Inkjet-printed flexible piezoelectric sensor for self-powered biomedical monitoring

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Abstract. Printed electronics has opened up new insights towards fabrication of electronic components and devices. This manufacturing technique has been successfully employed as a complementary fabrication approach to conventional nanolithography and microfabrication processes to create flexible and stretchable electronics. Fluoropolymers are crucial components in electronic manufacturing, owing to their piezoelectric, triboelectric, pyroelectric, ferroelectric, and dielectric properties. In this research, we report fabrication of an inkjet-printed piezoelectric sensor based on poly(vinylidenefluoride trifluoroethylene) (PVDF-TrFE) and amine functionalized graphene oxide (AGO) for biomedical monitoring. The piezoelectric inkjet ink was obtained by optimizing the fluid mechanic properties based on Reynold and Weber numbers. The inkjet-printed freestanding film was characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), wide-angle X-Ray scattering (WAXS), and differential scanning calorimetry (DSC). The piezoelectric sensor was fabricated out of the printed film by painting electrodes on each side, followed by wiring and encapsulation. The sensor was subjected to an electric field of 1500 kV/cm to align the internal dipoles and induce a net polarization. The obtained flexible piezoelectric sensor was employed for monitoring biomedical signals such as finger tapping, joint bending, and swallowing.

Keywords: Inkjet; Ink Formulation; Organic Electronics; Pressure sensor; Strain Sensor

1- Introduction

In the past two decades, the world has witnessed a stunning advancement in electronics technology. Wearable and flexible electronic technologies along with artificial intelligence (AI) and internet of things (IoT) are currently three main areas of research to build futuristic electronic devices. Going from existing rigid electronics towards flexible and wearable devices requires development of novel electronic materials and manufacturing processes [1, 2]. Materials to be used in next-generation wearable devices need to demonstrate features such as flexibility, mechanical robustness, excellent electrical properties, low cost, good solubility (preferably in water), biocompatibility, recyclability, and lightweight. Furthermore, they should also be conformable with different printing techniques to allow fast and roll-to-roll manufacturing [3].
Inkjet technology is the most widely used digital and non-contact printing technique in printed electronics. This technology operates based on drop ejection from a series of computer-controlled nozzles to reproduce digital patterns [4]. To have an optimal inkjet printing, the inks need to meet certain fluid mechanic requirements that are described by two dimensionless numbers known as Reynolds ($Re$) and Weber ($We$) numbers (Equations 1 and 2) [5].

\[
Re = \frac{\nu pd}{\eta} \quad (1)
\]

\[
We = \frac{\nu^2 pd}{\gamma} \quad (2)
\]

Where $\nu$, $d$, $\eta$, $\gamma$ and $\rho$ are velocity of ink droplets, ink density, nozzle diameter, dynamic viscosity, and ink surface tension, respectively. An optimal inkjet ink need to fall within four boundary conditions. Rheological requirement of inkjet inks is defined by $Z$ value ($Z = \frac{Re}{\sqrt{We}}$), where $4 < Z < 14$ is considered as printable interval [6]. The upper interval indicates the start point of satellite drop formation and the lower boundary determines the maximum fluid thickness, above which the ink droplets cannot be ejected by inkjet actuation mechanisms [7]. The third boundary condition determines the minimum droplet velocity to overcome the inks surface tension and create discrete droplets, which is defined by Equation 3 [8]. Moreover, the upper boundary condition determines the maximum allowable droplet velocity before splashing while impingement on substrate, which is defined by Equation 4 [9, 10].

\[
We_{\text{min}} = \frac{\nu_{\text{min}} \rho d}{\gamma} = 4 \quad (3)
\]

\[
We^{1/2} Re^{1/d} = K(r) \quad (4)
\]

Where $K(r)$ is a function of substrate’s surface roughness.

Ferroelectric polymers are a class of semicrystalline materials with at least one polar non-centrosymmetric crystalline phase [11]. Poly (vinylidenefluoride) (PVDF) and its copolymers such as poly (vinylidenefluoride trifluoroethylene) (PVDF-TrFE) and poly (vinylidenefluoride trifluoroethylene chlorotrifluoroethylene) (PVDF-TrFE-CTFE) are the most well established examples of organic ferroelectric. PVDF-based materials can crystallize into four different polymorphs ($\alpha$, $\beta$, $\gamma$, and $\delta$) depending on the processing conditions [12-14]. The $\alpha$-phase is the most thermodynamically favorable polymorph with $TGTG$ ($T =$ Trans, $G =$ Gauche) conformation [15]. This phase is non-polar and centrosymmetric, therefore does not demonstrate ferroelectric behavior, while $\beta$-phase with all trans (TTTT) conformation is polar and ferroelectric [16]. The $\gamma$ and $\delta$ phases demonstrate lower polarity compared with the $\beta$-phase, and are only obtained under specific thermodynamic conditions [17]. Ferroelectric polymers are piezoelectric, which means that they can convert mechanical stress into electric field and vice versa [18]. Piezoelectric materials are crucial components in electronic industry, which are extensively used in fabrication of sensors, energy harvesters, ultrasonic transducers, sonars systems, actuators, and self-powered devices [19-22].
This work presents fabrication of inkjet printed flexible piezoelectric sensor based on PVDF-TrFE and amine functionalized graphene oxide (AGO). The main reason for using AGO nanosheets is due to presence of primary amine and hydroxyl groups that offer strong hydrogen bonding with polymer chains, which results in dipole alignment, lamellae enlargement, and inducing polar β-phase formation as shown in our previous work [23]. The fabricated sensor was then used to monitor biomedical signals such as joint bending, finger taps, and swallowing. This work can be used for real-time and remote monitoring of physical signals in patients, which is an important step towards delocalization of medical practices and reduce the costs.

2- Results and Discussion

2.1- Ink Formulation and Inkjet Printing

Fabrication of inkjet ink is a challenging task, as it requires optimization in several aspects. Fluid mechanic properties determines the drop ejection behavior of inks. Common problems associated with improper fluid mechanic properties are satellite drop formation, coffee ring effect, and splashing. Drop ejection behavior of PVDF-TrFE – AGO ink was investigated by a drop-watcher camera integrated in a Dimatix Inkjet printer. Figure 1a corroborates the ideal jetting behavior of the ink, characterized by formation of singular droplets per jet and proper tail detachment. The jetting process was monitored for 5 minutes and no sign of nozzle clogging nor satellite drop formation was observed. The ink’s surface tension was obtained by contact angle measurements. As shown in Figure 1b, the ink droplet formed a contact angle of $10^\circ \pm 1.5$ ($\gamma = 30.2 \text{ mN/m}$) with the substrate, corroborating excellent surface wettability. Wettability is a crucial factor in inkjet printing, which determines how well discrete ink droplets can spread over the substrate and create uniform structures. Wettability is controlled by two opposing macroscopic factors known as cohesive forces, which hold the molecules of a droplet tight together, and adhesive forces, which causes the droplet to cling the surface it rests. The substrate’s surface energy, porosity, and roughness have crucial influence on the printing quality. The borosilicate glass substrate used in this research demonstrated excellent compatibility with PVDF-TrFE – AGO ink, thus allowed a uniform film formation and smooth peel-off. Figure 1c is the flow curve of the ink at shear rates ranging from 3 – 75 (s$^{-1}$) at different temperatures. As observed, the overall viscosity of the ink decreased by increasing the temperature similar to non-Newtonian fluids that obey Arrhenius-type equation of viscosity. Moreover, the ink experienced increase in the apparent viscosity with increasing the shear rate, confirming the dilatant (shear-thickening) nature of the fluid. This behavior can be explained by Odell-Keller theory of flow-induced chain fracture in linear macromolecules [24]. According to this model at zero shear condition, the linear polymer chains of PVDF-TrFE copolymer form a random coil structure to attain the lowest available energy by forming intermolecular hydrogen bonding between fluorine and hydrogen atoms [25]. This configuration minimizes the polymer-solvent and polymer-filler electrostatic interactions, which leads to low viscosity values. However, by applying shear forces the polymer chains experience elongation, therefore their effective occupied surface area in the solution remarkably increases. This chain elongation brings about stronger dipole-dipole interactions and hydrogen bonding forces between polymer-DMF and polymer-AGO components, which translates into higher viscosity. At room temperature, the ink demonstrated the viscosity of 1.2 cP at shear rate of 3 s$^{-1}$, while this value increases to 5.57 cP at 75 s$^{-1}$. 
Another critical requirement for inkjet inks with insoluble components is good particle dispersibility and proper size distribution. To prevent nozzle clogging during jetting, particles should be around 20 times smaller than the nozzle diameter. Dynamic light scattering (DLS) method was employed to investigate the size distribution of AGO nanosheets in PVDF-TrFE ink (Figure 1d). DLS measurements on four samples of the same ink led to four Gaussian curves with mean values of 491, 512, 574, and 589 nm. Assuming that the average size of AGO is equal to the average of the mean values (541.4 nm), it can be inferred that the AGO nanosheets are in average 39 times smaller than the inkjet nozzle diameter (21 µm), which significantly reduces the possibility of nozzle clogging due to the particle aggregation. Figure 1e is the photograph of inkjet printed PVDF-TrFE – AGO nanocomposite film with the area of 2.5 × 2.5 cm² on the borosilicate glass substrate after annealing at 140 °C.
2.2- Chemical, Structural, and Morphological Characterizations

FT-IR spectrum of the printed nanocomposite film demonstrated two absorption bands at 852 and 1287 cm\(^{-1}\) corresponding to CF\(_2\) symmetric stretching, which also associate with \(\beta\) crystalline phase (Figure 2a). The strong absorption bands at 1400 and 887 cm\(^{-1}\) are respectively associated with CH\(_2\) wagging vibrations and asymmetric CF\(_2\) stretching [26]. Endothermic differential scanning calorimetry (DSC) thermograph of annealed and unannealed PVDF-TrFE – AGO nanocomposite film is shown in Figure 2b. Both thermographs demonstrated two peaks corresponding to Curie transition, where the ferroelectric domains lose their spontaneous polarization and become paraelectric, and melting transition, where crystalline phases turns from a solid to a viscous liquid [27]. The Curie transition for the unannealed film took place at 99 °C with the enthalpy of \(-5.13\) J/g, while for the annealed sample the transition peak was located at 104 °C with the enthalpy of \(-13.18\) J/g. This confirms that the annealing led to transforming a portion of paraelectric phases into a polar ferroelectric phase. Similarly, the melting peak had a shift from 145 to 147.5 °C; however, the melting enthalpy remained almost unchanged for both samples (~ 23 J/g). Considering narrowing of the melting peak after annealing and increase of Curie enthalpy, it is inferred that a portion of
α phase transformed into β phase upon annealing without changing the total degree of crystallinity ($\chi_c = 51\%$).

Wide angle X-ray scattering (WAXS) has been employed to quantify the percentage of α and β polymorphs in the annealed film. The 2D WAXS image demonstrated well-defined ring-shape structures, implying the isotropic nature of the inkjet printed PVDF-TrFE – AGO nanocomposite film (Figure 2c). The corresponding 1D WAXS profile obtained from cross-section of the 2D diffraction pattern is shown in the Figure 2d. The plot was deconvoluted into five peaks, two of which corresponding to the α-phase (located at 1.37 and 2.78 Å$^{-1}$), and the rest associated with the β-phase (located at 1.41, 2.48, and 2.86 Å$^{-1}$). By integrating the area under the peaks corresponding to each polymorph and then dividing to the total area, it turned out that the β-phase constituted 62 % of the total crystalline content ($\chi_c = 51\%$), and the remaining 38% was the α-phase. Scanning electron microscopy (SEM) image of the film exhibited in-plane arrangement of microstructured crystalline domains within an amorphous matrix (Figure 3a). Atomic force microscopy (AFM) was employed to capture a detailed 3D and 2D topographic images of the inkjet printed film (Figure 3b and c). As can be seen, crystalline domains formed interlaced needle-like structures with random orientation. Each domain was made of stacked edge-on lamellae, which consisted of tightly packed polymer chains with zigzag configuration. The mean surface roughness ($R_a$) of the printed film was obtained from the cross-sectional profile of the 2D AFM image, which was equal to $R_a = 6.51$ nm (Figure 3d). AFM scans from 10 different points on the film also showed similar surface roughness value of $R_a = 7.48 \pm 2.11$, indicating a uniform and high-quality printing.
2.3- Mechanical and Electrical Characterization

Mechanical properties of piezoelectric polymers have critical influence on their electrical properties and device performance. Electromechanical coupling coefficient \( k_{3i} \) of piezomaterials is directly proportional to the square root of the Young’s modulus \( Y \) (modulus of elasticity) according to the Equation 5.

\[
k_{3i} = d_{3i} \sqrt{\frac{Y_{ii}}{\varepsilon_{33}}}
\]

Where \( d_{3i} \) is the piezoelectric charge coefficient and \( \varepsilon_{33} \) is the dielectric permittivity. Moreover, the elastic compliance determines the extend of which a piezoelectric sensor can withstand bending, stretching, and compression stresses. Figure 4a demonstrates the stress-strain plot and its corresponding linear fit for the printed PVDF-TrFE – AGO nanocomposite film, which indicates the \( Y = 43.8 \) GPa. The Dielectric measurement was carried out in the frequency range of 300 Hz – 10 MHz (Figure 4b). The film experienced a notable decrease in the permittivity with increasing the frequency, which is mainly due the reduction of space-charge effects. On the other hand, the dielectric loss demonstrated an opposite behavior, indicating that the energy significantly dissipates in the form of heat at high frequencies. At 1 kHz, the film exhibited a relative permittivity of 17.5 and a loss factor of 0.05. Figure 4c is the bipolar polarization – electric field (P-E) loops acquired at different applied electric. The film demonstrated broad and nearly saturated hysteresis loops at high electric fields, indicating
ferroelectric domain switching due to reversing the direction of applied electric field. The P-E hysteresis loop of PVDF-TrFE – AGO film at 2000 kV/cm demonstrated a remnant polarization of $P_r^+ = 7.6 \mu C/cm^2$ and a coercive field of $E_c^+ = 575$ kV/cm. The current density – electric field (I-E) plots is shown in Figure 4d, which indicates that the coercive field slightly increases with the increase of applied electric field. At the applied field of 1200 kV/cm, the domain switching current, peaked at 501 kV/cm, while at 2000 kV/cm the peak shifted to 575 kV/cm.

2.4- Sensing Performance

To evaluate the performance of the fabricated sensor, the open circuit voltage signals generated as result of finger taps, finger bending, and saliva swallowing were recorded by an oscilloscope. Figure 5a exhibits the generated signals in the piezoelectric sensor by applying finger taps with three different intensities. By employing a digital force gauge, the magnitude of force applied to the sensor in each tapping region was measured to be 0.3, 0.6, and 1.0 N, which corresponds to 3, 6, and 10 kPa, respectively. The average intensity of the generated voltage signals at 3 kPa was $0.22 \pm 0.01$ V, while this value at 6 and 10 kPa was $0.53 \pm 0.01$ and $1.09 \pm 0.05$, respectively, demonstrating good linearity. Joint monitoring systems are crucial to detect and
control musculoskeletal disorders. To investigate the feasibility of employing the fabricated piezoelectric sensor for joint bending monitoring, the sensor was taped to a finger joint and the generated open circuit voltage was recorded at different bending angles. As shown in Figure 5b by increasing the bending angle the voltage signal increased proportionally. At bending angles around 30º the signal peaked at around 0.3 V, while at 90º the peak voltage was around 1.0 V. The bending signals were comprised of positive and negative pulses corresponding to finger bending and finger straightening, respectively. Swallowing disorders also known as dysphagia are common symptoms of several diseases that can cause malnutrition and deterioration of patient’s life quality [22]. Swallowing is always accompanied with laryngeal movement, which can be converted into electric signals by using a conformable piezoelectric sensor. Figure 5c demonstrates the electric signals generated by three consecutive saliva swallowing. Each swallowing signal was comprised of two phases, corresponding to upward and downward laryngeal prominence excursions. The first phase of the signal was corresponded to the moment that laryngeal prominence moved upward and passed the sensor, and the second phase was obtained when laryngeal prominence returned to its initial position [22].

3- Conclusion

In this study, we report fabrication an inkjet printed self-powered piezoelectric sensor based on poly(vinylidene fluoride trifluoroethylene) (PVDF-TrFE) and amine functionalized graphene oxide (AGO) for monitoring biomedical signals such as finger tapping, joint bending, and swallowing. This work is only a showcase to confirm fluoropolymer nanocomposites with piezoelectric, ferroelectric, pyroelectric, and dielectric properties can be successfully printed to form flexible electronic components with versatile applications.

4- Methods

4.1- Ink Formulation and Printing: 600 mg PVDF-TrFE (70 mol% VDF and 30 mol% TrFE) powder (Sigma Aldrich, France) was dissolved in 100 ml DMF at 60 ºC for 1 h to form a 6 mg/ml solution. A 1.20 mg/ml AGO dispersion in DMF was synthesized according to the procedure described in our previous work [23]. 0.5 ml of AGO dispersion was added to the

Figure 5a Open-circuit output voltage generated in the piezoelectric sensor in response to finger taps with different intensities. b The strain signals generated due to bending of finger joints. c Voltage signals corresponding to upward and downward laryngeal prominence excursions due to saliva swallowing.
PVDF-TrFE solution and mixed thoroughly to form a 0.1 wt% AGO nanocomposite inkjet ink. A Dimatix drop-on-demand inkjet printer (Fujifilm DMP-2850, USA) equipped with a drop watcher and a fiducial camera was used to print the nanocomposite ink. The ink was passed through a PP filter with pore size of 2 µm to remove possible impurities and then injected into a 10 pL inkjet cartridge with piezoelectric printhead. The PVDF-TrFE – AGO nanocomposite ink was printed on a borosilicate glass substrate with trigger voltage of 37 V, cartridge temperature of 35 ºC, drop spacing of 12 µm, and platen temperature of 50 ºC with 1693 DPI printing resolution. A ~ 20 µm thick nanocomposite freestanding film with the area of 2.5 × 2.5 cm² was obtained by 100 passes of printing. Then the film was annealed at 140 ºC for 2 h followed by rapid quenching.

3.2- Material Characterizations: The ink droplet’s contact angle was measured by a Theta Flex Optical Tensiometer (Gothenburg, Sweden). The surface tension of the ink was obtained by the Young’s equation (Equation 6).

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \theta
\]

Where \( \gamma_{sl} \), \( \gamma_{lv} \), and \( \theta \) are solid–liquid interfacial surface energy, liquid surface energy, and the contact angle, respectively. Field emission scanning electron microscope (FE-SEM) (Magellan 400, USA) was used to study the surface morphology of the printed nanocomposite film. Atomic force microscopy (AFM) (Bruker Dimension Edge, US) equipped with RTESP-300 silicon tip (Bruker, US) with spring constant of 40 N/m was used to image the topography of inkjet printed film and measure the surface roughness. AFM image was obtained by scanning 1 µm × 1 µm area of the film in tapping mode. PerkinElmer Fourier transform infrared spectroscopy (FT-IR) (Waltham, US) with attenuated total reflectance (ATR) was used to investigate the chemical structure of the printed film. The measurements were carried out in the spectral region of 2000 – 400 cm⁻¹ with a resolution of 2 cm⁻¹ at 10 scans per sample. The total degree of crystallinity (\( \chi_c \)) was measured by differential scanning calorimetry (DSC) (DSC 3 Mettler Toledo, USA). 1 mg of nanocomposite film was placed in an aluminum crucible and heated from 30 to 160 ºC under nitrogen gas flow with heating rate of 10 ºC/min. The \( \chi_c \) was obtained according to the Equation 7.

\[
\chi_c = \frac{\Delta H_m}{\Delta H_0} \times 100
\]

Where \( \Delta H_0 \) is the melting enthalpy for fully crystalline PVDF-TrFE, which was reported to be 45 J/g [28], and \( \Delta H_m \) is the melting enthalpy obtained by integrating the endothermic melting peak. The ratio of \( \alpha \) and \( \beta \) crystalline phases was obtained using wide angle X-ray scattering (WAXS) carried out with Nano-inXider (Xenocs, France) equipped with Genix3D micro-focus X-ray Cu K\( \alpha \) source. After background subtraction, the WAXS plot was deconvoluted into five peaks located at scattering vectors of 1.37 \((110)\alpha\), 1.41 \((110)(200)\beta_{ter}\), 2.48 \((001)\beta\), 2.78 \((002)\alpha\), and 2.86 \((201)(111)\beta\) Å⁻¹. The ratio of each phase was calculated by dividing the integrated area of its corresponding peaks to the total peak areas. Rheology measurement was carried out using DVNext LV Rheometer (BUCH & HOLM, Denmark) at shear rates of 3 – 75 s⁻¹ at 15, 25, 35, and 45 ºC. Particle size distribution of AGO in PVDF-TrFE solution was measured by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Pananalytical Ltd, UK).

3.3- Sensor Fabrication and Electrical Measurements. A flexible piezoelectric sensor was fabricated out of the inkjet printed PVDF-TrFE – AGO nanocomposite film as active layer.
The electrodes were painted on both sides of the film and the wires were integrated to the electrodes followed by encapsulation with soft Kapton. The fabricated sensor was poled at an electric field of 1500 kV/cm for 10 min using a TF1000 (aixACCT, Germany) equipped with a TFSHU thin film sample holder (aixACCT, Germany). The voltage signals were acquired using an Oscilloscope (Keysight DSOX 1204 A, USA).

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Conflicts of Interest

The authors declare no conflict of interest.

Data availability

The authors declare that all data supporting the findings of this study are available within the paper and its Supplementary Information file or from the corresponding author upon reasonable request.

References


