₃ -doped polyvinylidene fluoride electrospinning fibers and polydimethylsiloxane microcylindrical structures for the dielectric layer.	Capacitive Pressure Sensor	Fabrication involved Photolithography, electrospinning, moulding and multiple chemical reactions. Only measured pulse waveform and not blood pressure	No	No
Zhang et al.	Created resistive pressure sensors based on g-MWCNTs composite	Resistive Pressure Sensor	Fabrication was time-consuming, involving multiple reactions and filtrations.	No	No
Kyuyoung Kim et al.	Developed a liquid metal-based pressure sensor (3D-BLiPs) with a sensitivity of 0.158 kPa-1	Liquid Metal-based Pressure Sensor	Fabrication involved making molds, producing microchannels, and integrating microbumps monolithically.	No	No
Kirev et al.	Proposed thin graphene-based tattoos for measuring blood pressure from bioimpedance	Graphene-based Tattoos	Fabrication required chemical vapor deposition (CVD) growth of graphene which is	No	No

			Complex fabrication process		
Yu-Jen Wang et al.	Proposed use of photoplethysmography (PPG) sensor and strain gauge to measure Blood pressure by measuring pulse transit time.	Strain Gauge based	Requires use of more than one sensor and complex mathematical modelling	No	No
Wang et al.	Employed PZT-based piezoelectric-based sensors to measure beat-to-beat blood pressure using a simple calibration technique	Piezoelectric-based Sensor	Use of commercially available sensor. Sensors used were rigid which might readily cause air gaps to develop with prolonged daily usage.	Yes	No
Manh et al.	Proposed sensor with two stacked components made of polyvinylidene fluoride and polydimethylsiloxane, simultaneously measures heart and breathing rates.	Piezoelectric-based Sensor (PVDF)	Only measured the PPW and heart rate and not the blood pressure.	Yes	No

CHAPTER 3 RESEARCH OBJECTIVES

3.1 Problem identification

AM, due to its inherent properties of reduced material waste, speed, and customizable production, simplifies the creation of wearable sensors by eliminating the need for complex and multi-step fabrication processes.[1, 3]. Specifically, AM's application in fabricating PVDF based piezoelectric sensors can eliminate the need for bulky batteries, resulting in lightweight sensors.[8, 10-12]. These sensors, developed through DIW, are biocompatible and flexible, making them suitable for critical medical applications.[5, 36] One such vital area is blood pressure monitoring, where real-time and regular monitoring can potentially improve disease diagnosis.[75, 76] In the event of a medical emergency such as a heart attack, a computerized CPR system, which involves continuous BP monitoring, can be instrumental in saving lives. Traditional methods using bulky cuffs are limited to intermittent monitoring, whereas the invasive method suffers from risks such as infections bleeding, and thrombosis.[16, 54] Fabrication of soft wearable sensors for continuous blood pressure measurement often demands complex manufacturing processes and the sensors are not always biocompatible or flexible.[18, 67-69, 71, 74]. All the clean-room techniques require masks for making sensors, which in case of personalization becomes very expensive whereas 3D printing can print small quantities with a lot of design variations. Therefore, given the advantages of 3D printing, self-powered capabilities, biocompatibility, and flexibility of PVDF, it is imperative to develop 3D printed blood pressure sensors and validate their potential for real-time monitoring.

3.2 Research objectives

The main objective of this research is **to design and fabricate PVDF nanocomposite-based sensors using direct ink write 3D printing technique for continuous blood pressure measurement**. The main objective is divided into three specific objectives as listed below:

1. **SO1:** Optimize the printing parameters for maximizing the piezoelectric coefficient of the PVDF-BaTiO₃ sensors through characterizing the material properties.
2. **SO2:** Increase the sensitivity of 3D printed sensors through thermal contact poling and to characterize the sensor behaviour.
3. **SO3:** Verify the suitability of the PVDF nanocomposite sensor for measuring heart rate and continuous blood pressure.

CHAPTER 4 ARTICLE 1: 3D PRINTING OF POLYVINYLIDENE FLUORIDE BASED PIEZOELECTRIC SENSORS FOR NON-INVASIVE CONTINUOUS BLOOD PRESSURE MONITORING

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We present successful fabrication and application of 3D printed piezoelectric sensors, made from polyvinylidene fluoride-barium titanate (PVDF-BaTiO₃) nanocomposites, for continuous blood pressure monitoring. Our sensors are fabricated using direct-ink write 3D printing technique possessing excellent flexibility, rendering them ideal for wearable applications. We optimize key printing parameters, such as nozzle size and pressure, to achieve a β -phase of 70% and an overall crystallinity of 48.3%. Our sensors are characterized under dynamic pressures and show excellent linearity with a coefficient of determination (R^2) of 0.99 and a pressure sensitivity of 0.024 V kPa⁻¹, and demonstrate durability over 3600 cycles. We compare the performance of our piezoelectric sensors with a standard blood pressure monitoring device for

a subject and find a strong correlation with standard deviation of 3.87 mmHg and 0.63 mmHg for SBP and DBP, respectively. The development of sensors through 3D printing, as demonstrated in this study, represents a significant scientific advancement in the field of personalized healthcare. Our novel approach enables the creation of customized wearable devices tailored for real-time health monitoring of blood pressure and heart rate.

4.1 Introduction

3D printing of biomedical devices offers immense prospects for the future of medical device manufacturing due to its quick production time, ability to produce personalized and complex-shaped parts, and ease of fabrication.^[1, 3] The capability of 3D printing to create small and intricate objects with greater design flexibility can be exploited to produce customizable sensors for wearable applications.^[1, 77] PVDF is a semi-crystalline polymer that exhibits a piezoelectric effect.^[14, 31, 32] Piezoelectricity is the property of a material to generate charges when mechanical stress is applied to it or *vice versa*. The sensors made with PVDF are self-powered and hence, do not require batteries, which are often bulky, increase the weight of wearables, and require frequent replacement.^[11, 12, 78] The 3D printing of polyvinylidene fluoride (PVDF) based sensors has been applied to various biomedical applications like respiration monitoring,^[32] tactile sensing,^[32] and gait analysis.^[14]

PVDF predominantly exists in five different phases namely α , β , γ , δ , and ϵ .^[30, 34, 79] Among these the β -phase is the most electroactive and exhibits the highest piezoelectricity due to a high net dipole moment within its polymer chains.^[27, 29, 30, 34, 79] The α -phase is nonpolar whereas the γ -phase exhibits piezoelectricity lower than the β -phase.^[27, 29, 30, 34, 79] The β -phase in PVDF can be obtained and improved by the addition of fillers,^[12, 29, 31] the use of polar solvents,^[12, 27, 31, 79] stretching,^[11, 79] annealing,^[34, 79] and electrical poling.^[13, 15, 43] Adding 10% by weight of barium titanate nanoparticles (BaTiO₃) to PVDF has shown to improve the β -phase content in 3D printed PVDF sensors.^[31]

Given the biocompatibility of BaTiO₃, it is a viable option to be used as a filler for PVDF in the preparation of efficient piezoelectric wearable sensors. At the same time, PVDF is recognized for its excellent biocompatibility, chemical resistance, and flexibility.^[4-8] These properties make it suitable for use in wearable health monitoring devices. One such vital health parameter that requires regular monitoring is human blood pressure (BP). High blood pressure leads to hypertension, which can result in a heart attack or stroke.^[75, 76] The standard method

for measuring blood pressure uses an oscillometric device, where a cuff is placed around the forearm.^[80, 81] Blood pressure values are measured by inflating the cuff above the individual's systolic blood pressure to stop the blood flow and then deflating it to measure the systolic pressure and diastolic blood pressure by listening to the Korotkoff sounds.^[16] However, the cuff-based devices only provide average value over period of time and not the continuous beat-to-beat blood pressure measurement.^[57, 82, 83] Continuous measurement of blood pressure provides a pulse pressure waveform (PPW), which indicates the rise and fall of blood pressure with each cardiac cycle. This is a critical feature, as it enables detection of rapid, situational or positional changes in blood pressure and provides deeper insights into the cardiovascular health of an individual.^[75, 76, 80] By analyzing the pulse pressure waveform (PPW), doctors can detect variations and trends in blood pressure, potentially identifying underlying health issues or the effectiveness of treatments. Additionally, BP sensors can be integrated into computerized CPR systems, enabling precise real-time feedback on the effectiveness of chest compressions.

In the rapidly advancing field of wearable health technology, several researchers have been making significant strides in developing sensors for continuous blood pressure monitoring. For example, Joshua Kim et al. developed soft wearable capacitive pressure sensors using Polydimethylsiloxane (PDMS) to continuously monitor blood pressure.^[84] However, the fabrication of these sensors involves complex and expensive clean-room processes like sputtering and etching. Zhang et al. created resistive pressure sensors based on g-MWCNTs composite for measuring blood pressure, nonetheless, the fabrication process was time-consuming, involving multiple reactions and filtrations.^[85] Kyuyoung Kim et al. developed a liquid metal-based pressure sensor (3D-BLiPs) with a microchannel filled with Galinstan, demonstrating a sensitivity of 0.158 kPa^{-1} .^[86] The downside was that the fabrication involved making molds, producing microchannels, and integrating micro bumps monolithically, which creates an obstacle for rapid sensor production. Kirev et al. proposed thin graphene-based tattoos for measuring blood pressure from bioimpedance, but the preparation of these tattoos required chemical vapor deposition (CVD) of graphene, another complex process in itself.^[87] Recently, Wang et al. employed piezoelectric sensors to measure beat-to-beat blood pressure using a simple calibration technique.^[88] However, the sensors used were rigid which resulted in poor attachment to the skin, making them uncomfortable for long-term use. In conclusion, most of the reported blood pressure monitoring sensors were manufactured using expensive, time-consuming, and elaborate procedures.

In this work, we present an efficient fabrication process to produce flexible blood pressure sensors using 3D printing. We 3D printed PVDF-BaTiO₃ sensors using the direct-ink write (DIW) 3D printing approach. We investigated the impact of nozzle sizes (0.1 mm and 0.25 mm), annealing temperatures (80°C, 100°C, and 120°C), and print-bed temperatures (no heating, 40°C, 60°C, 80°C and 100°C) on the appearance of phases and crystallinity of PVDF and thereafter on the sensitivity of the sensors. Subsequently, we determined optimized poling parameters to enhance sensitivity in the thickness (d_{33}) direction of the sensors, the direction critical to this application. To verify their applicability in measuring blood pressure, the sensors were characterized using a compression device under dynamic pressure between 6 kPa and 20 kPa at 1 Hz. The hysteresis of the sensors were also determined in the same pressure range. The sensors were then tested for 1 hour to validate the continuity and repeatability of measurements. Finally, we calibrated the sensors with a standard cuff-based oscillometric device and measured the blood pressure of a subject by placing the sensor near the radial artery. The measured blood pressure from the sensors was compared against a standard oscillometric device (A&D Medical, UA-767FAM) to assess its accuracy in detecting blood pressure and heart rate. Our results confirm the potential to use our 3D printed sensors to measure heart rate and continuous blood pressure.

4.2 Result and discussion

4.2.1 Sensor development

Figure 4.1a illustrates the DIW process employed to print PVDF-BaTiO₃ films. During the printing process, the BaTiO₃ nanoparticles form agglomerates and serve as nucleating agents for the β - and γ -phases in polymer chains. The shear stress of up to 1.4 MPa from pressures applied during the extrusion combined with the stretching from the printing speed of 20 mm.s⁻¹ induce the alignment of the electroactive β - and γ -chains in PVDF.^[8] Essentially, the greater the shear stress the higher the production of β - and γ -phases, the more the polymer chains are stretched, and higher the alignment of β - and γ -phases, and hence increased piezoelectricity.

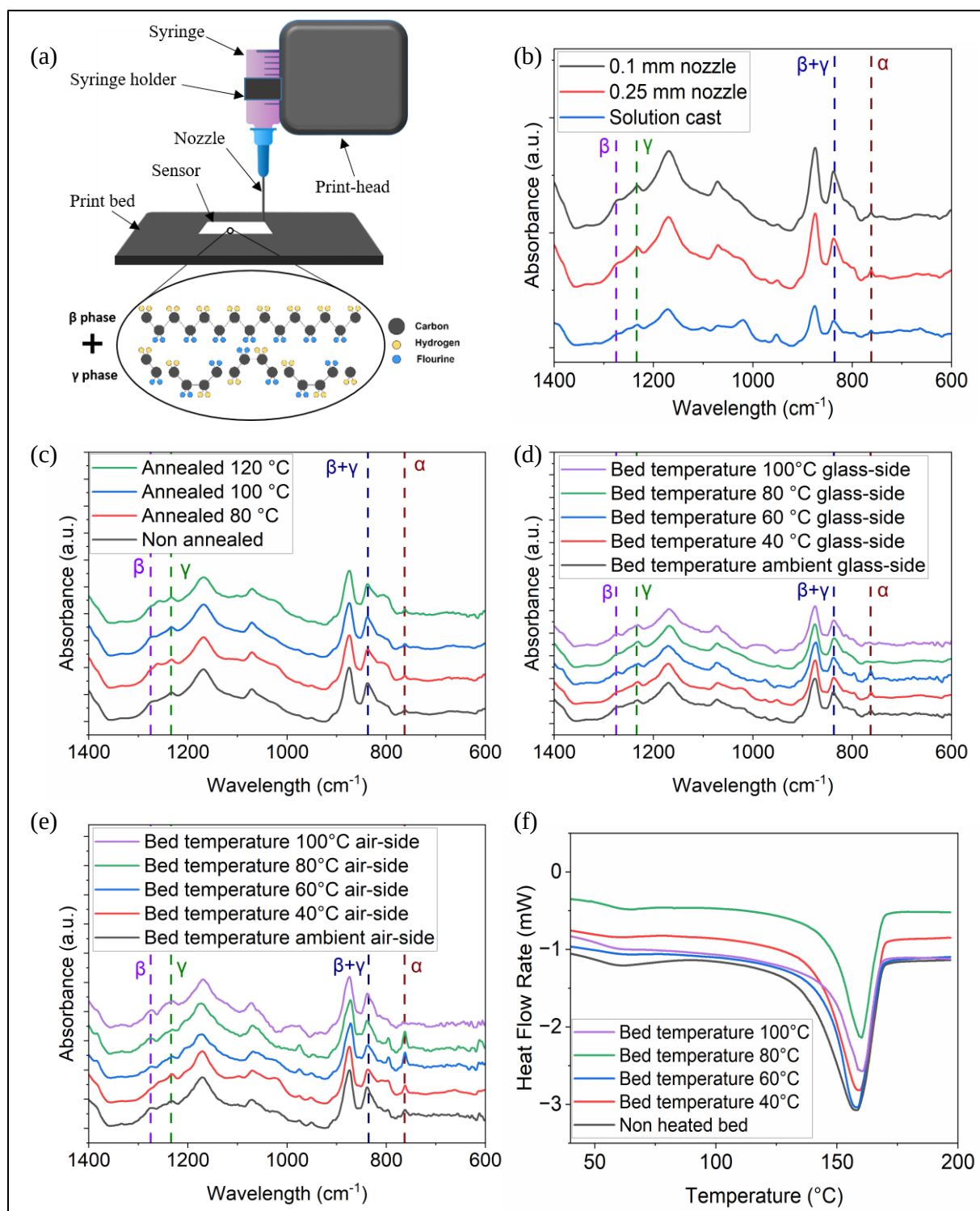


Figure 4.1 a) A schematic of the direct-ink write (DIW) 3D printing of PVDF-BaTiO₃ sensors. Fourier-transform infrared (FTIR) spectra showing b) the effect of varying print nozzle size on the phases of PVDF (Printing speed: 20 mm.s⁻¹; bed temperature: ambient; printing pressure: 140 kPa for 0.25 mm nozzle and 1.4 MPa for 0.1 mm nozzle, respectively), c) the impact of annealing on the phases of PVDF at various temperatures (Printing speed: 20 mm.s⁻¹, nozzle

diameter: 0.1 mm, printing pressure: 1.4 MPa, bed temperature: ambient, annealing time: 3 hours). FTIR spectra for sensors printed with bed temperatures: No heating, 40°C, 60°C, 80°C, and 100°C as tested on d) the glass-side e) the air-side. (Printing speed: 20 mm.s⁻¹, nozzle diameter: 0.25 mm, printing pressure:140 kPa), f) Differential Scanning Calorimetry (DSC) analysis of PVDF nanocomposite films printed at bed temperatures: No heating, 40°C, 60°C, 80°C, and 100°C. (Printing speed: 20 mm.s⁻¹, nozzle diameter:0.25 mm, printing pressure:140 kPa)

Figure 4.1b presents the FTIR spectra of PVDF nanocomposite films printed with 0.1 mm and 0.25 mm diameter nozzles, alongside a sample prepared through solution casting. The presence of a peak at 763 cm⁻¹ represents the presence of the α -phase, while the peak at 840 cm⁻¹ indicates the existence of a combination of the electroactive β - and γ -phases.^[89] Additionally, peaks at 1234 cm⁻¹ and 1275 cm⁻¹ are distinct peaks for γ - and β -phases, respectively.^[89] Figure 4.1b shows that the 840 cm⁻¹ peak is highest for the sample printed with a 0.1 mm nozzle at 1.4 MPa, compared to PVDF nanocomposite films printed with a 0.25 mm nozzle at 140 kPa and the solution cast sample, confirming that the higher shear stress resulted in an increase in the electroactive phases. The printing pressure for the 0.25 mm nozzle is lower compared to a 0.1 mm nozzle to achieve the same thickness of the film, as the printing speed was kept constant at 20 mm.s⁻¹.

We calculated the β -phase is performed using the Beer-Lambert law, as represented by the following equation:

$$F_{\beta} = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}} \quad (4,1)$$

where, A_{α} and A_{β} represent the absorption fractions of the α - and β -phases at 763 cm⁻¹ and 840 cm⁻¹, respectively. Additionally, 1.26 stands for the ratio of absorption coefficients 7.7×10^4 and 6.1×10^4 cm² mol⁻¹ for the β - and α -phases, respectively.

Using Beer-Lambert's law, the average percentages of the β -phase in the PVDF nanocomposite films are calculated as 70%, 64%, and 55% for the 0.1 mm nozzle, 0.25 mm nozzle, and solution-cast films, respectively. These results confirm that printing at higher pressures causes more stretching in PVDF polymer and hence an increase in the β -phase.

Various authors have reported an increase in the β -phase after annealing PVDF,^[25, 33] while others have observed no change in phase after the annealing process.^[34] To investigate the

impact of annealing in our experiments, the PVDF nanocomposite films printed with a 0.1 mm nozzle, at a pressure of 1.4 MPa, and speed of 20 mm.s⁻¹ were annealed for three hours at 80°C, 100°C, and 120°C. The post-annealing FTIR results are presented in Figure 4.1c. It appears that the peaks at 840 cm⁻¹ and 763 cm⁻¹ are consistent in height across all PVDF nanocomposite films, suggesting no significant increase in the β -phase for the annealed PVDF nanocomposite films. The average β -phase percentages calculated from Beer-Lambert's law are 70%, 69%, 69%, and 68% for the non-annealed, annealed at 80°C, 100°C, and 120°C, respectively which also confirms that annealing had no quantitative effect on the β -phase content in the PVDF nanocomposite films. [34]

As the phase of PVDF also depends on the temperature at which the films are crystallized, it is important to study the effect of the printing bed temperatures. To the best of our knowledge, no such study has been done before. Figures 4.1d and 4.1e present the FTIR plots of two different surfaces of the PVDF nanocomposite films printed at varying bed temperatures. Figure 4.1d shows the plot for the smoother surface facing the heated bed, *glass-side*, while Figure 1e illustrates the rougher surface exposed to the air, *air-side* during the printing process. For this study, a 0.25 mm nozzle was used as the 0.1 mm nozzle was prone to clogging when printing at elevated bed temperatures, as the higher bed temperatures resulted in faster evaporation of the solvents. Observations from Figure 4.1d reveal that the amplitude of the peak at 763 cm⁻¹ initially increases as we progress from the ambient bed temperature to 60°C, then decreases for films printed at 80°C and 100°C bed temperatures. This pattern suggests an increase in the α -phase and a reduction in the β - and γ -phases up to 60°C, followed by an increase in the β - and γ -phase formation and a decrease in the α -phase beyond this temperature. Figure 4.1e reflects similar trend for the *glass-side*, with the sole exception occurring at 80°C where the α -phase surpasses the β - and γ -phases. The average β -phase values calculated from the Beer-Lambert's law for the *air-side* of PVDF nanocomposite films, which were 65%, 62%, 59%, 51%, and 70% when printed on a bed at ambient temperature, 40°C, 60°C, 80°C, and 100°C, respectively as shown in table 4.1. Meanwhile, for the surfaces of films facing the *glass-side*, the values were 62%, 58%, 51%, 77%, and 72% printed on a bed at ambient temperature, 40°C, 60°C, 80°C, and 100°C, respectively. The formation of the β -phase also depends on the solvent evaporation rate, [39] and the temperature at which the polymer crystallizes. [37] As the bed temperature increases, the solvent evaporation rate also increases, favoring the formation of β - and γ -phases as per Ostwald's step rule. [39] However, higher temperatures also favor the more

thermodynamically stable α -phase.^[37] Thus, the final phase composition depends on a competition of these factors.^[28, 34, 37] Also, the phase compositions are different for the films on the two surfaces as there is a difference in temperature and evaporation rates between them (film thickness of 0.1 mm).^[28] The *air-side* of the films have faster evaporation rates compared to the *glass-side* and the conditions are reversed for the temperature for the two sides. This explains the appearance of higher β - and γ -phase on *air-side* up to 60°C. At temperatures of 80°C and 100°C, evaporation occurs throughout the film, due to boiling of solvents. This can be inferred from the presence of pores, (supporting information, Fig. 4.6). Consequently, the β - and γ -phases are more pronounced on the side of the *glass-side*.

Table 4.1 Effect on β -phase and total crystallinity of printed PVDF nanocomposite films (Printing speed: 20 mm.s⁻¹, nozzle diameter: 0.25 mm, printing pressure: 140 kPa)

Print Bed Temperature (°C)	β-phase on air-side (%)	β-phase on glass-side (%)	Average β-phase of both sides (A_β) (%)	Total Crystallinity (χ_c) (%)	Effective β-phase ($A_\beta \times \chi_c / 100$) (%)
No-heating	65	62	63.5	48.4	30.73
40	62	58	60	43.5	26.1
60	59	51	55	42.4	23.22
80	51	77	64	31.2	19.96
100	70	72	71	33.7	23.92

Printing at high bed temperatures influences the crystallization time, which can, in turn, affect the total crystallinity of the polymer.^[26] Therefore, it is important to study the total crystallinity of samples printed on a heated bed. Figure 4.1f presents the total crystallinity of the PVDF nanocomposite films printed at different bed temperatures. The total crystallinity was calculated using the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^o} \times 100 \quad (2)$$

where ΔH_m is the melting enthalpy of the sample, $\Delta H_m^o = 104.7 \text{ J.g}^{-1}$ is the enthalpy of the hypothetically 100% crystallized PVDF. The total crystallinity, calculated from DSC analysis, for PVDF nanocomposite films printed at ambient, 40°C, 60°C, 80°C, and 100°C bed temperatures was found to be 48.4%, 43.5%, 42.4%, 31.2%, and 33.7%, respectively. The highest crystallinity is observed in the PVDF nanocomposite films printed at ambient bed temperature, and it decreases as the bed temperature increases. This decline is attributed to decreased available crystallization time with increased evaporation rate at higher bed temperatures.^[26] Despite exhibiting a higher β -phase, PVDF nanocomposite films printed at elevated bed temperatures demonstrated a reduced total crystallinity as presented in table 4.1. This shows that the effective β -phase is reduced as shown in table 4.1. So, printing at ambient bed temperature is considered to be the optimal condition to achieve higher piezoelectric. It was also observed that, printing with a nozzle diameter of 0.1 mm at a pressure of 1.4 MPa induced high shear stress which leads to a β -phase of 70% as compared to 0.25 mm at 140 kPa which produced only 64% of β -phase. Hence, the PVDF nanocomposite films printed with the nozzle of 0.1 mm and pressure of 1.4 MPa at a speed of 20 mm.s^{-1} at ambient bed temperature were chosen for the printing of blood pressure sensors. Annealing did not necessarily increase the β -phase but the PVDF nanocomposite films needed to be dried to get rid of solvents, as explained in the following section.

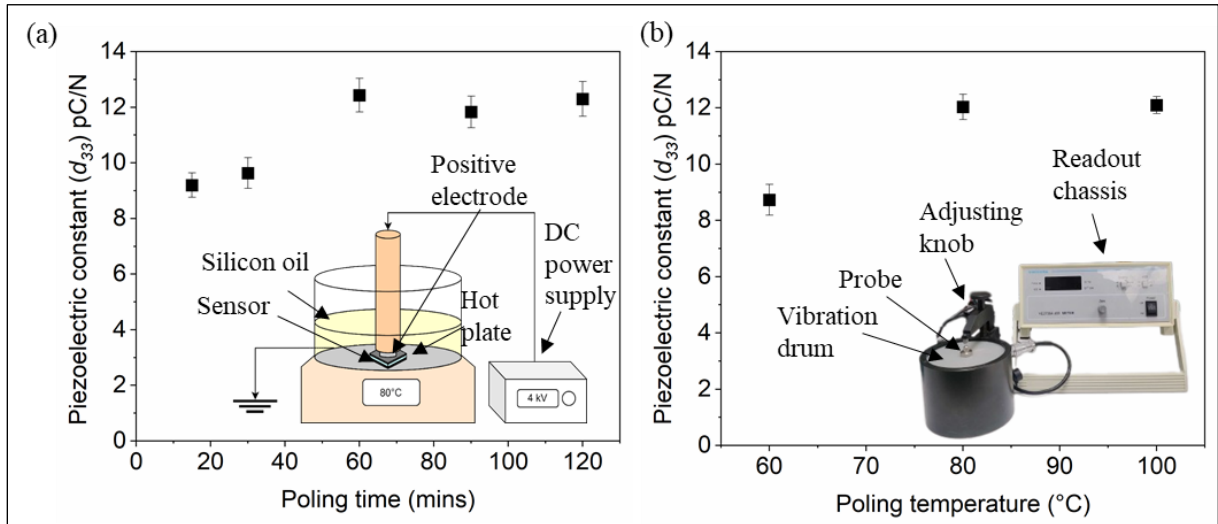


Figure 4.2 a) The variation of piezoelectric constant with varying poling time (15 min, 30 min, 60 min, 120 min) while maintaining a constant poling field of 50 MV m^{-1} and bath temperature

of 100 °C with the insert showing the poling setup b) The variation of piezoelectric constant with varying oil-bath temperatures (60 °C, 80 °C, 100 °C) with poling time and poling field kept constant at 60 minutes and 50 MV m⁻¹ respectively (the insert shows a photograph of the d_{33} meter used for measuring the piezoelectric coefficient).

Poling is a process where a high electric field is applied across a piezoelectric material to align all the dipoles. This step enhances the material's piezoelectric response. After the DIW printing of the nanocomposite films and drying at ambient temperature for 18 hours, there was still some residual solvent present in the films. This residual solvent limited the poling fields to less than 10 MV m⁻¹ as the solvents created an electrical short circuit. To alleviate this problem, the PVDF nanocomposite films were placed in a vacuum oven for 18 hours prior to poling, to evaporate all the traces of the solvents. Subsequently, silver conductive paint was applied to the opposite sides of the PVDF nanocomposite films to form the electrodes. To ensure uniform poling, the PVDF nanocomposite films were immersed in a silicone oil bath. Silicone oil was chosen due to its high dielectric breakdown voltage (10-15 MV m⁻¹) compared to air (3 MV m⁻¹).^[90] The thicknesses of the poled PVDF nanocomposite films were around 0.1 ± 0.02 mm. An electric field of 50 MV m⁻¹ was used for poling as higher values led to a breakdown in the PVDF nanocomposite films.

Figure 4.2a presents the values of the piezoelectric constant (d_{33}) for different poling durations, keeping the electric field and bath temperature constant at 50 MV m⁻¹ and 100°C, respectively. At first, the piezoelectric constant increases from 9.2 pC N⁻¹ to 12.4 pC N⁻¹ with time, saturating after a duration over 60 minutes. Figure 4.2b shows the piezoelectric constant for different poling temperatures while keeping the electric field and time constant at 50 MV m⁻¹ and 60 minutes, respectively. The piezoelectric constant increases from 8.7 pC N⁻¹ to 12.1 pC N⁻¹ when increasing poling temperatures up to 80°C, while showing a plateau at higher temperatures. The increase in temperature elevates the mobility of the polymer chains and aids in the poling process. However, at temperatures around 120°C, the PVDF nanocomposite films experienced frequent breakdown due to decrease in dielectric breakdown strength of polymer with increase in temperature. Therefore, the optimal parameters for poling were thus identified as an electric field of 50 MV m⁻¹, a poling duration of 60 minutes, and a bath temperature of 80°C, yielding a d_{33} value of 12 ± 1.5 pC/N.

4.2.2 Sensor Characterization

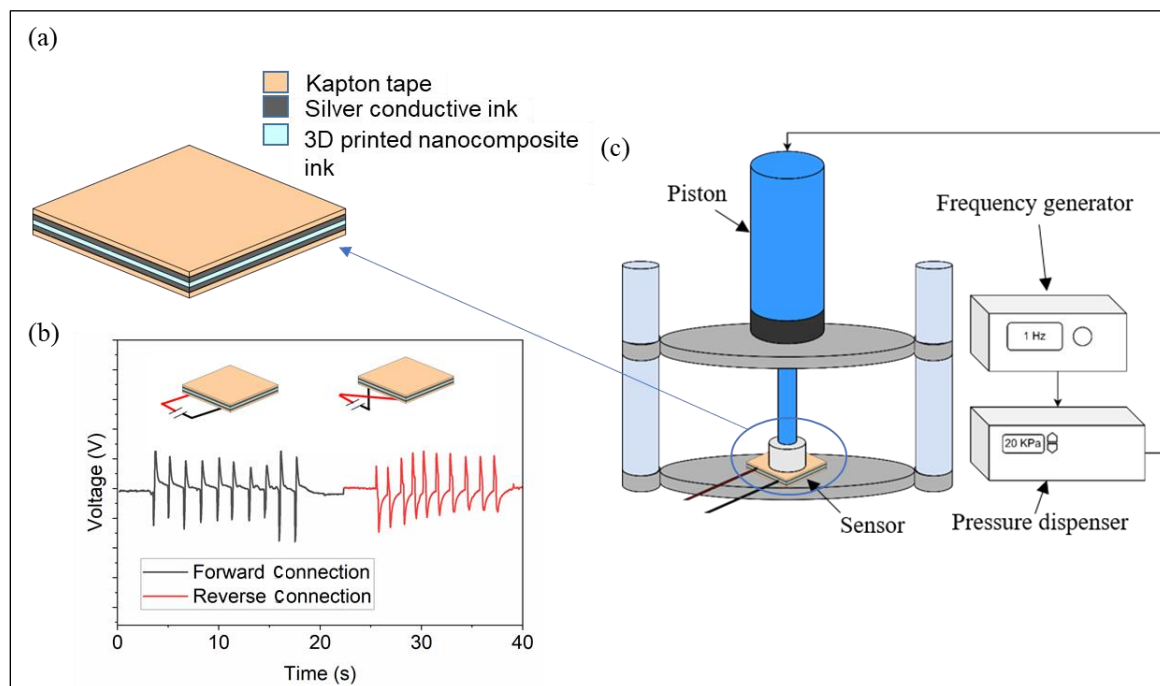


Figure 4.3 a) Schematic of the test setup for dynamic testing of the PVDF nanocomposite sensors in compression mode, b) Schematic of the PVDF nanocomposite sensor. c) Voltage response of the sensor tested in both forward and reverse connections.

Figure 4.3a presents the schematic of the PVDF nanocomposite sensor, where the 3D printed film is sandwiched between two layers of conductive silver paint and a Kapton tape. Kapton tape insulates the sensor and protects it from wear and tear. Wires are connected to the silver electrodes using aluminum tape. Figure 4.3b illustrates the output voltage when the sensor is pressed with a finger, both in forward connection and reverse connection (achieved by swapping the contact wires). The reversal of the graph, when the connection is inverted, confirms that the signal originates from the piezoelectric effect and not from contact electrification.^[91] Figure 4.3c presents the testing setup used for sensor characterization. It consists of a piston connected to a pressure dispenser and a frequency generator. The piston applies dynamic compressive force to the sensors at various pressures (6 kPa – 20 kPa) and frequencies (1 Hz – 3 Hz). Physical contact between the sensors and the piston was continuously maintained during the pressing of the sensor to eliminate any effects from contact electrification or triboelectricity.^[91]

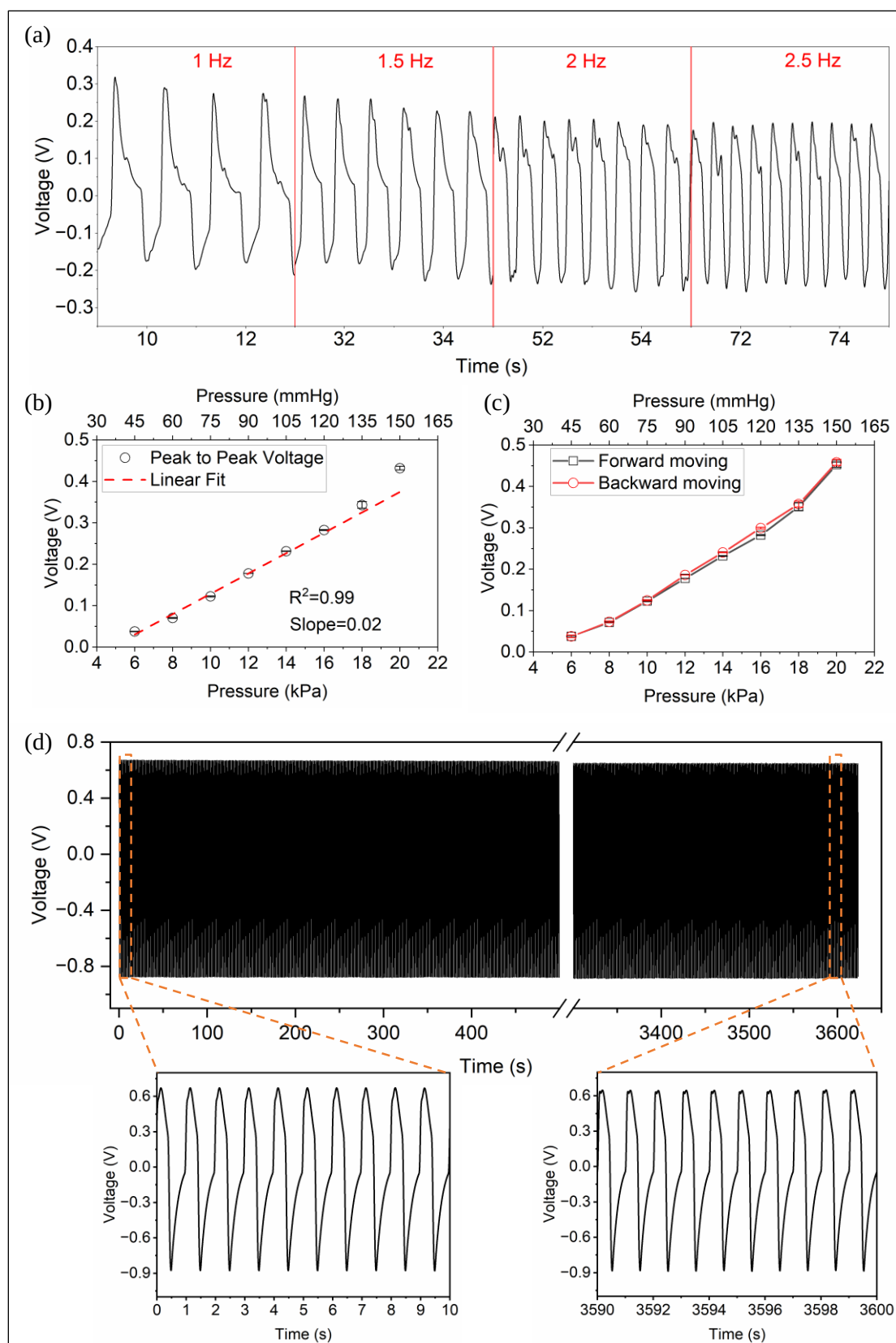


Figure 4.4 a) Voltage response of the PVDF nanocomposite sensor tested at various frequencies at an applied 16 kPa pressure (equivalent to 120 mmHg). b) Plot of the peak-to-peak output voltage versus applied pressure chosen within the range of typical human blood pressures (each sensor tested five times). c) Hysteresis plot of the sensor when increasing dynamic pressures from 6 kPa to 20 kPa and back from 20 kPa to 6 kPa. d) Sensor tested for 1 hour (3600 cycles) at 1Hz and 40 kPa.

In Figure 4.4a, the sensor is tested for frequencies of 1 – 2.5 Hz, which is within the range of human pulse rate at a constant pressure of 16 kPa (120 mmHg). 16 Kpa is chosen as it is a value close to normal systolic blood pressure. The frequency response demonstrates it's applicability to monitor beat-to-beat changes in blood pressure. Figure 4.4b displays the peak-to-peak voltage output from a sensor when a frequency of 1 Hz is applied at pressures between 6 kPa and 20 kPa – a typical range for the adult blood pressure.^[80, 82] We observe that the sensor output voltage is linear with applied pressure, (coefficient of determination, R^2 of 0.99), and we measure a corresponding pressure sensitivity of 0.024 V kPa^{-1} . The sensitivity of sensors in previous works varied with the pressure from range 6-20 kPa,[18, 74] because of their capacitive nature but our sensors shows a excellent linearity ($R^2 = 0.99$) without any change in sensitivity throughout the pressure range, confirming their reliability. Figure 4.4c presents the hysteresis of the sensor when a dynamic pressure of 1 Hz is applied, first by increasing it from 6 kPa to 20 kPa, then by reducing it down to 6 kPa. Hysteresis in piezoelectric pressure sensors refers to a phenomenon where the response of the sensor is dependent on the loading history which means the output of the sensor does not follow the same path when the applied pressure is increasing compared to when it is decreasing.^[18, 74] The small area within the hysteresis loops shows our sensor has negligible hysteresis. In Figure 4.4d, the results of a sensor's endurance test are shown for 1 hour (3600 operational cycles) at 1 Hz and 40 kPa. The insets confirm no changes in performance even after 1 hour, thus indicating the robustness and repeatability of our sensor to work continuously for 1 hour (3600 cycles).

4.2.3 Sensor application

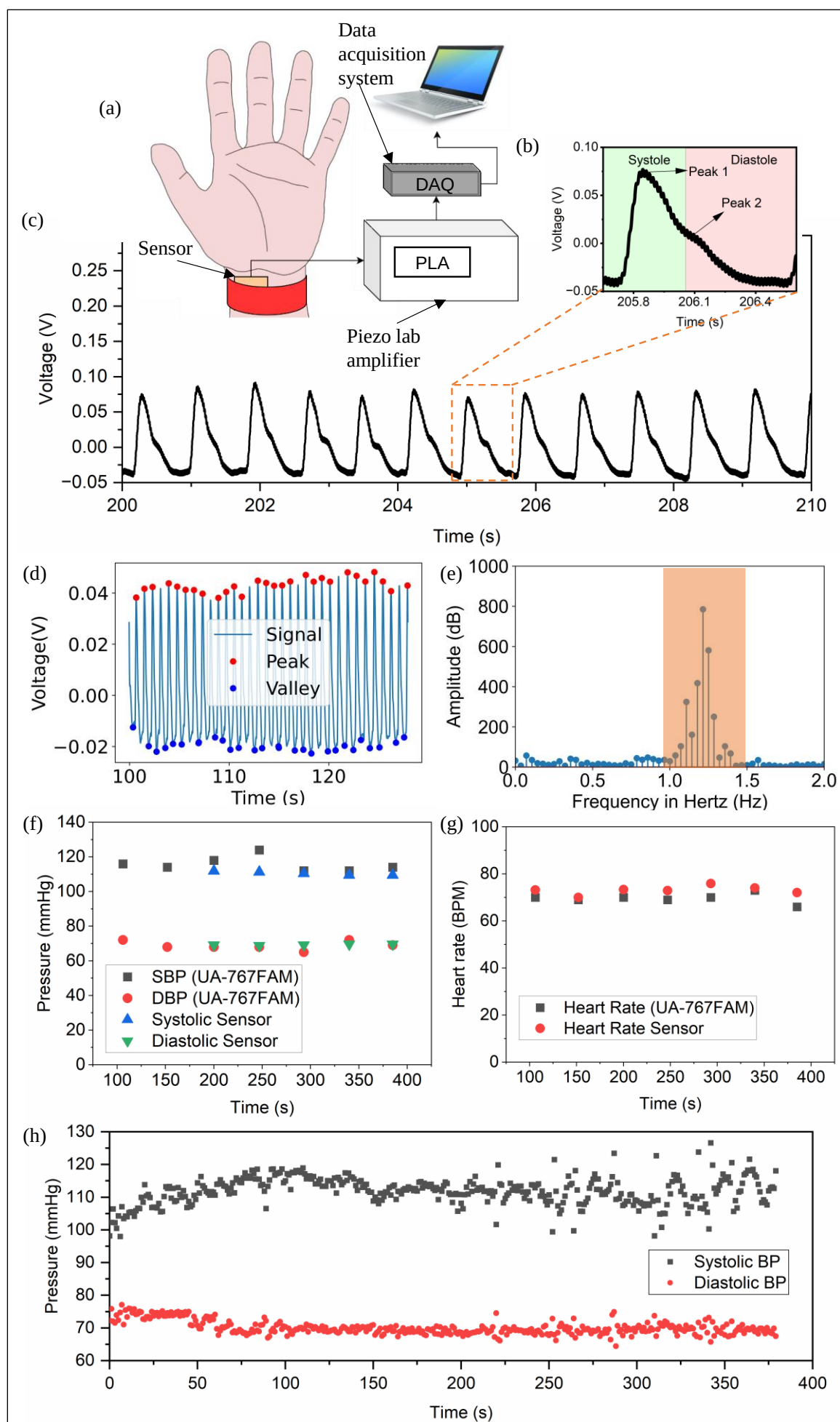


Figure 4.5 a) Schematic illustrating the process of pulse pressure wave (PPW) collection using the 3D printed sensor. b) Peak 1 and peak 2 represent systolic pressure and diastolic pressures, respectively. c) PPW captured by the sensor over a span of 10 seconds from a human subject. d) Identification of peaks and valleys in the pulse pressure wave. e) Fourier transform (FFT) of the pulse pressure wave. f) Comparison of blood pressure values estimated by the 3D printed sensor and a standard blood pressure monitoring device. g) Comparison of heart rate values estimated by the sensor and a standard blood pressure monitoring device. h) Beat-to-beat systolic and diastolic blood pressure estimates provided by the 3D printed sensor for a subject.

Figure 4.5a illustrates the method for acquiring pulse pressure wave (PPW) data from the radial artery. The sensor is positioned on the skin near the radial artery and then fastened securely with a wrist strap. The charges from the sensor were acquired through a piezo lab amplifier that amplified and convert them into readable voltages. The PPW represents the pressure exerted on the arteries by blood with each heartbeat.^[16]

As the heart contracts, blood is pumped to the body, causing an increase in arterial pressure which leads to the expansion of the artery wall. The strain, proportional to the arterial pressure, is transferred through tissue and skin to the sensor. The sensor produces equivalent charges captured in the form of voltage signals by the amplifier, reflecting the increase in blood pressure. When the heart expands, the pressure drops to diastolic pressure which is the pressure in the arteries when the heart is not pumping. Figure 4.5c displays the pulse pressure wave (PPW) collected using the sensor for 10 seconds. Two peaks can be observed in the PPW as highlighted in figure 4.5b. The peak 1 is reached when the blood pressure is highest, i.e., *systolic pressure*. When the pressure drops, we observe a second peak in the signal known as the dicrotic notch. This slight pressure increase occurs when the heart transitions from contraction to expansion and backflow is restricted due to the aortic valve. The pressure then drops to the lowest point or the valley i.e., *diastolic pressure* before it rises again in the next cycle.

An important thing to note is that the piezoelectric sensors cannot measure absolute pressures. They can only measure pressure changes. In our work, they measure the pulse pressure i.e., the difference between systolic and diastolic pressure. As the piezoelectric sensors cannot measure the absolute pressure, the lowest point i.e., the diastolic pressure needs to be measured with a separate device (in this case the standard device, Life Source UA-767FAM) and then the increase in pressure gives the value of systolic pressure. For example: suppose the diastolic

pressure is D , and systolic pressure is S . Value of D is obtained from the standard device. Our sensor measures Pulse Pressure (PP). Then the systolic pressure is given by $S = D + PP$.

The pulse pressure measured by the sensor depends on damping due to tissue and skin thickness of an individual and also on hand orientation.^[92] Hence, for best results we need to calibrate the values with a standard device for an individual before measuring the blood pressure continuously. The prominent peaks (peak 1) and valleys are extracted using a python program and then are used to predict blood pressure after the calibration step (explained in the **supporting information, c**). Figure 4.5d illustrates the Fast Fourier Transform (FFT) of the curve in Figure 4.5c, with the highest peak observed at 1.3 Hz. This value represents the frequency of pulse rate during that duration, which is in coherence with the subject's heart rate.

For calibration and testing, the sensor is positioned on the right hand of the subject, and data is collected as demonstrated in Figure 4.5a. A standard blood pressure monitoring device (UA-767FAM) is placed on the left hand, and blood pressure is measured simultaneously from both the devices. The time taken by the standard BP device for each measurement is noted and later matched with sensor data for the same duration for calibration and comparison. The first two measurements from the standard device serve as calibration, and the rest of the measurements serve as comparisons.

The time duration taken by the standard BP device to measure blood pressure is denoted by t . For calibration, the average peak-to-valley amplitude of all data points over the duration t is calculated (A), and it is proportional to the difference between systolic BP and diastolic BP calculated by the standard device ($SBP_c - DBP_c$). The SBP and DBP at point i can be given by[68]:

$$SBP_i = SBP_{i-1} + \frac{(SBP_c - DBP_c)}{A} \times (a_i - a_{i-1}) \quad (4.3)$$

$$DBP_i = DBP_{i-1} + \frac{(SBP_c - DBP_c)}{A} \times (b_i - b_{i-1}) \quad (4.4)$$

where $(a_i - a_{i-1})$ and $(b_i - b_{i-1})$ represent the difference in peak values and valley values at position i and $i-1$, respectively.

For the calculation of heart rate, the FFT of sensor data over the duration t is performed, and the frequency where the amplitude is highest in the FFT graph is used for calculation. The heart rate in beats per minute can then be given by:

$$\text{Heart Rate} = F \times 60 \quad (4.5)$$

where F is the frequency of the highest peak.

Figure 5f displays the comparison of SBP and DBP data between the sensor and standard BP device for the subject. The comparison between the sensor and the standard BP device reveals a strong correlation for both SBP and DBP, with a minor standard deviation of 3.87 mmHg and 0.63 mmHg respectively within acceptable limits ± 8 mmHg.^[68] This confirms the sensor's accuracy in measuring blood pressure. Figure 4.5g presents the comparison of heart rate calculated from the sensor and the standard BP device. We see that the heart rate calculated from the sensor aligns closely with that of the standard BP device with a standard deviation of 2.4 b.p.m (beats per minute), indicating the sensor's capability in heart rate monitoring. Figure 5h shows the continuous BP values measured from the sensor for the subject after calibration for over 300 seconds which shows the capability of sensors for continuous beat-to-beat BP measurements. Given these results, the sensor demonstrates promising performance in capturing both continuous blood pressure waveform and heart rate. However, additional studies with a larger sample size and varying conditions might be necessary before fully recommending its use in medical settings.

The accuracy of these results could be enhanced further by employing machine learning techniques and comparing the results against invasive BP measurements. These findings offer a promising avenue for the development of 3D printed, self-powered blood pressure monitoring sensors for remote healthcare monitoring.

4.3 Conclusion

This study presents a novel fabrication process for biomedical sensors using DIW 3D printing, which is simple, fast, and inexpensive. These fabricated biocompatible and flexible sensors are used for real-time monitoring of vital health functions like heart rate and blood pressure. The reported blood pressure sensors are well suited for integration into smart wearable fabrics because they are thin (<0.1 mm), flexible and printed at room temperature, making possible continuous real-time health monitoring and remote diagnosis. More precisely, we first investigated and optimized suitable printing parameters for the sensor material, PVDF-BaTiO₃, using the characterization techniques: FTIR, DSC, d_{33} meter, and optical microscopy. For the first time, the printing of PVDF nanocomposite sensors is studied in detail at different bed temperatures to analyze its effect on the phases and total crystallinity of PVDF nanocomposite.

It was found that a 0.1 mm nozzle size with a pressure of 1.4 MPa and 20 mm.s⁻¹ yields the highest β -phase of 70%. We observed that annealing did not significantly increase the β -phase presence in PVDF nanocomposite films. The effect of printing on a heated bed differed for the two film surfaces (facing the bed or air) due to variations in solvent evaporation rates. Both evaporation rates and bed temperatures impacted the final crystalline phase composition of the films. While printing at a high bed temperature of 100°C increased the β -phase from 65% to 70% compared to a normal bed temperature, the total crystallinity decreased from 48.4% to 33.7%. Hence, the overall effective β -phase actually decreases, as it is dependent on total crystallinity. This finding suggests that printing at ambient bed temperature is preferable.

Secondly, to further enhance their piezoelectric response, the sensors were poled, and the optimal poling parameters were determined to be an electric field of 50 MV m⁻¹, a temperature of 80 °C, and a duration of 60 minutes. It was also noted that the films needed to be thoroughly dried in a vacuum oven to eliminate solvents for a successful poling process.

To evaluate the feasibility of our sensors for real-time blood pressure monitoring, we examined the sensor properties. For this purpose, the sensor was characterized at dynamic pressures ranging from 6 kPa to 20 kPa (45 mmHg to 150 mmHg) at a frequency of 1 Hz, which falls within the typical range for human blood pressure. The sensor's durability was then confirmed over continuous testing for 1 hour (3600 cycles) with no apparent changes in performance noticeable. The sensor shows a sensitivity of 0.024 V kPa⁻¹, much higher than those found in the literature, with an excellent linearity ($R^2=0.99$), which proves its potential for clinical biomedical applications.

Lastly, the sensor was employed to monitor blood pressure and heart rate, demonstrating its applicability and potential for continuous and real-time monitoring. We compared the sensor's performance with a standard blood pressure monitoring device to assess its accuracy in measuring both blood pressure and heart rate. It was observed that the wrist needed to be slightly hyperextended so the sensor can press against the radial artery with appropriate pressure to capture the pulse pressure waveform. Also, it was essential to keep the hand still, as any motion artifacts can introduce noise into the signals and interfere with the measurements.

This research paves the way for future efforts to develop medical devices using 3D printing. Such technology is particularly useful as devices can be rapidly produced in emergencies and at remote locations.

4.4 Experimental section/methods

Materials: Polyvinylidene fluoride (PVDF) powder (Sigma-Aldrich) and barium titanate nanoparticles (BaTiO_3 ; 99.9% purity, 100 nm; Nanostructured & Amorphous Materials Inc.) were used as materials for the sensors. The solvents used were acetone, N, N-dimethylformamide (DMF; Alfa Aesar), and dimethyl sulfoxide (DMSO; Sigma-Aldrich; 65 g L^{-1}), with a concentration ratio of 3:2:0.3. Silver paint (MG Chemicals 842AR-15ML) was used to form the electrodes. Kapton tape was used to package the sensors.

Ink preparation: 1.8 g PVDF powder and 0.2 g BaTiO_3 nanoparticles (9:1 ratio) were added to the ball milling cylinder. To dissolve the PVDF powder and facilitate the mixing of the nanoparticles, a solvent mixture of 6 ml of acetone, 4 ml of DMF, and 0.6 ml of DMSO (3:2:0.3) was added to the ball-milling cylinder. The resulting mixture was then ball-milled for 20 min to ensure uniform nanoparticle dispersion and the highest percentage of beta phase.^[6] The ball milling was carried out using a high-energy ball mill (SPEX SamplePrep 8000, Series Mixer/Mil) with a rotation speed of 1080 rpm and zirconia balls with a ball-to-solution weight ratio of 1:1.

3D Printing: The piezoelectric ink was 3D printed using a custom-built attachment fixed to the printhead of an FDM 3-D printer (Crealitiy Ender 3 v2), a syringe-nozzle system (3 mL), and a pressure dispensing system (Ultimus V and HP-7X; Nordson EFD). The ink was extruded through a stainless steel nozzle with an inner diameter of 0.1 mm and 0.25 mm at a pressure of 1.4 MPa and 140 kPa respectively and a speed of 20 mm.s^{-1} . The films were designed in Solidworks and sliced using an open-source slicing software, Cura, and the G-code was transferred to the 3D printer. The dimensions of the films were 25 mm x 25 mm x 0.1 mm. After printing, the films were dried at ambient temperature on the print bed for 6 h to allow evaporation of the solvents and avoid shrinkage and curling of films. To remove any remaining solvents, the films were further dried in a vacuum oven (10 kPa) at 100 °C for 18 h.

Thermal Poling: Silver conductive paint was painted on the opposite sides of the films to achieve uniform contact poling. Contact poling of PVDF nanocomposite films was carried out using a poling setup where PVDF nanocomposite films were immersed in a silicone oil bath. A voltage of 5 kV was applied across the film using a high-voltage DC power source.

Sensor Fabrication: The PVDF nanocomposite film was sandwiched between two silver electrodes, which were painted using the commercially available silver conductive paint.

Aluminum tape (3M) was used to connect the wires to the electrodes. The entire sensor assembly was insulated using a Kapton tape to prevent electrical interference.

Characterization:

FTIR Analysis: An additional solution-cast film was prepared on a glass slide to compare with the 3D printed film. To investigate the effect of printing pressures on the β -phase of the films, FTIR analysis was carried out using a Perkin-Elmer, Spectrum 65 FTIR spectrometer between 600 cm^{-1} to 1400 cm^{-1} wavelength with a step size of 4 cm^{-1} . The films were scanned two times each at random locations on both surfaces in absorption mode.

DSC Analysis: The crystallinity of the PVDF nanocomposite films was measured using a Differential Scanning Calorimeter (DSC) from TA Instruments (DSC Q100). Close to 5 mg of the specimens were punched out from the nanocomposite film and placed into an aluminum pan. Measurements were performed twice for each sample printed at different bed temperatures. Heating scans were carried out from 0°C to 200°C at the rate of $10^{\circ}\text{C min}^{-1}$.

D33 Measurement: The piezoelectric coefficient (d_{33}) of the PVDF nanocomposite films was measured using a YE2730 d_{33} meter on both sides of the sensors three times each and the average was calculated.

Electrical Characterization: To investigate the sensor's behavior under different pressures and at different frequencies, a cyclic compression testing device was custom-built by connecting a pressure dispenser (Ultimus V and HP-7X; Nordson EFD) to a frequency generator. The sensor was compressed using the pressure dispenser, and the electrical response was recorded.

Data Acquisition: To collect data from the sensors, a piezo lab amplifier (Measurement Specialties) and a data acquisition system (NI-9239) were used. The piezo lab amplifier was set to a gain of 1 with voltage mode, input impedance 10 G (50PF), and the filter was set between 0.1 Hz and 10 Hz . A MATLAB (R2022a) code was used to control the data acquisition system and collect the data, which were stored on a computer. The collected data were analyzed using the Python 3 Software package.

Heart Rate and Continuous Blood Pressure Monitoring: To monitor heart rate and continuous blood pressure, the PVDF nanocomposite sensor was placed on the wrist near the radial artery to record the pulse pressure wave. The sensor was attached to the skin using Tegaderm tape (3M) and a wristband was used to ensure proper contact-pressure on the sensor for detecting

the pulse pressure wave. The data from the sensor were collected using the same piezo lab amplifier and data acquisition system described above. The collected data were analyzed using Python 3 Software package.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

There are no conflicts to declare.

4.5 Supporting Information

a. Microscopic images of PVDF nanocomposite films printed under various conditions

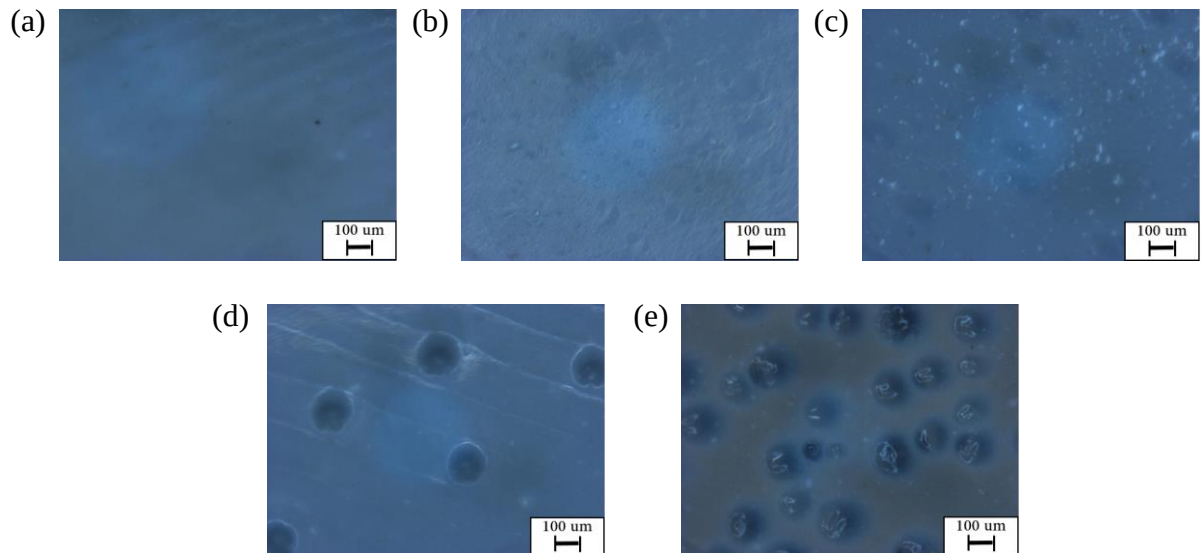


Figure 4.6 Microscopic images of PVDF nanocomposite films printed under various conditions: a) at ambient bed temperature, b) with a bed temperature of 40°C, c) 60°C, d) 80°C, and e) 100°C. (Printing speed: 20 mm.s⁻¹ nozzle diameter:0.25 mm, printing pressure:140 kPa, surface: air-side)

Figure 4.6 displays microscopic images of the films printed at various bed temperatures. Figures 4.6a, 4.6b, and 4.6c show no pores in the PVDF nanocomposite films subjected to ambient, 40°C, and 60°C bed temperatures. Conversely, Figures 4.6d and 4.6e illustrate the presence of pores when the films are subjected to bed temperatures of 80°C and 100°C. This pore formation is likely due to a faster evaporation rate.^[93] These pores create challenges for the electrical poling process, as they serve as weak points where the electric field gets concentrated and causes dielectric breakdown at low electric fields, i.e., less than 10 MV m⁻¹.^[94]

b. Sensor attachment and Hand support for wrist hyperextension and avoid movements

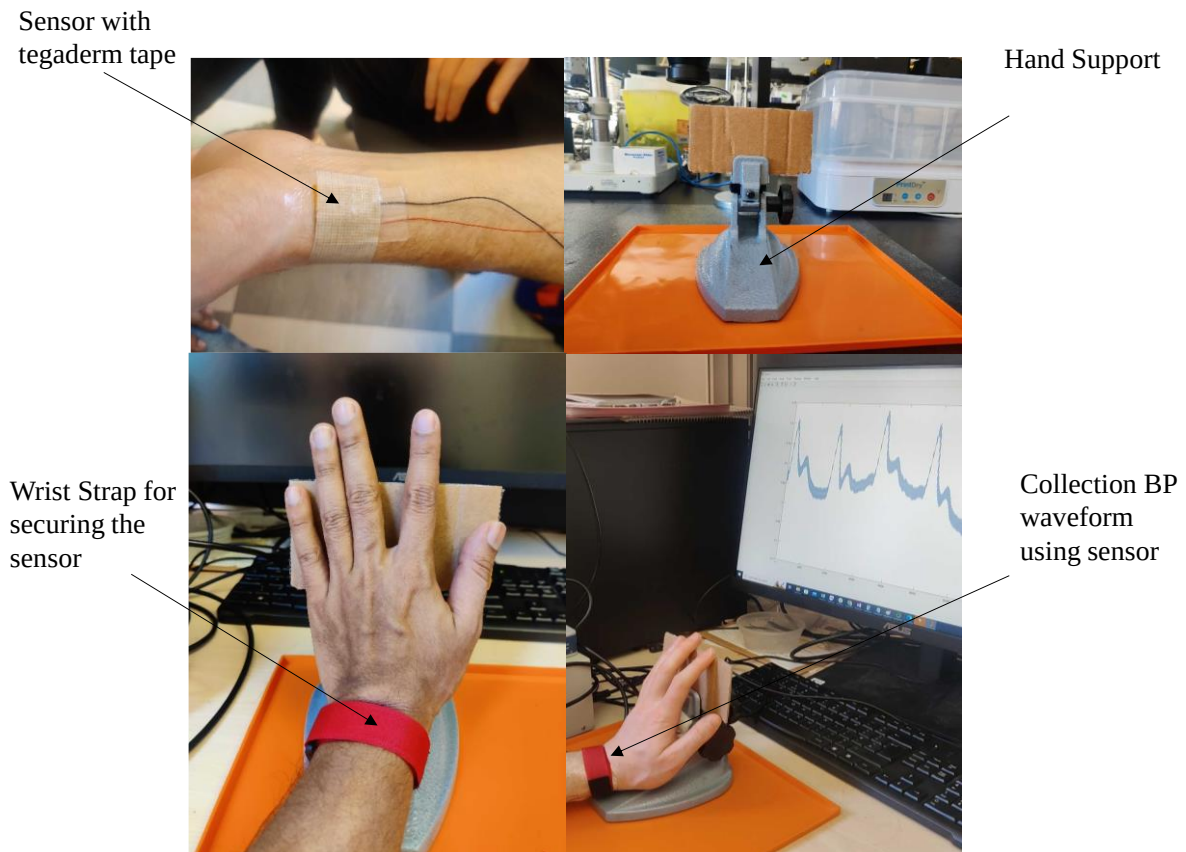


Figure 4.7 Hand support for taking (pulse pressure wave) PPW measurement from sensors

c. Determination of radial artery location using ultrasonic probe

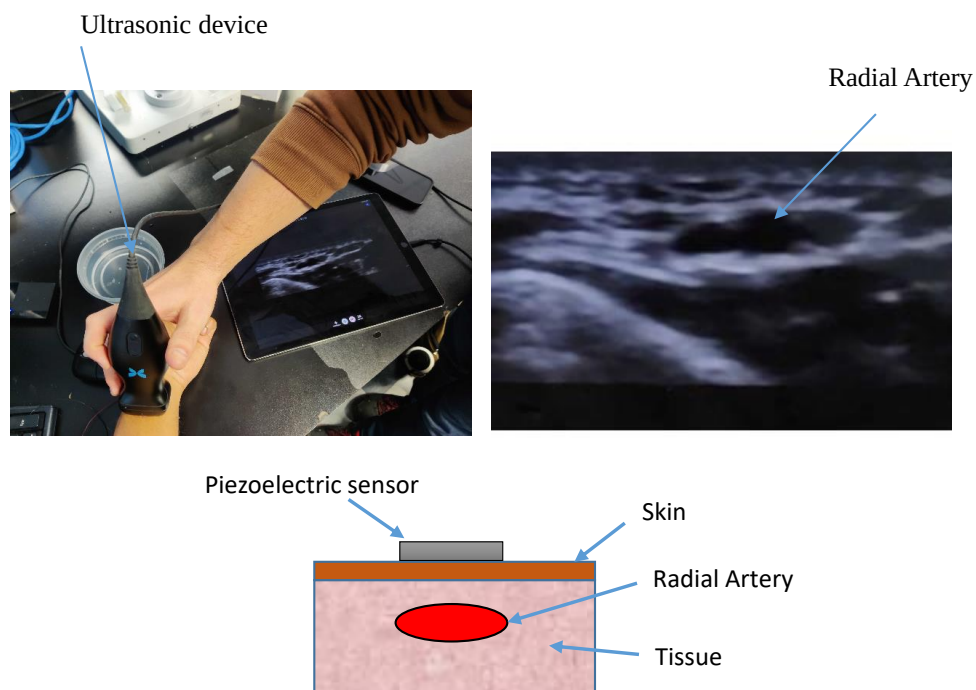


Figure 4.8 Ultrasonic view and schematic of radial artery

d. Calibration Process

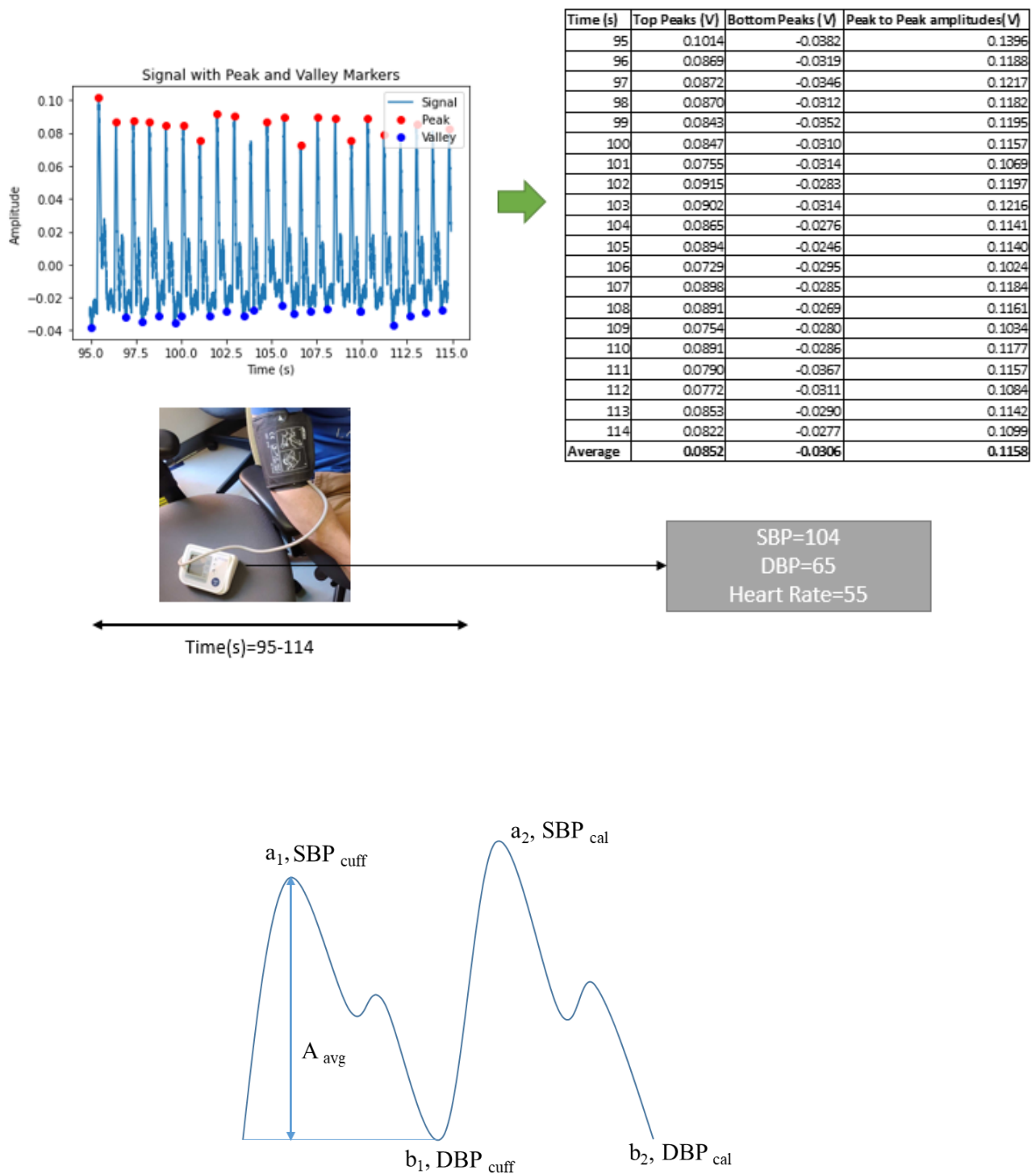


Figure 4.9 Calibration process of sensors with standard BP device (UA-767FAM)

First, the peak-to-peak amplitudes are calculated from the sensor data for the same time period as taken by the cuff to measure the blood pressure. As the cuff-based BP device give values

over a period of time, we take out the average of peak to peak values of BP waveform from the sensor data and then use it for calibration as follows:

$$\text{Calibration ratio} = (\text{SBP}_{\text{cuff}} - \text{DBP}_{\text{cuff}}) / A_{\text{avg}}$$

$$\text{SBP}_{\text{cal}} = \text{SBP}_{\text{cuff}} + \text{Calibration ratio} * (a_2 - a_1)$$

$$\text{DBP}_{\text{cal}} = \text{DBP}_{\text{cuff}} + \text{Calibration ratio} * (b_2 - b_1)$$

where,

SBP_{cuff} = Systolic BP measured by the cuff based device (Life Source UA-767FAM)

DBP_{cuff} = Diastolic BP measured by the cuff based device

A_{avg} = Average amplitude (in Volts) calculated from the sensor data for the time span taken by the cuff device to measure the BP

SBP_{cal} = SBP calculated from sensor data after calibration

DBP_{cal} = DBP calculated from sensor data after calibration

a_1 = Average of the peak voltage (in Volts) calculated from the sensor data for the time span taken by the cuff device to measure the BP

a_2 = Peak voltage for the next subsequent measurement after the calibration process

b_1 = Average of the valley voltage calculated from the sensor data for the time span taken by the cuff device to measure the BP

b_2 = Valley voltage for the next subsequent measurement after the calibration process

Then the calculated values from sensor after calibration are compared with cuff-based BP device for subsequent data collection.

e. Amplifier Information



Figure 4.10 Piezo film lab amplifier

Piezo Film Lab amplifier (TE connectivity) was used to take measurement from the sensor using following settings:

- Mode: Voltage Mode
- Input Impedance: 1G (50 PF)
- Input Attenuator switch: 0 dB
- Low frequency Selector: 0.1 Hz
- High frequency Selector: 10 Hz

CHAPTER 5 GENERAL DISCUSSION

In our study, we investigated the effectiveness of 3D printed piezoelectric sensors—made from a biocompatible and flexible nanocomposite of PVDF-BaTiO₃—in monitoring blood pressure and heart rate. The 3D printing method employed, known as direct ink write (DIW), facilitates the stretching of PVDF, an advantage not seen in the fused deposition modelling (FDM) printing technique where the material must be separately stretched to achieve the electroactive β -phase. Notably, annealing did not considerably augment the β -phase content of the PVDF nanocomposite films. We also discovered that printing on a heated bed induced variations in the final crystal phase composition of the films due to changes in solvent evaporation rate and temperature across the two film surfaces. Printing at a high bed temperature of 100 °C raised the β -phase from 65% to 70% as compared to a normal bed temperature, but overall crystallinity dropped from 48.4% to 33.7% for a 0.25 mm nozzle at 140 kPa and a speed of 20 mm.s⁻¹. Thus, printing at a normal bed temperature is more advantageous because of the enhanced total crystallinity. Furthermore, we identified ideal poling parameters to improve the piezoelectric activity of the sensors. Optimal results were obtained with an electric field of 50 MV m⁻¹, a temperature of 80 °C, and a duration of 60 minutes. For effective poling, the films needed to be thoroughly dried in a vacuum oven to remove solvents, with higher temperatures facilitating chain alignment due to increased molecular chain mobility.

To verify our sensors' feasibility for real-time blood pressure monitoring, we assessed their sensing properties under dynamic pressures between 6 kPa and 20 kPa at a frequency of 1 Hz, in-line with the typical blood pressure range. We conducted durability tests over 3600 cycles and found the sensor to display a sensitivity of 0.02 V kPa⁻¹ with an exceptional linearity ($R^2 = 0.99$), suggesting its potential for critical biomedical applications.

Finally, we applied the sensors for continuous blood pressure and heart rate testing by positioning them near the radial artery. Given the sensors' low piezoelectric constant, a charge amplifier was used to boost the voltage output, and a band-pass filter was implemented to eradicate noise caused by breathing at frequencies lower than 0.5 Hz and

higher frequencies of 10 Hz. The sensor was required to be firmly pressed against the wrist to capture the pulse pressure wave signal. Keeping the wrist slightly hyperextended ensured clearer signals. It was also necessary to immobilize the hand during signal recording to minimize noise, posing a challenge for ambulatory measurements. Nevertheless, accurate measurements can be achieved if hand movements are limited during the process.

During critical medical situations like cardiopulmonary resuscitation (CPR), being able to continuously monitor a patient's blood pressure can make a significant difference in the success of the treatment. This is the core focus of a project we're working on in partnership with IMPACK CPR, a pioneering start-up based in Montreal that's developing a computerized system for administering CPR. Their mission is to design an automatic device that first responders can use to carry out CPR more efficiently. Their innovative proposal involves the use of a pressure sensor patch placed directly on the patient. This patch will measure blood pressure continuously with every chest compression during CPR. The real-time data gathered from these sensors would then be utilized to regulate the computerized CPR device's pressure output, thereby enhancing the precision and effectiveness of the life-saving procedure.

This study lays a foundational groundwork for future advancements in wearable smart sensor fabrication. With the application of 3D printing, more complex projects, such as fully printed hearts with integrated sensors, can be pursued.

CHAPTER 6 CONCLUSION AND RECOMMENDATION

6.1 Conclusions

In this thesis, our aim was to develop 3D-printed piezoelectric sensors for use in blood pressure and heart rate monitoring. This objective was further divided into three sub-objectives.

The first part of the study involved characterizing the material properties of direct ink write 3D-printed PVDF-BaTiO₃ films to identify the optimal printing parameters. We investigated the impact of printing at nozzle sizes of 0.1 mm and 0.25 mm to induce β - and γ - phases. It was discovered that a 0.1 mm nozzle with higher pressure induces more of the β -phase due to increased shear stress during the printing process. We also studied the effect of the printing bed temperature on the β - phase and total crystallinity. The β - phase initially decreased with an increase in bed temperature, but then increased, even as the total crystallinity decreased with rising print bed temperatures. This reduced the effective β -phase, leading us to conclude that printing at the normal bed temperature was optimal.

In the second part, we improved the sensitivity of the PVDF films using contact poling and determined the optimum poling parameters (electric field, time, and temperature). Subsequently, we characterized the sensors to assess their performance under different pressures and frequencies, akin to blood pressure and pulse rate. The repeatability of the sensor was analyzed by testing the sensor across 1 hour (3600 cycles).

The third part involved testing the sensors on a human subject. The sensors was tested on a subject and the results were compared with a standard BP monitoring device. This comparison depicted a strong correlation for both SBP and DBP, with a minor standard deviation of 3.87 mmHg and 0.63 mmHg respectively within acceptable limits ± 8 mmHg within acceptable error margins.

6.2 Recommendations

- In this study, only 2D printed films were used, but 3D shapes can provide better sensitivity due to the increased amount of strain. However, printing 3D shapes with DIW is challenging and requires slow printing speeds of about 1 mm s⁻¹. Detailed

simulations and studies are required to find an optimum 3D shape for sensors without compromising on its conformability to skin. This could be an area of future research, helping to unleash the full potential of the 3D printing process for the development of wearables.

- In this study, a separate poling station was used for poling. A system can be designed to have an integrated 3D printing and poling setup. The poling process requires the use of a high electric field, heat, and sufficient time, which may pose a challenge to integrate with the 3D printing process to achieve the same sensitivity as obtained by poling separately.
- The standard blood pressure device we used for comparison purposes wasn't a continuous monitoring device. This aspect might render the comparison less accurate than desired, as there could be intra-cycle variations missed by intermittent measurements. For a more precise evaluation of our sensor's performance, it would be beneficial to compare it with continuous beat-to-beat standard blood pressure monitors or even with invasive blood pressure measurement devices.
- A comprehensive investigation into the impact of sensor dimensions on the output signal would contribute significantly to optimizing sensor design. Different geometries may influence the signal quality or sensitivity of the sensors, as they may affect factors like contact surface area, pressure distribution, or mechanical stress on the sensor. By systematically studying the relationship between sensor design and output, we can fine-tune the physical properties of the sensors to enhance their performance.
- Before introducing these sensors into the human clinical setting, rigorous animal testing must be undertaken to evaluate biocompatibility, safety, and functionality under various physiological conditions. Also, extensive clinical trials on human subjects will be essential to validate the sensor's accuracy, reliability, and real-world applicability. These tests must be conducted in compliance with ethical guidelines and in a controlled, representative population to ensure that the sensors can be widely implemented in healthcare monitoring without unforeseen complications or risks.

This comprehensive validation approach would build confidence in the technology and pave the way for its integration into standard medical practice.

- A crucial aspect that warrants further research is the effect of time on the sensitivity of PVDF-BaTiO₃ films. Sensitivity could deteriorate over time due to factors such as material degradation, environmental exposure, or repeated stress cycles. A study tracking the change in sensor sensitivity over extended periods would provide invaluable data on the life expectancy and reliability of these devices. This information is critical for applications, where the sensor may need to operate effectively over prolonged periods.

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APPENDIX A : MATLAB AND PYTHON CODE

MATLAB code for data real time data collection from sensors:

Code for connecting to NI device:

```
% Chris R. KAMAL YOUSSEF
clear; clc;
global x; % To save data
global seconds; % time in seconds

path_txt = '\\dionysos.meca.polymtl.ca\lis\Public\Chih-l Luo\test\'; % Path to
the folder which you want to save data
path_plot = '\\dionysos.meca.polymtl.ca\lis\Public\Chih-l Luo\test\'; % Path
to the folder which you want to save image
seconds = 100; % Time in seconds

%d = daqlist("ni");
%deviceInfo = d{1, "DeviceInfo"};

dq = daq("ni");
ch = addinput(dq, "cDAQ1Mod1", "ai2", "Voltage");

dq.ScansAvailableFcn = @read_RealTime;
start(dq,"Duration",seconds)

% Copy .this in Command Window after finishing the test
% to save data and plot
% save_files(path_txt, path_plot, seconds)

% If you don't want to save: copy this instead :

x = [];
```

Code for reading real time data:

```
% Chris R. KAMAL YOUSSEF
function read_RealTime(obj,~)
    global x;
    global seconds;
% obj is the DataAcquisition object passed in. evt is not used.
    data = read(obj,obj.ScansAvailableFcnCount,"OutputFormat","Matrix");
    x=[x;data];
    plot(x)
    %xlim([0 seconds])
end
```

Code for saving files:

```

function save_files(path, path_im, tt)
    name = input("test 1 : ','s') %Name of txt and plot
%% Prepare the txt file
    global x;
    t = datetime;
    format =
append(string(year(t)), '_', string(month(t)), '_', string(day(t)), '_', name);

    time = (1/length(x)) : (tt/length(x)) : tt;
    % Create the .txt file to store data
    fileID = fopen(fullfile(path, append(format, '.txt')), 'w');
    fprintf(fileID, '%s \n\n', name);
    %fprintf(fileID, '%s \n', 'write comments here');
    fprintf(fileID, '%s %s\n', 'time', 'data');
    fprintf(fileID, '%.8f , %.8f\n', [time;x]);
    %fprintf(fileID, '%.3f , %.3f\n', [x;y]);
    fclose(fileID);
    plot(time,x);
    title(string(datetime));
    xlabel('Time [sec]');
    ylabel('Voltage [V]');
    f = gcf;
    % save the graph
    exportgraphics(f, fullfile(path_im, append(format, '.png')));

    x=[];
end

```

NOTE: Save these code as three separate MATLAB files. Open all the three and after giving proper parameters, run the first file.

Python codes for blood pressure data analysis:

```

#!/usr/bin/env python
# coding: utf-8

# In[2]:

import scipy.io.wavfile
import scipy.signal
import numpy as np
import matplotlib.pyplot as plt
import pandas as pd

```

```

# In[34]:

import os

dir_containing_file = r'\\poseidon.meca.polymtl.ca\lis\Public\Chih-1
Luo\Blood pressure test data\Test on subjects\Arijit 2\Test 1'
# 📁 change to directory containing file
os.chdir(dir_containing_file)
print(os.getcwd())

# In[35]:

os.listdir()

# In[57]:

#To get the data between particlular time range
ts=200 #start time for data
#To get the data between particlular time range
t1= ts*1612
tn=10 #duration from the starting time
t2= tn*1612
#Array to time to save in text file with peak data
time_values = np.arange(ts, ts + tn)
print(time_values)

# In[58]:

Data=np.genfromtxt("2023_5_26_test 1.txt",delimiter=',',skip_header=t1,
max_rows=t2 )

# In[59]:

t = Data[:,0]
x = Data[:,1]

fig, ax = plt.subplots()
ax.plot(t, x)
ax.set_xlabel('Time [s]')
ax.set_ylabel('Signal amplitude');

# In[60]:

y=t[2]-t[1]

```

```

f_s=1/y
print(f_s)
fs=int(f_s)

# In[61]:

from scipy import fftpack

X = fftpack.fft(x)
freqs = fftpack.fftfreq(len(x)) * f_s

fig, ax = plt.subplots()

ax.stem(freqs, np.abs(X))
ax.set_xlabel('Frequency in Hertz [Hz]')
ax.set_ylabel('Frequency Domain (Spectrum) Magnitude')
#ax.set_xlim(-f_s / 2, f_s / 2)
ax.set_xlim(0.5,2)
ax.set_ylim(-5, 1000)
#ax.axis([0.5, 1.5, 15, 20])

# In[62]:

# Define the frequency range of interest
f_min = 0.5 # Hz
f_max = 10.0 # Hz

# Create a filter that attenuates the frequencies outside the range of
interest
filter = np.logical_and(freqs >= f_min, freqs <= f_max).astype(int)

# Apply the filter to the frequency-domain representation of the signal
X_filtered = X * filter

# Compute the inverse FFT of the filtered signal
x_filtered = np.fft.ifft(X_filtered).real

# Plot the original and filtered signals
plt.figure()
plt.plot(t, x, label='Original signal')
plt.plot(t, x_filtered, label='Filtered signal')
plt.legend()
plt.xlabel('Time (s)')
plt.ylabel('Amplitude')
plt.show()

# In[63]:

```

```

plt.plot(t, x_filtered, label='Filtered signal')

# In[299]:

# Define the range of frequency values of interest
min_freq = 0.5
max_freq = 2.0

# Find the indices of the frequency values within the range
freq_indices = np.where((freqs >= min_freq) & (freqs <= max_freq))[0]

# Find the magnitude of the signal within the frequency range
mY_range = np.abs(X_filtered[freq_indices])

# Find the location and value of the maximum peak within the range
peak_loc = freq_indices[np.argmax(mY_range)]
peak_val = np.max(mY_range)

# Get the actual frequency value corresponding to the peak location
freq_peak = freqs[peak_loc]
freqY=freq_peak
# Print the results
print("Peak frequency: {:.2f} Hz".format(freq_peak))
print("Peak magnitude: {:.2f}".format(peak_val))

# In[300]:

# Divide the signal into 1-second segments
segment_size = fs # Number of samples per segment
num_segments = len(x_filtered) // segment_size
x_segments      =      np.reshape(x_filtered[:num_segments*segment_size],
(num_segments, segment_size))

# Calculate the peak amplitudes of each segment
max_amplitudes = np.max(x_segments, axis=1)
min_amplitudes = np.min(x_segments, axis=1)
#      peak_amplitudes      =      np.maximum(np.abs(max_amplitudes),
np.abs(min_amplitudes))
peak_amplitudes = np.max(x_segments, axis=1) - np.min(x_segments, axis=1)

# Plot the signal and mark the peaks
fig, ax = plt.subplots()
ax.plot(t, x_filtered, label='Signal')
for i in range(num_segments):
    start = i * segment_size / fs
    end = (i + 1) * segment_size / fs
    max_peak = np.argmax(x_segments[i])
    min_peak = np.argmin(x_segments[i])

```

```

        ax.plot(t[i*segment_size + max_peak], x_filtered[i*segment_size +
max_peak], 'ro', label='Peak' if i==0 else None)
        ax.plot(t[i*segment_size + min_peak], x_filtered[i*segment_size +
min_peak], 'bo', label='Valley' if i==0 else None)
    ax.legend()
    ax.set_xlabel('Time (s)')
    ax.set_ylabel('Amplitude')
    ax.set_title('Signal with Peak and Valley Markers')

# Print the peak amplitudes
print('Top Peaks:',max_amplitudes)
print('Bottom Peaks:',min_amplitudes)
print('Peak to Peak amplitudes:', peak_amplitudes)

# In[287]:

dpi_value = 600
font_size=20

# Plot the signal and mark the peaks
fig, ax = plt.subplots()
ax.plot(t, x_filtered, label='Signal')
for i in range(num_segments):
    start = i * segment_size / fs
    end = (i + 1) * segment_size / fs
    max_peak = np.argmax(x_segments[i])
    min_peak = np.argmin(x_segments[i])
    ax.plot(t[i*segment_size + max_peak], x_filtered[i*segment_size +
max_peak], 'ro', label='Peak' if i==0 else None)
    ax.plot(t[i*segment_size + min_peak], x_filtered[i*segment_size +
min_peak], 'bo', label='Valley' if i==0 else None)
ax.legend()
ax.set_xlabel('Time (s)',fontsize=font_size)
ax.set_ylabel('Voltage(V)',fontsize=font_size)

plt.legend(fontsize=font_size,loc='center')

# Set the font size for the tick labels
plt.tick_params(axis='x', labelsz=font_size)
plt.tick_params(axis='y', labelsz=font_size)

fig.savefig('peakvalues.jpg',
dpi=dpi_value,bbox_inches='tight',format='jpg')

# In[288]:

# stack the arrays horizontally
result = np.hstack((time_values.reshape(-1,1), max_amplitudes.reshape(-
1, 1), min_amplitudes.reshape(-1, 1), peak_amplitudes.reshape(-1, 1)))

```

```

#result      =      np.hstack((      max_amplitudes.reshape(-1,      1),
min_amplitudes.reshape(-1, 1), peak_amplitudes.reshape(-1, 1)))

# ask user to input a file name
file_name = input("Enter a file name to save the arrays: ")

# define column headers
headers = "Time,Top Peaks,Bottom Peaks,Peak to Peak amplitudes" #add txt
at the end of the file name
#headers = "Top Peaks,Bottom Peaks,Peak to Peak amplitudes" #add txt at
the end of the file name
# save the arrays to a file
np.savetxt(file_name, result, delimiter=",",header=headers, comments="")

```

Python code for heart rate measurement in beats per minute:

```

# Arijit M. 2022
# In[158]:

import numpy as np
import matplotlib.pyplot as plt

# In[251]:

import os

dir_containing_file = r'\\poseidon.meca.polymtl.ca\lis\Private\Arijit
Mandal\04_Masters Research\Experiments\Blood pressure measurement pulse
rate measurement using pvdv film\testing on subject\Aymen 2'
# 🖱️ change to directory containing file
os.chdir(dir_containing_file)
print(os.getcwd())

# In[252]:

os.listdir()

# In[380]:

#To get the data between particlular time range
ts= 514 #start time for data
t1= ts*1612
tn= 31 #duration from the starting time
t2= tn*1612

```

```

# In[381]:

#Data=np.genfromtxt("2023_5_5_t1.txt",delimiter=',',skip_header=10000,
skip_footer=1000)

# In[382]:

Data=np.genfromtxt("2023_6_2_aymen.txt",delimiter=',',skip_header=t1,
max_rows=t2 )

# In[383]:

t = Data[:,0]
x = Data[:,1]

fig, ax = plt.subplots()
ax.plot(t, x,)
ax.set_xlabel('Time [s]')
ax.set_ylabel('Signal amplitude');

# In[386]:

y=t[2]-t[1]
f_s=1/y
print(f_s)

# In[387]:

from scipy import fftpack

X = fftpack.fft(x)
freqs = fftpack.fftfreq(len(x)) * f_s

fig, ax = plt.subplots()

#dpi_value = 600
# font_size=0
ax.stem(freqs, np.abs(X))
ax.set_xlabel('Frequency in Hertz (Hz)')
ax.set_ylabel('Amplitude (dB)')

# Set the font size for the tick labels
# plt.tick_params(axis='x', labelsiz=font_size)

```

```

# plt.tick_params(axis='y', labelsz=font_size)

#ax.set_xlim(-f_s / 2, f_s / 2)
ax.set_xlim(0,2)
ax.set_ylim(0, 1000)
#ax.axis([0.5, 1.5, 15, 20])

#fig.savefig('output.jpg',
dpi=dpi_value,bbox_inches='tight',format='jpg')

# In[388]:

# Define the frequency range of interest
f_min = 0.5 # Hz
f_max = 10.0 # Hz

# Create a filter that attenuates the frequencies outside the range of
interest
filter = np.logical_and(freqs >= f_min, freqs <= f_max).astype(int)

# Apply the filter to the frequency-domain representation of the signal
X_filtered = X * filter

# Compute the inverse FFT of the filtered signal
x_filtered = np.fft.ifft(X_filtered).real

# Plot the original and filtered signals
plt.figure()
plt.plot(t, x, label='Original signal')
plt.plot(t, x_filtered, label='Filtered signal')
plt.legend()
plt.xlabel('Time (s)')
plt.ylabel('Amplitude')
plt.show()

# In[389]:

plt.plot(t, x_filtered, label='Filtered signal')

# In[391]:

# Define the range of frequency values of interest
min_freq = 0.5
max_freq = 2.0

# Find the indices of the frequency values within the range
freq_indices = np.where((freqs >= min_freq) & (freqs <= max_freq))[0]

```

```

# Find the magnitude of the signal within the frequency range
mY_range = np.abs(X_filtered[freq_indices])

# Find the location and value of the maximum peak within the range
peak_loc = freq_indices[np.argmax(mY_range)]
peak_val = np.max(mY_range)

# Get the actual frequency value corresponding to the peak location
freq_peak = freqs[peak_loc]
freqY=freq_peak
# Print the results
print("Peak frequency: {:.2f} Hz".format(freq_peak))
print("Peak magnitude: {:.2f}".format(peak_val))

# In[393]:

BPM= 60*freqY
print("Beats per minute =", BPM)

```