

3D Printing of Polyvinylidene Fluoride-Based Piezoelectric Sensors for Noninvasive Continuous Blood Pressure Monitoring

Arijit Mandal, Alban Morali, Maksim Skorobogatiy, and Sampada Bodkhe*

The successful fabrication and application of 3D-printed piezoelectric sensors, made from polyvinylidene fluoride-barium titanate nanocomposites, for continuous blood pressure (BP) monitoring, is presented. The sensors are fabricated using direct-ink write 3D printing technique possessing excellent flexibility, rendering them ideal for wearable applications. Key printing parameters, such as nozzle size and pressure, are optimized to achieve a β -phase of 70% and an overall crystallinity of 48.3%. The 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. The performance of our piezoelectric sensors is compared with a standard BP monitoring device for a subject, and a strong correlation with a standard deviation of 3.87 and 0.63 mmHg for systolic BP and diastolic BP, respectively, is found. The development of sensors through 3D printing, as demonstrated in this study, represents a significant scientific advancement in the field of personalized healthcare. This novel approach enables the creation of customized wearable devices tailored for real-time health monitoring of BP and heart rate.

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.^[1,2] 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.^[2,3] Polyvinylidene fluoride (PVDF) is a

semicrystalline polymer that exhibits a piezoelectric effect.^[4–6] 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.^[7–9] The 3D printing of PVDF-based sensors has been applied to various biomedical applications like respiration monitoring,^[6] tactile sensing,^[6] and gait analysis.^[5]

PVDF predominantly exists in five different phases namely α , β , γ , δ , and ϵ .^[10–12] 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.^[10–14] The α -phase is nonpolar whereas the γ -phase exhibits piezoelectricity lower than the β -phase.^[10–14] The β -phase in PVDF can be obtained and improved by the addition of fillers,^[4,7,14] the use of polar sol-

vents,^[4,7,10,13] stretching,^[8,10] annealing,^[10,11] and electrical poling.^[15–17] Adding 10% by weight of barium titanate nanoparticles (BaTiO_3) to PVDF has been shown to improve the β -phase content in 3D-printed PVDF sensors.^[4]

Given the biocompatibility of BaTiO_3 , 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 BP leads to hypertension, which can result in a heart attack or stroke.^[18,19] The standard method for measuring BP uses an oscillometric device, where a cuff is placed around the forearm.^[20,21] BP values are measured by inflating the cuff above the individual's systolic blood pressure (SBP) to stop the blood flow and then deflating it to measure the systolic pressure and diastolic blood pressure (DBP) by listening to the Korotkoff sounds.^[22] However, the cuff-based devices only provide average value over a period of time and not the continuous beat-to-beat BP measurement.^[23–25] Continuous measurement of BP provides a pulse pressure waveform (PPW), which indicates the rise and fall of BP with each cardiac cycle. This is a critical feature, as it enables detection of rapid, situational, or

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DOI: 10.1002/adem.202301292

positional changes in BP and provides deeper insights into the cardiovascular health of an individual.^[18–20] By analyzing the PPW, doctors can detect variations and trends in BP, potentially identifying underlying health issues or the effectiveness of treatments. Additionally, BP sensors can be integrated into computerized cardiopulmonary resuscitation (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 BP monitoring. For example, Joshua Kim et al. developed soft wearable capacitive pressure sensors using polydimethylsiloxane to continuously monitor BP.^[26] 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 BP, nonetheless, the fabrication process was time-consuming, involving multiple reactions and filtrations.^[27] 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} .^[28] The downside was that the fabrication involved making molds, producing microchannels, and integrating microbumps monolithically, which created an obstacle for rapid sensor production. Kirev et al. proposed thin graphene-based tattoos for measuring BP from bioimpedance, but the preparation of these tattoos required chemical vapor deposition of graphene, another complex process in itself.^[29] Recently, Wang et al. employed piezoelectric sensors to measure beat-to-beat BP using a simple calibration technique.^[30] 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 BP monitoring sensors were manufactured using expensive, time-consuming, and elaborate procedures.

In this work, we present an efficient fabrication process to produce flexible BP 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 and 0.25 mm), annealing temperatures (80, 100, and 120 °C), and print-bed temperatures (no heating, 40, 60, 80 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 BP, the sensors were characterized using a compression device under dynamic pressure between 6 and 20 kPa at 1 Hz. The hysteresis of the sensors was also determined in the same pressure range. The sensors were then tested for 1 h to validate the continuity and repeatability of measurements. Finally, we calibrated the sensors with a standard cuff-based oscillometric device and measured the BP of a subject by placing the sensor near the radial artery. The measured BP from the sensors was compared against a standard oscillometric device (A & D Medical, UA-767FAM) to assess its accuracy in detecting BP and heart rate. Our results confirm the potential to use our 3D-printed sensors to measure heart rate and continuous BP.

2. Result and Discussion

2.1. Sensor Development

Figure 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.^[31] 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 1b presents the Fourier-transform infrared (FTIR) spectra of PVDF nanocomposite films printed with 0.1 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.^[32] Additionally, peaks at 1234 and 1275 cm^{-1} are distinct peaks for γ - and β -phases, respectively.^[32] Figure 1b shows that the 840 cm^{-1} peak is the 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

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

where, A_{α} and A_{β} represent the absorption fractions of the α - and β -phases at 763 and 840 cm^{-1} , respectively. Additionally, 1.26 stands for the ratio of absorption coefficients 7.7×10^4 and $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ 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,^[33,34] while others have observed no change in phase after the annealing process.^[11] 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 3 h at 80, 100, and 120 °C. The postannealing FTIR results are presented in Figure 1c. It appears that the peaks at 840 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%

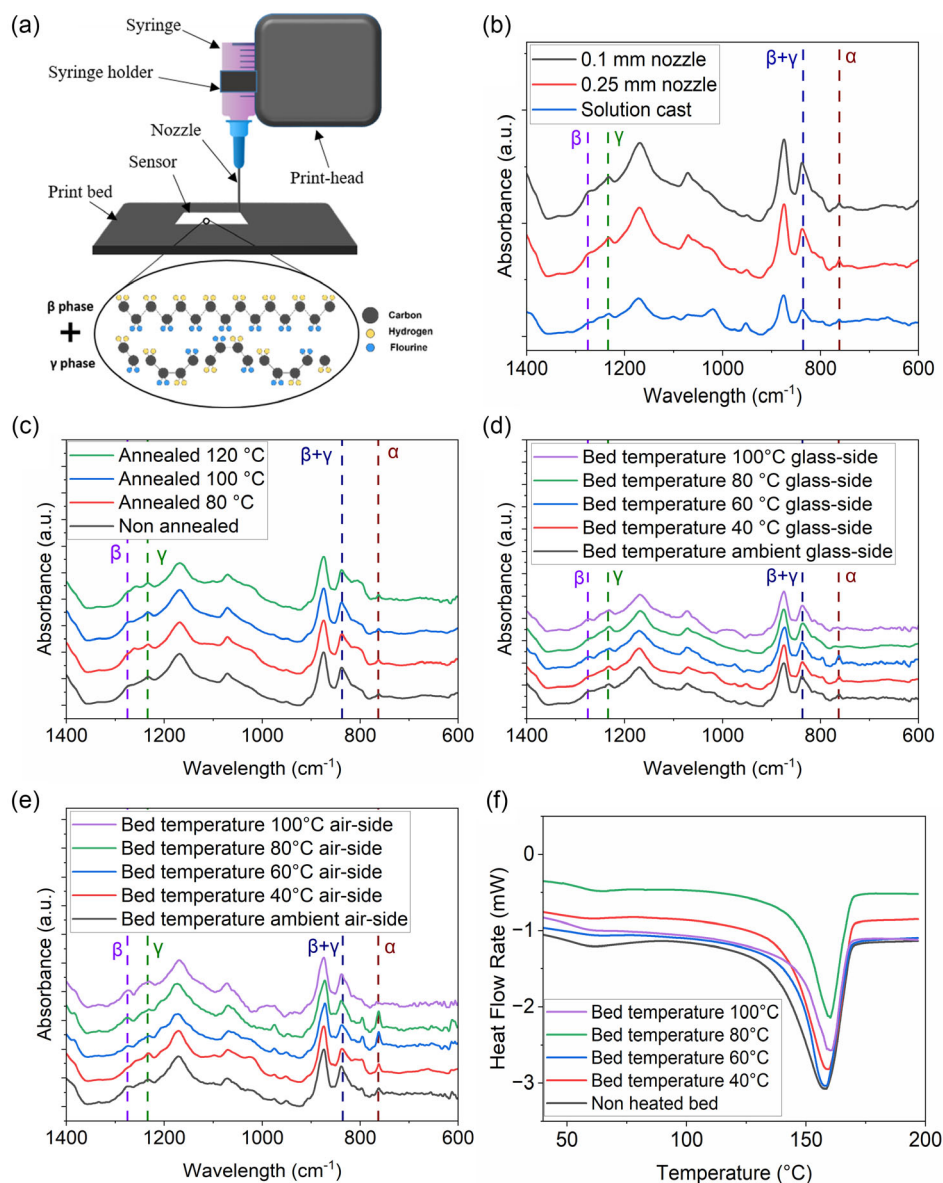


Figure 1. a) A schematic of the DIW 3D printing of PVDF-BaTiO₃ sensors. FTIR spectra showing, b) the effect of varying print nozzle size on the phases of PVDF (printing speed: 20 mm s⁻¹; bed temperature: ambient; printing pressure: 140 kPa for 0.25 mm nozzle and 1.4 MPa for 0.1 mm nozzle, respectively), 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 h). FTIR spectra for sensors printed with bed temperatures: No heating, 40, 60, 80, 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) DSC analysis of PVDF nanocomposite films printed at bed temperatures: No heating, 40, 60, 80, and 100 °C (printing speed: 20 mm s⁻¹, nozzle diameter: 0.25 mm, printing pressure: 140 kPa).

for the nonannealed, annealed at 80, 100, and 120 °C, respectively, which also confirms that annealing had no quantitative effect on the β -phase content in the PVDF nanocomposite films.^[11]

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. Figure 1d,e presents the FTIR plots of two different surfaces of the PVDF nanocomposite

films printed at varying bed temperatures. Figure 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 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 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 -phases formation and a decrease in the α -phase beyond this temperature. Figure 1e reflects a 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 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, 60, 80, and 100 °C, respectively, as shown in **Table 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, 60, 80, and 100 °C, respectively. The formation of the β -phase also depends on the solvent evaporation rate,^[35] and the temperature at which the polymer crystallizes.^[36] 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.^[35] However, higher temperatures also favor the more thermodynamically stable α -phase.^[36] Thus, the final phase composition depends on a competition of these factors.^[11,36,37] 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).^[37] The air-side of the films has 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 -phases on air-side upto 60 °C. At temperatures of 80 and 100 °C, evaporation occurs throughout the film, due to boiling of solvents. This can be inferred from the presence of pores, (Figure S1, Supporting Information). Consequently, the β - and γ -phases are more pronounced on the side of the glass-side.

Printing at high bed temperatures influences the crystallization time, which can, in turn, affect the total crystallinity of the polymer.^[38] Therefore, it is important to study the total crystallinity of samples printed on a heated bed. Figure 1f presents the total crystallinity of the PVDF nanocomposite films printed at different bed temperatures. The total crystallinity was calculated using the following equation

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (2)$$

where ΔH_m is the melting enthalpy of the sample and $\Delta H_m^0 = 104.7 \text{ J g}^{-1}$ is the enthalpy of the hypothetically 100% crystallized PVDF. The total crystallinity, calculated from

differential scanning calorimetry (DSC) analysis, for PVDF nanocomposite films printed at ambient, 40, 60, 80, 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.^[38] Despite exhibiting a higher β -phase, PVDF nanocomposite films printed at elevated bed temperatures demonstrated a reduced total crystallinity, as presented in Table 1. This shows that the effective β -phase is reduced, as shown in Table 1. A schematic illustrating the crystalline composition (α , β , γ) of samples post-3D printing on a heated bed is shown in Figure S6, Supporting Information, for further clarity. 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 BP 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.

Poling is a process where a high electric field is applied across a piezoelectric material to enhance the material’s piezoelectric response. This step facilitates the alignment of the β -phase chains, thereby amplifying the piezoelectric effect.^[8] It also assists in conversion of γ -phase to β -phase which is explained in more detail in the Figure S7, Supporting Information. After the DIW printing of the nanocomposite films and drying at ambient temperature for 18 h, 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 h 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 ($10\text{--}15 \text{ MV m}^{-1}$) compared to air (3 MV m^{-1}).^[39] The thicknesses of the poled PVDF nanocomposite films were around $0.1 \pm 0.02 \text{ mm}$. An electric field of

Table 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

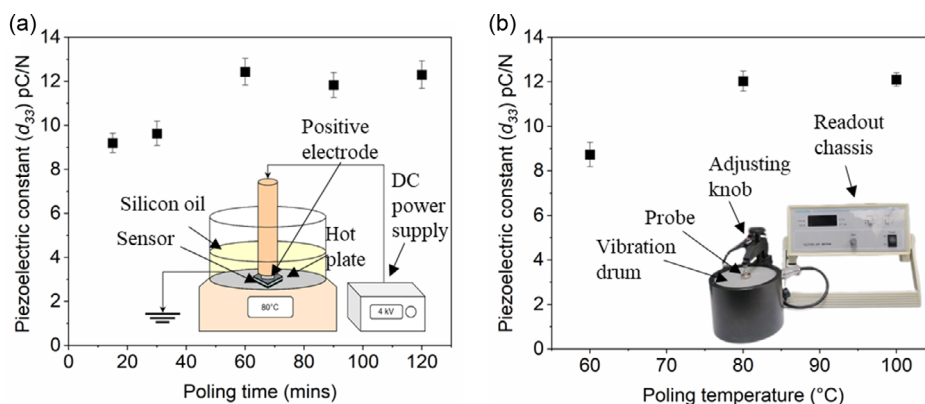


Figure 2. a) The variation of piezoelectric constant with varying poling time (15, 30, 60, 120 min) while maintaining a constant poling field of 50 MV m^{-1} and bath temperature of 100°C with the insert showing the poling setup. b) The variation of piezoelectric constant with varying oil-bath temperatures ($60, 80, 100^\circ\text{C}$) with poling time and poling field kept constant at 60 min and 50 MV m^{-1} , respectively (the insert shows a photograph of the d_{33} meter used for measuring the piezoelectric coefficient).

50 MV m^{-1} was used for poling as higher values led to a breakdown in the PVDF nanocomposite films.

Figure 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 to 12.4 pC N^{-1} with time, saturating after a duration over 60 min. **Figure 2b** shows the piezoelectric constant for different poling temperatures while keeping the electric field and time constant at 50 MV m^{-1} and 60 min, respectively. The piezoelectric constant increases from 8.7 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 a decrease in the dielectric breakdown strength of the polymer with an 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 min, and a bath temperature of 80°C , yielding a d_{33} value of $12 \pm 1.5 \text{ pC/N}$.

2.2. Sensor Characterization

Figure 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 3b** illustrates the output voltage when the sensor is

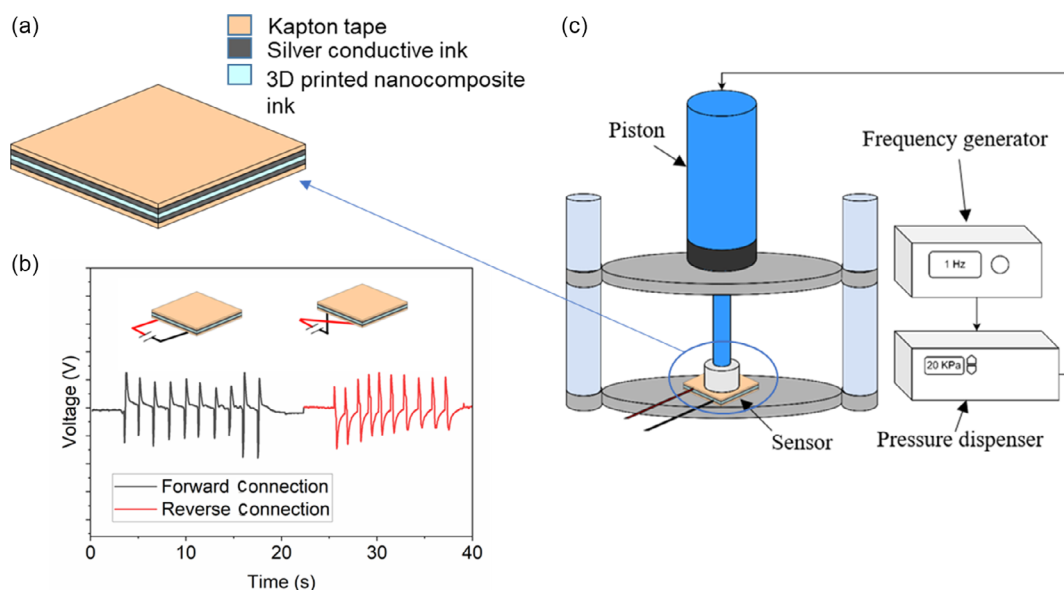


Figure 3. a) Schematic of the test setup for dynamic testing of the PVDF nanocomposite sensors in compression mode, b) schematic of the PVDF nanocomposite sensor. c) Voltage response of the sensor tested in both forward and reverse connections.

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.^[40] Figure 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 (6–20 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.^[40]

In Figure 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 mm Hg). 16 Kpa is chosen as it is a value close to normal SBP. The frequency response demonstrates its applicability to monitor beat-to-beat changes in BP. Figure 4b displays the peak-to-peak voltage output from a sensor when a frequency of 1 Hz is applied at pressures between 6 and 20 kPa—a typical range for the adult BP.^[20,23] 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 of 6–20 kPa,^[41,42] because of their capacitive nature but our sensors show excellent linearity ($R^2 = 0.99$) without any change in sensitivity throughout the pressure range, confirming their reliability. Figure 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.^[41,42] The small area within the hysteresis loops shows our sensor has negligible hysteresis. In Figure 4d, the results of a sensor's endurance test are shown for 1 h (3600 operational cycles) at 1 Hz and 40 kPa. The insets confirm no changes in performance even after 1 h, thus indicating the robustness and repeatability of our sensor to work continuously for 1 h (3600 cycles).

2.3. Sensor Application

Figure 5a illustrates the method for acquiring 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 converted them into readable voltages. The PPW represents the pressure exerted on the arteries by blood with each heartbeat.^[22]

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 BP. When the heart expands, the pressure drops to diastolic pressure which is the pressure in the arteries when the heart is not pumping.

Figure 5c displays the PPW collected using the sensor for 10 s. Two peaks can be observed in the PPW as highlighted in Figure 5b. The peak 1 is reached when the BP is highest, i.e., systolic pressure. When the pressure drops, we observe a second peak in the signal known as the diastolic 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.^[43] Hence, for best results, we need to calibrate the values with a standard device for an individual before measuring the BP continuously. The prominent peaks (peak 1) and valleys are extracted using a Python program and then are used to predict BP after the calibration step (explained in the Figure S4, Supporting Information). Figure 5e illustrates the Fast Fourier Transform (FFT) of the curve in Figure 5d, 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 are collected, as demonstrated in Figure 5a. A standard BP monitoring device (UA-767FAM) is placed on the left hand, and BP 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 BP 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^[44]

$$SBP_i = SBP_{i-1} + \frac{(SBP_c - DBP_c)}{A} \times (a_i - a_{i-1}) \quad (3)$$

$$DBP_i = DBP_{i-1} + \frac{(SBP_c - DBP_c)}{A} \times (b_i - b_{i-1}) \quad (4)$$

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 the highest in the FFT graph is used for calculation. The heart rate in beats per minute can then be given by

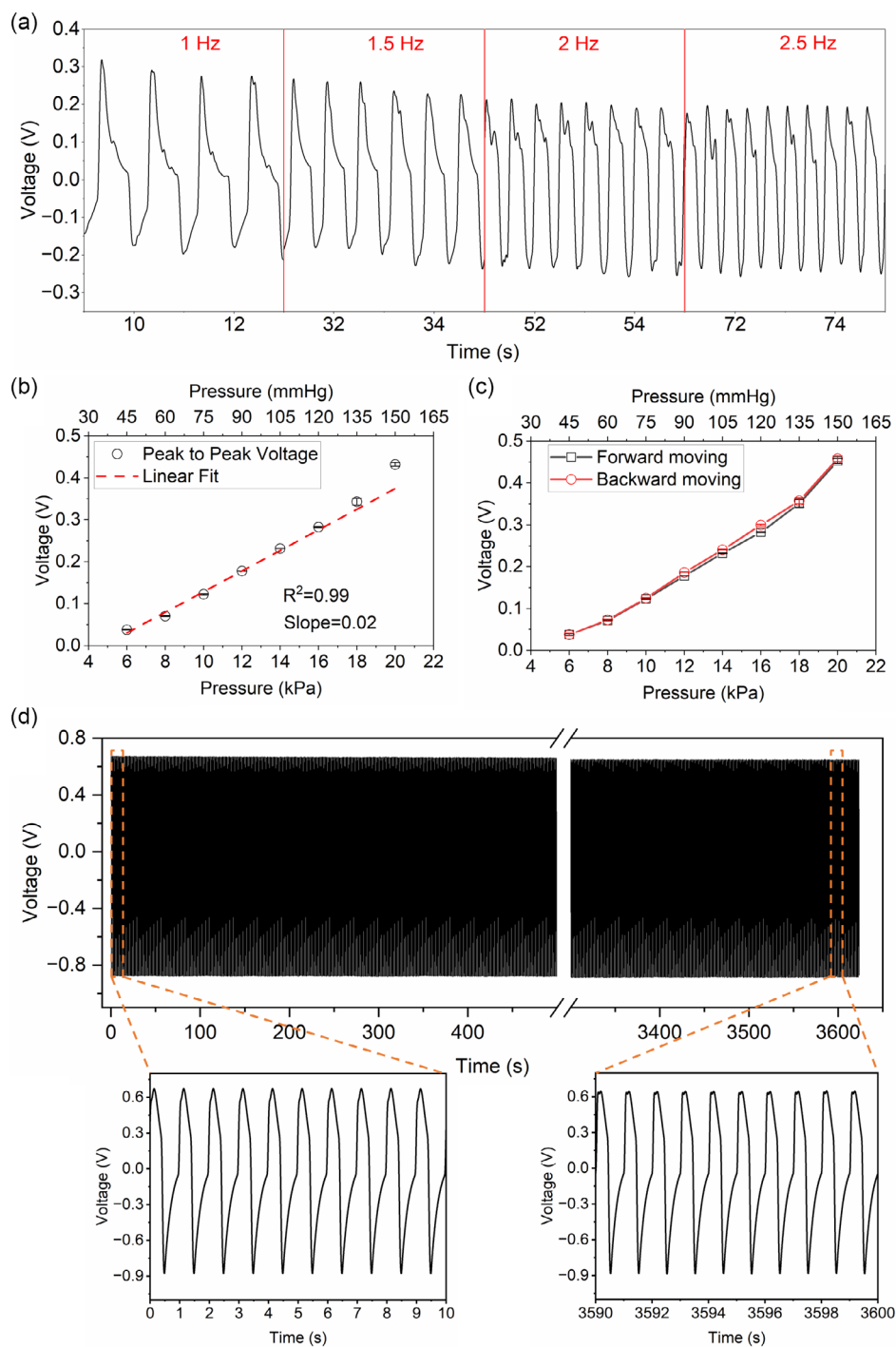


Figure 4. a) Voltage response of the PVDF nanocomposite sensor tested at various frequencies at an applied 16 kPa pressure (equivalent to 120 mm Hg). b) Plot of the peak-to-peak output voltage versus applied pressure chosen within the range of typical human BPs (each sensor tested five times). c) Hysteresis plot of the sensor when increasing dynamic pressures from 6 to 20 kPa and back from 20 to 6 kPa. d) Sensor tested for 1 h (3600 cycles) at 1 Hz and 40 kPa.

$$\text{Heart Rate} = F \times 60$$

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.

(5) 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 and 0.63 mm Hg, respectively, within acceptable limits ± 8 mm Hg.^[44] This confirms the sensor's accuracy in measuring BP. Figure 5g presents the comparison

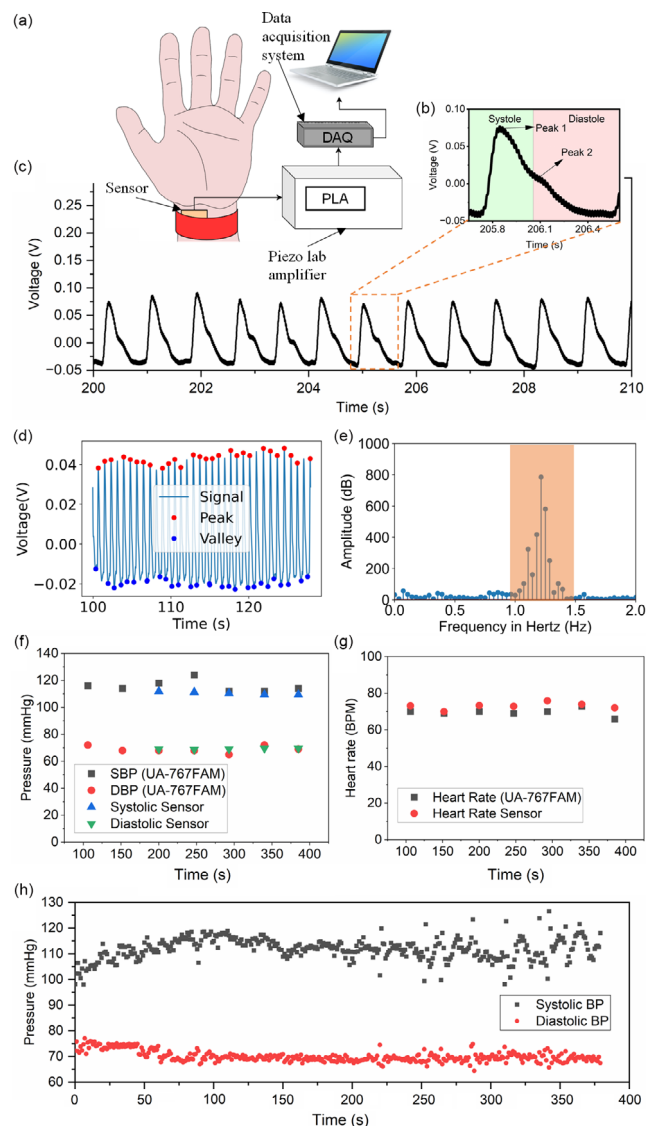


Figure 5. a) Schematic illustrating the process of PPW collection using the 3D-printed sensor. b) Peak 1 and peak 2 represent systolic pressure and diastolic pressures, respectively. c) PPW captured by the sensor over a span of 10 s from a human subject. d) Identification of peaks and valleys in the pulse pressure wave. e) FFT of the pulse pressure wave. f) Comparison of BP values estimated by the 3D-printed sensor and a standard BP monitoring device. g) Comparison of heart rate values estimated by the sensor and a standard BP monitoring device. h) Beat-to-beat systolic and diastolic BP estimates provided by the 3D-printed sensor for a subject.

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 bpm (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 s 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 BP 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 BP monitoring sensors for remote healthcare monitoring.

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 BP. The reported BP 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.

Second, 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 min. 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 BP monitoring, we examined the sensor properties. For this purpose, the sensor was characterized at dynamic pressures ranging from 6 to 20 kPa (45 to 150 mm Hg) at a frequency of 1 Hz, which falls within the typical range for human BP. The sensor's durability was then confirmed over continuous testing for 1 h (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 BP and heart rate, demonstrating its applicability and potential for continuous and real-time monitoring. We compared the sensor's performance with a standard BP monitoring device to assess its accuracy in measuring both BP and heart rate. It was observed that the wrist needed to be slightly hyperextended so the sensor could press against the radial artery with appropriate pressure to capture the PPW. 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. Experimental Section

Materials: 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-15 mL) 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 3D printer (Crealty 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 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 $25 \text{ mm} \times 25 \text{ mm} \times 0.1 \text{ mm}$. 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 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 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.

Characterization: DSC Analysis: The crystallinity of the PVDF nanocomposite films was measured using a 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 to 200°C at the rate of $10^\circ\text{C min}^{-1}$.

Characterization: d_{33} 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.

Characterization: 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 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 BP Monitoring: To monitor heart rate and continuous BP, 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 (3 M) 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.

Acknowledgements

This manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript. The authors acknowledge the financial support from Fonds de recherche du Québec (FRQNT) Établissement de la relève professorale for Sampada Bodkhe and NSERC (Natural Sciences and Engineering Research Council of Canada) Discovery Grants program and the MITACS Graduate Fellowship program for Arijit Mandal. The authors would also like to thank Micheal Flandez for his help with amplifier development, Chris Kamal Youssef for his help in MATLAB code for data acquisition, and Dr. Lawrence Leroux, anesthesiology, University of Montreal for his help and advice related to BP and its testing process.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

continuous blood pressure monitoring, piezoelectric sensors, polyvinylidene fluoride, 3D printing

Received: August 16, 2023

Revised: October 10, 2023

Published online: November 12, 2023

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