Fabrication of $\beta$-phase poly(vinylidene fluoride) piezoelectric film by electrospinning for nanogenerator preparations

H.U. Kumarasinghe*, L.R.A.K. Bandara, T.M.W.J. Bandara, G.K.R. Senadeera and C.A. Thotawatthage

**Highlights**

- Thin films consisting of uniform PVdF fibers were prepared by electrospinning.
- Electrospinning increases the fraction of $\beta$-phase in PVDF which promotes piezoelectricity.
- The fraction of $\beta$-phase in the electrospun PVdF film is 80.1%.
- The maximum voltage generated using the nano-generator is 1.3 V.
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Abstract: Electrospun poly (vinylidene fluoride) (PVdF) has been recognized as a potential candidate for making nano-generators in a broad range of applications. Through electrospinning, PVdF fiber films can be fabricated while enhancing the $\beta$-phase content within it. The electrospinning process was carried out with optimal parameters to obtain uniform and well-aligned fibers. The morphology of the PVdF fiber film, observed by Scanning Electron Microscopy (SEM), showed uniform, smooth and consistent fiber formation without beads, and the fiber diameters were in the range of 700 - 1000 nm. The crystalline phase of the PVdF was characterized by analyzing the X-ray Diffraction (XRD) pattern and Fourier-Transform Infrared (FTIR) spectrum. The $\beta$-phase content of the electrospun film was 80.1%, while that of the solvent cast PVdF film was 64.4%. This result shows that electrospinning has increased the percentage of the $\beta$-phase in the film. The force applied and the output voltage of the constructed nano-generator detected are linearly correlated within the measurement window. The maximum voltage generated was about 1.0 V with finger tapping and 1.3 V with a custom-designed tapping machine. Improvements to this PVdF piezoelectric nano-generator can be used in many potential applications in several fields, especially as energy harvesters, biomedical applications and sensors.

Keywords: Piezoelectricity; PVdF (polyvinylidene fluoride); electrospinning; nano-generator.

INTRODUCTION

Nano-generator based on piezoelectricity is a promising technology that converts mechanical energy produced by small physical changes into electricity, which has a great potential for a wide range of applications; for example, in energy harvesting devices, sensors and biomedical applications (Choi and Jiang, 2006; Wang and Shi, 2012; Shimada, 2013). Piezoelectric nano-generators gained significant importance and thus extensive investigations are being carried out on extracting and storing energy from the environment using these nano-generators. In numerous previous studies, piezoelectric ceramics such as lead zirconate titanate (PZT; piezoelectric coefficient $[(d_{33}) = 225$ pC N$^{-1}]$ and barium titanate (BaTiO$_3$; $d_{33} = 191$ pC N$^{-1}$) have been used for mechanical-electrical energy conversion because of their large piezoelectric coefficient (Helke and Lubitz, 2008; Acosta et al., 2017). Although these traditional solid-state piezoelectric ceramics were used in various fields, there were restrictions in some applications of these materials due to their rigid nature, and concerns have been raised regarding their impact on the environment due to the heavy content of Pb in the high-end piezoceramics (Rödel et al., 2015).

To overcome these drawbacks polymers are researched extensively as piezoelectric materials because of their unique properties and advantages over other materials. As a result, among many of the piezoelectric materials, PVdF has been recognized as a suitable candidate for making piezoelectric nano-generators because of its flexibility, non-toxicity, biocompatibility and high piezoelectric properties. PVdF is a semi-crystalline polymer with four different crystalline phases $\alpha$, $\beta$, $\gamma$ and $\delta$ depending on its chain conformation. The non-polar $\alpha$-phase is the most common, while the polar $\beta$-phase shows piezoelectric properties. There are various ways to increase the fraction of the $\beta$-phase in PVdF and thereby increase the piezoelectric properties. Mechanical drawing, melt quenching, solvent casting from a solution, and electric-field poling are some common methods reported (Lovingier, 1980; Mahato et al., 2015). When compared to other methods, electrospinning is more efficient in improving piezoelectric properties by converting $\alpha$-phase to $\beta$-phase. The PVdF fibers with a high content of $\beta$-phase could be fabricated directly by electrospinning without any post-treatment. The electrospinning process ensures the fiber polarization and formation of the $\beta$-phase within the structure of the PVdF fibers (Ramakrishna et al., 2006; Ribeiro et al., 2010).

This work is specifically focused on the fabrication of piezoelectric PVdF film to design a nano-generator by increasing the fraction of the $\beta$-phase through electrospinning. The electrospinning process was carried out with optimal parameters to enhance the $\beta$-phase. A nano-generator was prepared by sandwiching the fabricated film between two gold electrodes. The performance of the fabricated nano-generator was evaluated by detecting the output voltage with different tapping methods. The results showed that the fabricated nano-generator could generate an output voltage of about 1.0 V with finger tapping and 1.3 V with a custom-designed tapping machine. The force applied and the output voltage of the constructed nano-generator detected are linearly correlated within the measurement window.
PVdF fiber film between copper electrodes to test the output voltage variations. The piezoelectric response of the nano-generator was observed using a galvanostat.

MATERIALS AND METHODS

Chemicals and materials
Poly(vinylidene fluoride) pellets (MW 275000; Sigma-Aldrich, USA), N,N-dimethyl formamide (DMF, 99.5%; Sigma-Aldrich, USA), acetone (99.8%; S D Fine-Chem Limited, India) and copper foil were used for the preparation of PVdF films.

Preparation of solvent casted PVdF film
First, 11wt% (w/v) PVdF-DMF solutions were prepared by mixing PVdF and DMF for about 1 h at 60 °C using a magnetic stirrer. Next, the solution was cast on a glass plate by the method of drop-casting. The casted films were finally dried at 60 °C for 16 h in a vacuum oven.

Polymer solution preparation for electrospinning
The composition that was optimized in preliminary studies was used in order to fabricate beads-free fibers with the desired size. First, 11wt% (w/v) PVdF-DMF solution was prepared (Alhassan et al., 2018). Then the solution was stirred using a magnetic stirrer for 1 h at 60 °C. Next, acetone was added to the PVdF-DMF solution in a 1:2 volume ratio and stirred well, in order to fabricate the desired nano-fibers (He et al., 2021). Then, 10 mL of the final solution was loaded into the syringe of the electrospinning machine.

Electrospinning process
TL-01 Electrospinning and spray unit (Tong Li Tech) was used to prepare PVdF fibers. The electrospinning was performed with an applied voltage of 15 kV DC, the flow rate of 1 mL h⁻¹, tip-to collector distance of 15 cm and drum speed of 1500 rpm. To collect the electrospun fibers, aluminum foil was wrapped around the drum. The basic electrospinning setup and an image of electrospun PVdF film are shown in Figure 1.

Preparation of nano-generator and testing
The electrospun film was separated from the aluminum foil. The separated film was sandwiched between two flexible copper electrodes (with an effective area of 1.77 cm²) and external connecting wires were soldered as shown in Figure 2.

Characterization of electrospun film
The crystalline phases of the PVdF film samples were analyzed using the powder X-ray diffraction patterns obtained from the Bruker D8 Advanced Eco Powder X-ray Diffraction system. The diffraction patterns were recorded for 2θ from 10° to 70° with a step size of 0.01° at a rate of 1° min⁻¹ using Cu-Kα radiation of λ = 1.5406 Å. The formation and transformation of β and α phases were further confirmed by FTIR spectrum obtained using Jasco FTIR-6700 spectrometer with a resolution of 4 cm⁻¹, from the absorption bands measured over a range of 400 to 1500 cm⁻¹ at room temperature for both solvent cast and electrospun PVdF films. The surface morphology of the electro spun PVdF samples was observed by SEM images taken using Hitachi SU6600 Analytical Variable Pressure FE-SEM.

Figure 1: (a) Schematic diagram of basic electrospinning setup (b) Photographic image of electrospun PVdF film.

Figure 2: Photographic image of the prepared nano-generator.
**Characterization of piezoelectric nano-generator**

The output voltage of the nano-generator was investigated using the chronopotentiometry (CP) mode of the Metrohm Autolab Galvanostat. Nova 1.1 software was utilized in the analysis of the output voltage of the nano-generator. To produce a controllable periodic force with a constant amplitude, a custom-made tapping machine was used (shown in Figure 3). To measure the force applied to the sample by the custom-made tapping machine, a dual-range force sensor (DFS-BTA model) was used. Logger Pro 3.15 software from Vernier Software was utilized as the analytical tool for real-time graphing of the force versus time plot. The experimental setup used to characterize the nano-generator is shown in Figure 4.

**RESULTS AND DISCUSSION**

**PXRD analysis**

Figure 5 represents the XRD pattern obtained for the electrospun PVdF film. Strong peaks at 17.99° (100) and 20.06° (110), and medium peaks at 25.93° (021) show the presence of α-phase (Hasegawa et al., 1972; Esterly and Love, 2003; Lei et al., 2013; Cai et al., 2017). The broad peak around 20.6° refers to the sum of the diffraction in the (110) and (200) planes, which are a characteristic of the β-phase (Martins et al., 2014). Thus, the presence of both the β and α-phases is evident in the electrospun PVdF film.

**FT-IR analysis**

FT-IR characterization is useful to highlight the transformation of the non-polar α-phase to the polar β-phase of PVdF during electrospinning. The α-phase of PVdF can be easily detected by FT-IR absorption as it presents a large number of characteristic bands that are exclusive to it, such as the absorption bands at 489, 532, 614, 762, 795, 855 and 974 cm⁻¹ (Boccaccio et al., 2002). The bands at 431, 776, 812 and 833 cm⁻¹ are exclusive of the γ-phase, while those at 840 cm⁻¹ and 1276 cm⁻¹ are exclusive of the β-phase (Table 1).

The FT-IR absorption spectra of the solvent cast and electrospun PVdF films between 400 cm⁻¹ and 1500 cm⁻¹ wavenumber range are shown in Figure 6. The spectrum of solvent cast PVdF film shows dominant peaks that correspond to the α-phase. It has intensive peaks at 762 cm⁻¹ and 974 cm⁻¹, characteristics of the α-phase. However, the spectrum samples do not show a significant peak at 1276 cm⁻¹ (exclusive for the β-phase). When investigating the peak at 1276 cm⁻¹, it was noted that it is a shoulder peak and thus, the original spectrum was deconvoluted using the software Origin 6.0, so that a clear conclusion can be made. In the deconvolution process, peaks due to the α-phase 1181, 1209, 1233 and 1262 cm⁻¹ were selected, and the sum of the intensity of all the deconvoluted peaks was ensured to fit the original spectrum. Figure 7 shows the deconvoluted spectrum of the solvent cast film in the range between 1140 and 1300 cm⁻¹. It confirms that there is no peak at 1276 cm⁻¹ which is exclusive for the β-phase. Thus, the availability of a high content of the α-phase is evident. The fraction of β-phase (Fβ) can be calculated using Equation 1, where Aα is the absorbance at 766 cm⁻¹ and Aβ is the absorbance at 840 cm⁻¹ (Osaki and Kotaka, 1981; Gregorio and Cestari, 1994). According to Equation 1, the β-phase content calculated in the solvent cast film is 64.4%.

\[
F_\beta = \frac{A_\beta}{(1.3)A_\alpha + A_\beta}
\]  

The spectrum of electrospun PVdF fibers in Figure 6 shows dominant intensities for peaks characteristic to the β-phase and negligible intensities for peaks characteristic to α-phase. The sample shows a dominant peak at 1276 cm⁻¹ (exclusive for β-phase), while there are no peaks at 974 cm⁻¹ and 762 cm⁻¹ (exclusive for α-phase). Furthermore, the other characteristic peaks of the β-phase, such as at 473 cm⁻¹ and 1431 cm⁻¹ can be identified in the electrospun PVdF film. The content of the β-phase calculated for electrospun PVdF film using the same equation (Equation 1) is 80.1%. The analysis of FTIR absorption spectra concludes that the fraction of the β-phase in the sample fabricated using the electrospinning method is higher than the sample fabricated using the method of solvent casting.

**Scanning electron microscopy (SEM) analysis**

To reach a conclusion about the fiber formation through the electrospinning process, the fiber morphologies were analyzed using scanning electron microscopy. The SEM images of...
Figure 5: (a) XRD pattern of electrospun PVdF film and (b) Referred XRD pattern (Martins et al., 2014).

Figure 6: FT-IR absorption spectra of the solvent casted and electrospun fibers.

Figure 7: FT-IR deconvolution of solvent casted film at the band between 1140 cm\(^{-1}\) and 1300 cm\(^{-1}\).

Table 1: Characteristic FT-IR vibration modes of PVDF (Ramesh and D’Souza, 2018; Lanceros-Méndez et al., 2001).

| Wavenumber (cm\(^{-1}\)) | Vibration mode                                      | Phase |
|--------------------------|-----------------------------------------------------|-------|
| 489                      | CF\(_2\) bending and wagging                        | \(\alpha\)-phase |
| 614                      | CF\(_2\) bending and CCC skeletal vibration          | \(\alpha\)-phase |
| 762                      | In-plane bending or rocking                         | \(\alpha\)-phase |
| 776                      | CH\(_2\) rocking                                    | \(\gamma\)-phase |
| 812                      | CH\(_2\) out-of-phase wagging                       | \(\gamma\)-phase |
| 840                      | CH\(_2\) rocking and CF\(_2\) asymmetric stretching | \(\beta\)-phase |
| 974                      |                                                     | \(\alpha\)-phase |
| 1181                     | CF stretching vibration                              | \(\alpha\)-phase |
| 1209                     |                                                     | \(\gamma\)-phase |
| 1233                     |                                                     | \(\gamma\)-phase |
| 1276                     |                                                     | \(\beta\)-phase |
| 1453                     | CH\(_2\) in-plane bending or scissoring              |       |
the electrospun PVdF film showed very uniform, smooth and consistent fibers as shown in Figures 8 (a) and (b).

Since the SEM image did not show any beads and the fibers were very uniform, the values selected for parameters, such as polymer concentration, flow rate, applied voltage and tip to collector distance, can be confirmed as a suitable combination to form uniform fibers through the electrospinning process. The diameters of electrospinning fiber are varying from 700 - 1000 nm range. After plotting the diameter distribution curve of fibers, shown in the inset of Figure 8 (b), most of the fibers are found to be in the range of 850 - 900 nm. Further, the average thickness of the electrospun film is determined to be 156.5 μm as shown in [Figure 8 (c)].

**Piezoelectric properties of nano-generator**

To study the generated potential difference, the nano-generator designed was first subjected to an external force by finger tapping. Figure 9 shows the variation of voltage generated under different tapping frequencies. Results show that the potential difference generated is an AC signal. This AC behavior is due to the variation of induced potential difference from quick compression and expansion of the flexible polymer film at the moment of applying the force.

Even with heavy finger tapping, the maximum voltage generated was about 1.0 V. Instead of finger tapping, output voltages were measured by applying force using the custom-designed tapping machine. The tapping machine produces a controllable periodic force with constant amplitude. To explore the relationship between the output voltage and the applied force, the force was varied while the tapping frequency was kept at a constant value.

By extracting values for voltage and force from the above plots (Figure 10), the relationship between the output voltage and the magnitude of applied force is shown in Figure 11. The results showed the magnitude of force applied to the piezoelectric sample and the output voltage are linearly correlated. Finally, the present study reveals the development of an energy harvester that converts
mechanical energy to electrical energy via electrospun piezoelectric nano-generators. The nano-generators prepared may be suitable for low-power applications, such as wearable and portable charges and sensors. In addition, it can be more suitable to build force or pressure sensors since the applied force is directly proportional to the generated potential difference.

**CONCLUSION**

This study uncovers enhancement of piezoelectric properties of PVdF film prepared using the electrospinning method compared to that of the films prepared using the conventional method. PXRD and FT-IR analysis of the sample conclude that the electrospinning process increases the percentage of the $\beta$-phase within the film. SEM images of electrospun films confirm the formation of high-quality uniform fibers free of beads with 700 - 1000 nm diameter. Parameters used in this experiment have a favorable effect on the formation of well-aligned, uniform, and consistent fibers that promote the piezoelectric properties. The nano-generator prepared using the electrospun PVdF film generates a considerable potential difference when applying a force on it. The maximum output voltage generated was about 1.0 V by finger tapping and 1.3 V by the tapping machine. This kind of nano-generator can be used to generate voltage by mechanical deformation. Energy harvester that conserves energy from the ambient mechanical deformations and wearable sensors can be developed using PVdF-based piezoelectric nano-generators.

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**DECLARATION OF CONFLICT OF INTEREST**

The authors declare no conflict of interest.

**DATA AVAILABILITY STATEMENT**

All relevant data will be available on request from the corresponding author.

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