Enhanced piezoelectricity of PVDF nanofibers via a plasticizer treatment for energy harvesting

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Abstract
Enhancing the electrical outputs of energy harvesters is a great demand for researchers in recent years. In this work, the effect of the plasticizer treatment (Tetrahydrofuran [THF]) on the $\beta$ phase content (F[$\beta$]) of electrospun polyvinylidene fluoride (PVDF) fiber webs which are used as active layers to directly make a piezoelectric nanogenerator (PENG) is demonstrated. The results showed that during the plasticizer treatment, the F($\beta$) of the web increases when the initial length of the web ($L_0$) equals the distance between the two ends of the solid support (L) which the web fixed on it, whereas the F($\beta$) decreases when $L < L_0$ resulting in the formation of crimped fibers. Furthermore, the electrical outputs of the PENG based on the pristine web, and treated webs at different lengths are investigated. We believe this work can be used as a good reference for enhancing the electrical outputs of the PENG by enhancing the F($\beta$) of PVDF nanofiber webs using a plasticizer treatment.

1. Introduction
In the last decade, the demand for energy harvesters has increased sharply as evident from the development of product prototypes and the rising number of publications [1–8]. Running microelectronic devices with batteries such as watches, sensors, light-emitting diodes, and many others have difficulties owing to the disadvantages of batteries such as occupying a major weight and percentage of portable products, the need to recharge or replace them, the possible seepage of electrolyte solutions, and producing a significant environmental impact [9, 10]. Therefore, energy harvesting which is defined as collecting different amounts of energy from the surrounding environment and converting them into electric power for later use is the best choice for overcoming these limitations [1].

Piezoelectric polymers that can transform mechanical vibration into electrical energy are usually used for multiple applications such as wearable energy harvesting, artificial skin, sensors, and so on [1, 11–15].

Polyvinylidene fluoride (PVDF) which is a semi-crystalline polymer is considered one of the most favorable piezoelectric polymers owing to its outstanding piezo-, pyro-, and ferroelectric properties, low cost, excellent mechanical properties, high flexibility, good chemical stability, low density, ability to be formed in different structures, and so on [1, 16–21]. PVDF can be found in five polymorphs ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\epsilon$) [22]. The piezoelectric response of the PVDF is correlated with $\beta$ phase content [F($\beta$)] and polarization condition [23]. However, fabricated PVDF fiber webs with high F($\beta$) is still a big challenge for researchers. Different pre- and post-treatment methods were used to enhance the F($\beta$) of PVDF such as the mechanical drawing [24, 25], electrospinning [26, 27], electric poling [28], inclusion of nanofillers [29, 30], thermal treatment [31], hydrated salt [32], and so on.

Electrospinning is an effective process for producing fibers with diameters ranging to a few hundred nanometers [33–37], and to prompt the F($\beta$) of PVDF at the same time [1, 38, 39]. Poling and stretching of the
polymer at the high applied voltage during this technique can orientate the dipoles of PVDF molecular chains, resulting in an extra transformation of $\alpha$ to $\beta$ crystalline phase [40–43].

Previously, our group demonstrated the fabrication and characterization of electrospun PVDF fiber webs with different surface morphologies (wrinkled, smooth, and porous) based on randomly oriented and aligned fiber webs that can be used directly as active layers to make a piezoelectric nanogenerator (PENG). The results showed that the PENG based on the aligned wrinkled fiber web has the highest electrical their pillar wrinkled surfaces, supreme F($\beta$), interior pores, and fewer air gaps between the fibers [3].

Moreover, we studied the effect of the molecular weight of electrospun PVDF fibers (180000 g mol$^{-1}$, 275000 g mol$^{-1}$, and 530000 g mol$^{-1}$) on the electrical outputs of the PENG-based on the aligned wrinkled fiber webs [23]. We found that the electrical outputs of the PENG can be enhanced by increasing the molecular weight owing to their high F($\beta$) and high roughness.

Furthermore, we explored the effect of relative humidity on the piezoelectric properties of the PENG based on electrospun PVDF nanofibers [44]. The result showed that there is a positive relationship between the relative humidity and electrical outputs of the PENG owing to enhancing the F($\beta$) and the degree of roughness of nanofiber webs by increasing the relative humidity.

The main objective of this work is to enhance the electrical outputs of the PENG by enhancing its F($\beta$). In this work, a simple and cost-effective method is used to enhance the F($\beta$) of PVDF nanofibers based on the interaction between a plasticizer and the polymer. Furthermore, the electrical outputs of the treated webs are measured. We believe this work can be used as a good reference for enhancing the piezoelectric properties of PENGs using a plasticizer treatment.

2. Experimental

2.1. Materials

PVDF pellets (Mw = 530000 g mol$^{-1}$) were purchased from Sigma- Aldrich, USA. N, N-Dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Shanghai Chemical Reagents Co., Ltd, China. All chemicals were used without further purification.

3. Methods

After dissolving 15% (w/v) PVDF pellets in THF/DMF (1:2), the solution was added into a plastic syringe. A syringe needle with a 21 gauge was used as the spinneret and fixed on a syringe pump (KDS 100, KD Scientific Inc., USA) connected to a high-voltage supplier (Tianjin Dongwen Co., Ltd, China). A drum collector with a length of 40 cm length and a diameter of 20 cm was adjusted at the rotating speed of 2000 rpm to form aligned fibers (figure 1). The electrospinning process was performed at the relative humidity of 60%, working temperature of 22 °C, applied voltage of 18 kV, needle to collector distance of 18 cm, flow rate of 1.5 ml h$^{-1}$, which kept as constant for the entire study according to our previous works [3, 45–47].
4. Characterization

The surface morphology of the PVDF fibers was checked using field emission scanning electron microscopy (FE-SEM, S-4800 Hitachi, Japan). The diameter of fibers was measured using image analysis software (Adobe Acrobat X Pro 10.1.2.45). X-ray diffraction (XRD) was performed on a diffractometer (Panalytical XRD, Netherland) using Cu radiation 1.54 Å. All samples were scanned in the 2θ range of 5° to 30°. Fourier transform infrared (FTIR, USA) spectra were carried out on a Bruker Optics spectroscopy in ATR mode. Differential scanning calorimetry (DSC, USA) was measured by heating the samples from 40 to 190 °C at the heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. The thickness of the webs was checked using a micrometer (Anytime, USA). The design, working area, test conditions of PENG used in this work followed the same procedure described in our previous study [3].

5. Post-processing treatment

The electrospun PVDF nanofiber webs were cut into strips with dimensions of 6 × 2.5 cm², and then fixed on two solid supports with different lengths: L = L₀ and L = L₀/2, where L is the length of the support and L₀ refers to the initial length of webs (6 cm). After that, the fixed PVDF nanofiber webs were treated with THF and kept for 24 h at room temperature (figure 2).

6. Results and discussion

PVDF nanofiber webs were electrospun using 15% PVDF/ (THF: DMF) at the solvent ratio of 1:2 and relative humidity of 60% (figure 3(A)). The fiber webs were cut into 3 samples with dimensions of 6 × 2.5 cm². Before THF treatment, two of them were fixed on 2 solid supports with the length of L = L₀ and L = L₀/2, respectively. When L was set to be the same as L₀, the web maintained its initial length during THF treatment.
while it was 57.9%, and 50.6%, for the THF-treated samples at L0.

Crystalline phase characterization

The crystalline phase characterization of the pristine and treated samples was checked. The XRD patterns of the pristine and treated PVDF fibers electrospun are shown in figure 4(A). The phase showed peak at 2θ = 18.4°, corresponding to the (020) crystal plane, while the sum of β phase exhibited peak at 2θ = 20.6°, corresponding to the (110) and (200) plane. The THF-treated sample at L/L0 = 100% has the highest intensity of the β crystal phase, whereas the treated sample at L/L0 = 50% had the lowest intensity of the β crystal phase. To confirm the crystal phase structure, FTIR spectrophotometry was used. Figure 4(B) showed that the characteristic bands of the β phase crystals were observed at 840 cm−1 (CH2 rocking) and 1274 cm−1 (trans band), while α phase crystals were identified at bands 762 and 976 cm−1. PVDF can be found in five polymorphic phases: β phase (TTTT) all trans, α and δ phases (TGTG'), trans-gauche-trans-gauche, and γ and ε phases (T3GT3G'). Importantly, the F(β) of the PVDF fibers is correlated with the piezoelectric response. F(β) of the studied samples can be determined using equation S1. The F(β) of the untreated web was 84.77%, while it was 93% and 79% for the THF-treated samples at L/L0 = 100%, and L/L0 = 50%, respectively. DSC analysis was used to determine the crystallinity of samples (ΔXc) (figure 4(C)). We calculate the ΔXc content according to equation S2. The ΔXc of the untreated web was 53.5%, while it was 57.9%, and 50.6%, for the THF-treated samples at L/L0 = 100%, and L/L0 = 50%, respectively.

The results showed that the THF treated sample at L/L0 = 100% has the highest F(β) and ΔXc, whereas the THF treated sample at L < L0 has the lowest ones (table 1). These results should be ascribed to this reason. The PVDF polymer chains release the residual stress during THF treatment and thereby enhance the crystallinity if the length of the web is retained or induce the creation of a crimped structure if the length is allowed to shrink [48]. In other words, when the length of the nanofiber web retains, the energy released from the fibers during THF treatment will be used to rise the crystallinity. In contrast, when shrinkage is involved, the energy released from the fibers during THF treatment will be used to retract the fibers and create a crimped structure.

7. Crystalline phase characterization

To detect the effect of the THF treatment on the crystalline phases of the PVDF nanofibers webs, the crystal structure of the pristine and treated samples was checked. The XRD patterns of the pristine and treated PVDF fibers electrospun are shown in figure 4(A). The phase showed peak at 2θ = 18.4°, corresponding to the (020) crystal plane, while the sum of β phase exhibited peak at 2θ = 20.6°, corresponding to the (110) and (200) plane. The THF-treated sample at L/L0 = 100% has the highest intensity of the β crystal phase, whereas the treated sample at L/L0 = 50% had the lowest intensity of the β crystal phase. To confirm the crystal phase structure, FTIR spectrophotometry was used. Figure 4(B) showed that the characteristic bands of the β phase crystals were observed at 840 cm−1 (CH2 rocking) and 1274 cm−1 (trans band), while α phase crystals were identified at bands 762 and 976 cm−1. PVDF can be found in five polymorphic phases: β phase (TTTT) all trans, α and δ phases (TGTG'), trans-gauche-trans-gauche, and γ and ε phases (T3GT3G'). Importantly, the F(β) of the PVDF fibers is correlated with the piezoelectric response. F(β) of the studied samples can be determined using equation S1. The F(β) of the untreated web was 84.77%, while it was 93% and 79% for the THF-treated samples at L/L0 = 100%, and L/L0 = 50%, respectively. DSC analysis was used to determine the crystallinity of samples (ΔXc) (figure 4(C)). We calculate the ΔXc content according to equation S2. The ΔXc of the untreated web was 53.5%, while it was 57.9%, and 50.6%, for the THF-treated samples at L/L0 = 100%, and L/L0 = 50%, respectively.

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| F(β)(%) | ΔXc (%) |
|---------|---------|
| Samples | Pristine | L/L0 = 100% | L/L0 = 50% |
| F(β)(%) | 84.77   | 93%       | 79%       |
| ΔXc (%) | 53.5    | 57.9      | 50.6      |

(figure 3(B)). In contrast, when L < L0, the nanofibers were initially in a loose state resulting in the formation of the crimped fiber after THF treatment (figure 3(C)). The crimped structure was formed owing to the retraction of the elongated polymer chains in each fiber [48]. The diameter of the fibers increased from ~400 nm for the pristine web to ~825 nm after the THF treatment at L/L0 = 50% (Figure S1 and S2 (available online at stacks.iop.org/MRX/8/125001/mmedia)).
8. Piezoelectric properties of PVDF nanofiber webs

To explore the effect of the plasticizer treatment on the electrical outputs of the PENG, three PENGs based on pristine electrospun PVDF fiber web, THF-treated PVDF fiber web at $L/L_0 = 100\%$, and THF-treated PVDF fiber web at $L/L_0 = 50\%$ were fabricated. For an accurate comparison, the PENGs were tested under the same conditions (impact frequency of 5 Hz and peak force 10 N). The results exhibited that the electrical outputs of the PENGs were 2.1 V and 2.9 $\mu$A at the pristine web, 2.98 V and 4.2 $\mu$A at THF- treated web ($L/L_0 = 100\%$), and 1.69 V and 2.43 $\mu$A at THF- treated web ($L/L_0 = 50\%$) (figure 5 and S3). Herein, the highest voltage and current outputs of the PENGs based on the THF- treated web ($L/L_0 = 100\%$) is attributed to its high $F(\beta)$.

It is worth mentioning that the plasticizer treatment under specific conditions played a vital role in determining the electrical outputs of the PENG.

9. Conclusions

In summary, we demonstrated the effect of the THF treatment on the $F(\beta)$ of the electrospun PVDF nanofiber webs which can be used directly as active layers to make a PENG. The results showed that the $F(\beta)$ and $\Delta X_c$ of the PVDF fiber webs can be enhanced using THF-treatment at $L/L_0 = 100\%$ because the PVDF polymer chains released the residual stress during THF treatment. Whereas, the $F(\beta)$ and $\Delta X_c$ of the PVDF fiber webs decreased after the THF- treatment at $L/L_0 = 50\%$ because the retracted energy released from the shrinkage fibers during THF- treatment was used to create a crimped structure. Moreover, we found that the voltage and current outputs of the PENG based on the THF treated webs at $L/L_0 = 100$, are the highest compared with other studied samples owing to its high $F(\beta)$. We hope that this work can be used as a good reference for enhancing the electrical outputs of the PENG.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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