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FROM CNC-REINFORCED PVDF-HFP YARN TOWARDS PRESSURE SENSING TEXTILES

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ABSTRACT

The rise of interest on smart textiles with integrated sensing capabilities has led to increased research focus on flexible piezoelectric materials; such as, polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP). In this study, PVDF-HFP nanofibers were yarn-electrospun with sustainable cellulose nanocrystals (CNC) as fillers for pressure sensing. CNC reinforcement improved the properties of the PVDF-HFP yarns, as evidenced by increased β phase ratio, one-fold increase in mechanical properties, and approximately two-fold increase in piezoelectric output. The fabricated pressure sensor showed positive correlation with the exerted compressive loads, reaching a maximal output voltage of 20 V at 20 N. This work opens up new avenues in exploring the immense potential of electrospun PVDF-HFP/CNC yarns for flexible pressure sensing applications and smart textiles.

1 INTRODUCTION

Amidst the expanding interest in the field of wearable technology, yarns produced from piezoelectric polymers such as polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) still present unexplored advantages that can open up opportunities for a new generation of smart textiles suitable for self-powering, energy harvesting, and pressure sensing [1]. Piezoelectric effect allows the yarn to convert mechanical motion into electrical energy while the high flexibility of the yarn provides good wearability. The piezoelectric effect of PVDF and PVDF-based copolymers arises from the β phase, which is one of the crystalline conformations of PVDF with the highest polarizability [2]. The main challenge for commercializing the piezoelectric yarn is its comparatively lower piezoelectric performance than piezoelectric ceramics. Therefore, cellulose nanocrystal (CNC) is proposed in this work to enhance the piezoelectric performance of the PVDF-HFP yarn.

CNC is a biodegradable, biocompatible, and highly crystalline bio-based nanomaterial [3]. Incorporation of CNC in PVDF-HFP is hypothesized to promote formation of the β phase and improve the piezoelectric effect. Furthermore, the large aspect ratio, nano-size, and high modulus and strength of CNC can increase the mechanical properties of PVDF-HFP with minimal impact on flexibility [4].

Yarn electrospinning is an extremely flexible and tailorable fabrication method for generating twisted yarn structures composed of continuous nanofibers. High voltages with opposite polarity are applied to the spinnerets

facing each other so that the nanofibers with different charges can collide on a rotating cone placed in between the spinnerets. The entangled nanofibers are drawn into a piezoelectric yarn collected by a rotating cylinder.
Yarn electrospinning of PVDF-HFP was reported by several works [5–8]; however, most studies emphasized characterizing the mechanical and morphological properties of the yarns instead of their piezoelectric performance. Conversely, the piezoelectric characterizations were conducted for PVDF yarn or its composites [9–11], achieving output voltage ranging from 150-300 mV under compressive stress of 0.1 MPa [9] to 0.47-0.52 V under stress of 0.02 MPa [10].

In this work, we produced electrospun piezoelectric PVDF-HFP continuous yarn reinforced with CNC as a pressure-sensing textile. The impact of CNC on morphological, chemical, mechanical, and piezoelectric properties of PVDF-HFP yarn was analyzed. This study demonstrates immense research potential for the one-step production of piezoelectric nanofiber yarns and its application in flexible pressure sensors.

2 MATERIALS AND METHODS

2.1 Materials

PVDF-HFP (400 kDa) and anhydrous N, N-Dimethylformamide (DMF) with purity of 99.8% were obtained from Sigma Aldrich. Acetone and CNC were acquired from Fisher Scientific and CelluForce, respectively. 110 copper core was purchased from Master Carr.

2.2 Production of Nanofiber Yarn

1% (w/v) CNC was first dispersed in DMF/acetone (1/1 v/v) solvent in an ultrasound bath for 30 min. 20% (w/v) PVDF-HFP pellets were added to the CNC colloidal solution and mixed at a stirring speed of 500 rpm for 24 hours. Pristine PVDF-HFP solution was prepared for comparison.

The schematic layout of yarn electrospinning equipment is shown in Figure 1a. The positively charged spinneret (20 gauge blunt needle) was placed at 16 cm distance and with an angle of 30° from the center of the cone. The negatively charged spinneret was placed at 18 cm distance with an angle of 60° from the cone. Both the positive and negative voltages were 10 kV that were exerted by a DC power supplies (Gamma High Voltage). The flow rates were respectively 1.5 ml/hour and 0.5 ml/hour at the positive and negative spinnerets. A copper wire was fed through the cone as a structural support and a conductive core, which engineered the yarn to be readily applicable in sensor applications. The rotating speed of the cone was 130 rpm. After the nanofibers started to wrap around the copper core, the yarn was collected at a speed of 9.4 cm/min (1.5 rpm). The ambient environment was maintained at 21-22℃ and 10-15% relative humidity.

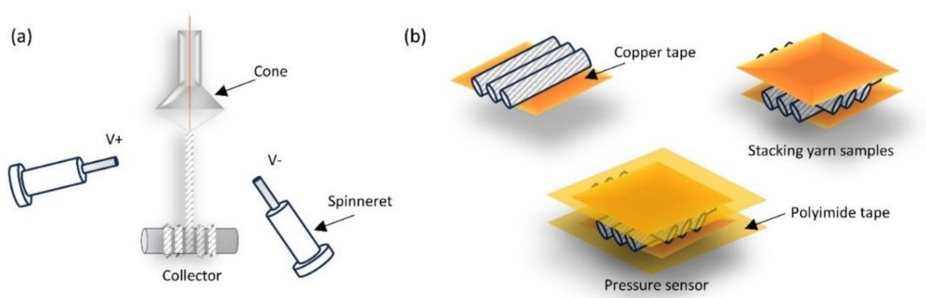

Figure 1. Schematic diagrams of (a) yarn electrospinning process and (b) pressure-sensor assembly.

2.3 Morphological Characterization

The morphological characterization was conducted by examining 5 mm-long gold-sputtered yarn samples under Hitachi field emission scanning electron microscope (FESEM). The accelerating voltage was 5 kV. The fiber diameter was measured using ImageJ (Fiji), presented as mean±standard deviation. The yarn size was measured by the Olympus optical microscope.

2.4 Chemical Characterization

The yarn samples were coiled into circular mats and characterized with Nicolet iS50 Fourier-transform Infrared Spectrometer (FTIR). The samples were scanned within the wavenumber range of 400 to 4000 cm^{-1}, averaging 32 scans with a resolution of 4 cm^{-1} for each sample. Baseline correction of the spectra was performed using Origin software to obtain the β phase ratio (R_β) [12],

$$R_\beta = \frac{A_\beta}{1.26A_\alpha + A_\beta} \tag{1}$$

where A_α and A_β were the absorbances at 764 and 840 cm^{-1}, corresponding to the α and β phases, respectively.

2.5 Mechanical Characterization

The yarn sample was mounted on a rectangular paper bracket using hot glue to avoid structural damage from the grippers. The mechanical test was performed with a tensile tester (Bose ElectroForce) with a gauge length of 30 mm and an elongation speed of 1 mm/second. The porosity ($\Phi_{PVDF-HFP}$) of the nanofibers wrapping on the copper core was estimated by,

$$\Phi_{PVDF-HFP} = 1 - \frac{(M_{yarn} - M_{copper})/\rho_{PVDF-HFP}}{V_{yarn}} \tag{2}$$

where M_{yarn} , M_{copper}, $\rho_{PVDF-HFP}$, V_{yarn} were the mass of the yarn, the mass of the copper, the density of PVDF-HFP, and the volume of the yarn, correspondingly. V_{yarn} was obtained by multiplying the average yarn diameter measured by the optical microscope and the length of the yarn. Then the effective stress (σ_{yarn}) of the yarn samples was calculated by,

$$\sigma_{yarn} = \frac{F}{A_{copper} + (A_{yarn} - A_{copper})(1 - \Phi_{PVDF-HFP})} \tag{3}$$

where *F* was the load, A_{copper} and A_{yarn} were the area of the copper core and the yarn.

2.6 Piezoelectric Testing and Stress Sensor

As shown in Figure 1b, 20 yarn samples were positioned across a square copper tape with an average side length of 6 mm. Then two of these tapes with yarn samples attached were stacked on top of each other. The yarns on the top layer were positioned perpendicular to those on the bottom layer. To shield the device from static, polyimide tapes were covered over the copper tape electrodes. The piezoelectric output was quantified using a source meter (Keithley 2612B) under a cyclic compressive load of 1.5 N and a frequency of 0.5 Hz. The output voltage was recorded when supplying 1 nA current, while the output current was recorded when supplying 1 V voltage.

To analyze the application of the PVDF-HFP/CNC yarn device containing 1 % CNC as a pressure sensor, open-circuit voltage was recorded with an oscilloscope (Tektronix 2024B) under varying compressive loads of 1.5-20 N.

3 RESULTS AND DISCUSSION

3.1 Morphological Analysis

The morphology of electrospinning PVDF-HFP yarn is shown in Figure 2. As 1% CNC was introduced, the nanofiber diameter showed insignificant change from 450±14 nm (0% CNC) to 435±174 nm (1% CNC), while the yarn diameter increased by around one-fold. There was no significant amount of defects, such as beads or fiber fusions, observed in the samples.

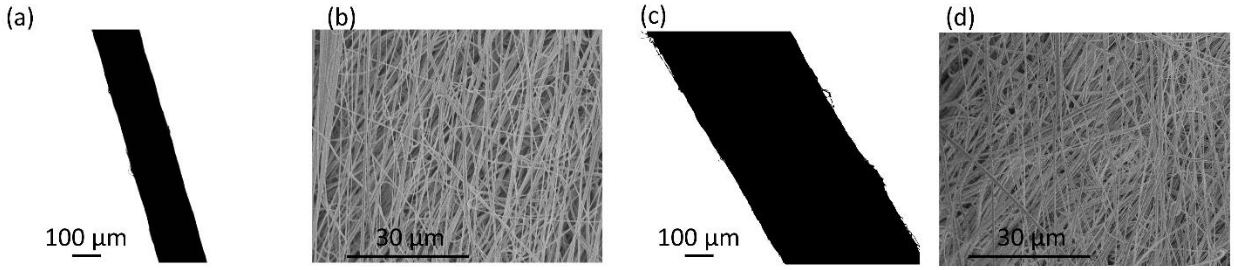

Figure 2. Morphology of (a) (b) PVDF-HFP yarn and (c) (d) PVDF-HFP/CNC (1% CNC) yarn.

3.2 FTIR Analysis

The FTIR spectra of PVDF-HFP and PVDF-HFP/CNC yarns are shown in Figure 3a. A notable reduction in the α phase was detected for the PVDF-HFP/CNC yarns. The decrease in the α phase gave rise to the higher R_β, which showed a 7.5% improvement compared to the pristine PVDF-HFP yarns.

3.3 Mechanical Characterization

The PVDF-HFP yarns reinforced with 1% CNC show considerable improvement in mechanical properties as shown in Figure 3b. A one-fold increase was observed for the ultimate tensile strength (UTS) and elastic modulus after including 1% CNC. Even though the mechanical properties of the yarn were dominated by the copper core, the CNC reinforcement was still demonstrated viable for PVDF-HFP nanofiber yarns.

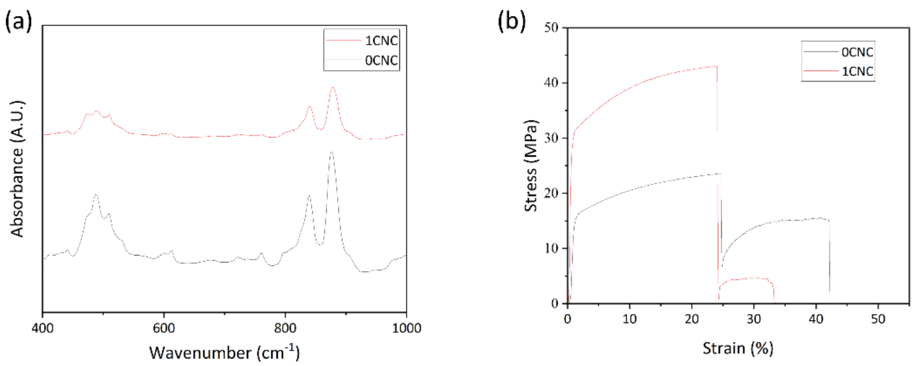

Figure 3. (a) FTIR spectra and (b) stress-strain curves of the PVDF-HFP yarn and PVDF-HFP/CNC yarn with 1% CNC.

3.4 Piezoelectric Characterization and Application

The positive effect of CNC addition on the piezoelectric performance of the PVDF-HFP yarns is demonstrated in Figure 4a. Addition of 1% CNC yielded increase of 2.1- and 2.6-fold in current sensitivity and voltage sensitivity, respectively. The improvement in the piezoelectric performance of the PVDF-HFP/CNC yarns was in agreement with the β phase ratio enhancement as analyzed in the FTIR characterization.

The PVDF-HFP/CNC yarns with 1% CNC were fabricated into pressure sensors. The positive correlation between the open-circuit voltages and the cyclic compressive loadings (varying between 1.5 and 20 N) is depicted in Figure 4b. A maximal output of ~20 V was achieved for compression force of 20 N (pressure of 56 MPa) with a frequency of 0.5 Hz. The successful application of electrospinning PVDF-HFP/CNC yarn as a pressure sensor not only demonstrates its practical utility but also broadens the research potential in flexible and sustainable wearable products.

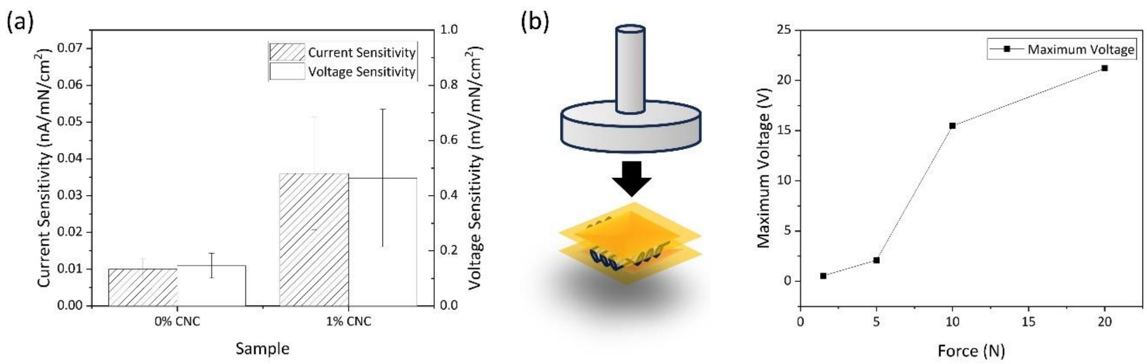

Figure 4. Piezoelectric characterizations of (a) current and voltage sensitivities and (b) pressure sensor application with a cyclic compressive load of 1.5-20 N.

4 CONCLUSION

In this study, we demonstrated the feasibility of enhancing the piezoelectric performance of electrospinning PVDF-HFP yarn by introduction of CNC. The PVDF-HFP/CNC samples produced by yarn electrospinning exhibited improved β phase ratio, better mechanical properties, and piezoelectric properties. Capitalizing on these advantages, the PVDF-HFP/CNC yarns were assembled into pressure sensors, which demonstrated great sensitivity to the applied compressive loads. The production of PVDF-HFP/CNC based flexible pressure sensors paves the way for the development of advanced and multifunctional wearable technologies.

5 REFERENCES

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