Fabrication of Aligned P(VDF-TrFE) Piezoelectric Nanofiber Bundles with Electrospinning Across Serrated Gaps

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Abstract: In this paper, we report a technique to generate aligned poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] co-polymer fibers with electrospinning method. The key features of the reported approach are that it offers a simple method to simultaneously form and align P(VDF-TrFE) fibers with several-micron diameters and that the resulting fibers are poled to provide piezoelectric properties along the length of the fibers. The technique is to use an inclined gap with the edges of the gap serrated to provide multiple field concentration points. The fibers were formed and collected mostly on the flat surface of the collector, and some were formed bridging two opposing tips of the serrated edges across the incline gap (Figure 2). The sharp points on the serrated teeth provide favorable charge dissipation points and thus fibers were preferentially formed bridging two closest sharp points across the gap. Our experiment showed that bundles of P(VDF-TrFE) fibers could be formed with controlled properties by optimizing the gap between the serrated edges, the geometry of the serrated teeth, and other electrospinning parameters. Detailed experimental approach and results are reported.

Keywords*: piezoelectric, nanofibers, electrospinning*

1. Introduction

Electrospinning is a well-developed method to generate ultrathin fibers with diameters ranging from a few nanometers to several micrometers. Since 1930s, this technology has been applied for the applications of filtration [1], suture threads [2], fuel cells [3], and scaffolds and substrates for tissue engineering applications [4-6]. This technique is based on applying a high potential difference between a liquid droplet from a syringe needle tip and an opposing collector. When the electric potential exceeds a certain threshold, the ejecting liquid will be guided along the strongest electric field line created between the needle tip and the grounded collector. Since charges are accumulated on the dielectric droplet during the process, the charged liquid is guided from the needle to the collector due to the transformation from electrical energy to dynamic energy. Further, due to columbic interactions, the electrospun fibers are usually randomly deposited on collectors [7].

During the last decade, different methods to generate aligned fibers have been reported, including the use of a wire drum collector [8], a rotating cylindrical collector [9, 10], an auxiliary electrodes [11], a grounded wheel-like bobbin [12], and an inclined gap collector [13, 14]. By using these approaches, fibers can be aligned in the same direction, but the distances between adjacent fibers are still uncontrollable. Here we present a new method to created fibers with a controlled separation distance. The technique is to use an inclined gap with the edges of the gap serrated to provide multiple field concentration points that are well defined. Experimental findings suggested that bundles of P(VDF-TrFE) fibers could be formed bridging two closest sharp points across the serrated gap.

2. Materials and Methods

Figure 1 illustrates our design and experimental set-up. The collector with an inclined gap was made by folding a 40-μm-thick sheet of stainless steel. A 5-μm-thick aluminum film laminated with a PVC film was cut to create serrated edges by using a Xeurographic machine (Graphtec Corp. FC5500-50). This aluminum film was attached onto the surface of the stainless steel frame such that the serrated edges extended beyond the edges of the inclined gap. This collector assembly was grounded during the electrospinning process to collecting fibers.

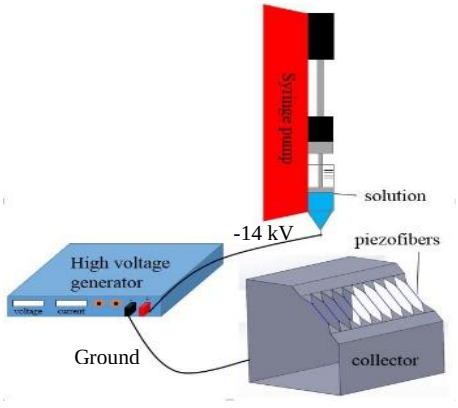

Figure 1. Illustration of the collector with serrated edges flanking an incline gap.

The polymer we used in this study was vinylidenefluoride (VDF) and trifluoroethylene (TrFE) copolymers with a 75/25 (w/w) ratio in VDF:TrFE. First, VDF and TrFE were disolved in a solvent containing 99% pure *N,N*-dimethyl acetamide (DMAc) and methyl

ethyl ketone (MEK) (25/75:v/v) to make 20%wt solution. This mixture was stirred overnight to ensure thorough mixing. The resulting mixture was drawn into a syringe which was then placed on a syringe pump held at a vertical position. A blunt stainless steel needle was attached to the syringe and biased at –14 kV during the electrospinning steps. The collector was grounded and placed below the needle tip. The pumping rate was maintained at 0.6 ml/hr during the electrospinning process.

3. Results

Figure 2(A) shows one of the experimental results of collected fiber bundles. In this experiment, there were a few fibers aligned across two sharp points nearest the edge of the collector assembly, although not on the other pairs of sharp points. It showed that the sharp points on the serrated teeth with favorable charge dissipation points indeed resulted in preferential fiber formation. Figure 2(B) shows an SEM image of this P(VDF-TrFE) fiber, measuring 3.84 mm in length.

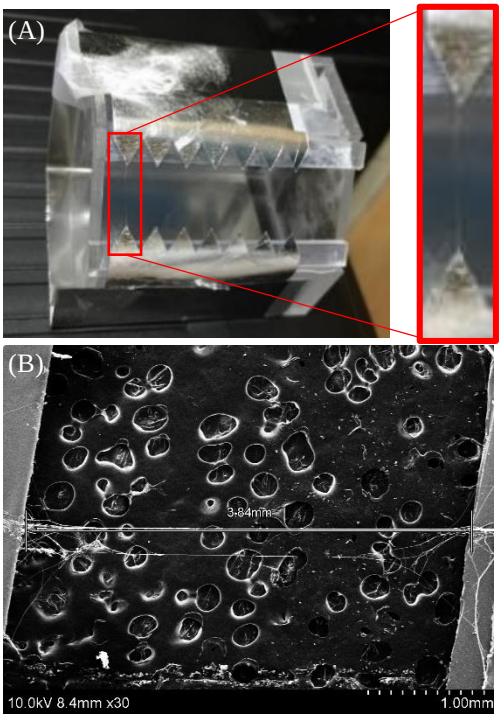

Figure 2. (A) Picture of a P(VDF-TrFE) fiber bundle bridging two opposing sharp tips across the inclined gap. (B) SEM picture of the same fiber, indicating a length of 3.84 mm.

This study included three different collector geometries to investigate the influence of the serrated teeth design on fiber alignment. The distance of the inclined gap was fixed at 15 mm while the sharpness of the teeth was varied by changing the tip angles at 30°, 45°, and 60°. The top side is placed near the needle tip. Based on our experimental results, we found that some fibers did bridge at the sharp points of two opposing teeth across the gap. However, some other fibers did not form at the exact opposing teeth but spanning the alternate ones after 12s of electrospinning with two different teeth angles [Figs. 3(B) and (C)]. Further, thicker and larger fiber bundles were formed after 30s to 60s of electrospinning [Figs. 3(D) and (E)]. After 300s, the longest electrospinning duration in this experimental work, a sheet of P(VEF-TrFE) fibers was formed spanning multiple teeth across the inclined gap [Fig. 3(F)].

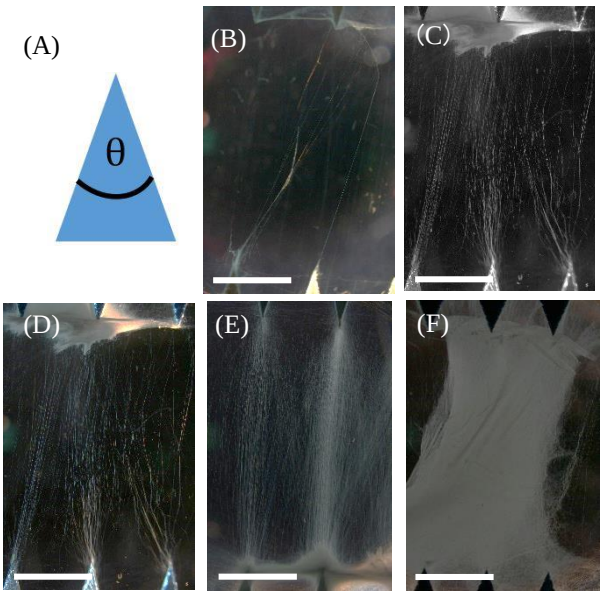

Figure 3. (A) Illustration of tooth angle θ. (B) θ = 30°, electrospun for 12s. (C) θ = 60°, 12s. (D) θ = 60°, 30s. (E) θ = 60°, 60s. (F) θ = 45°, 300s. Scale bar is 5 mm.

We found out that the P(VDF-TrFE) fiber bundles were not completely aggregated at the tips of the teeth. We postulated that it was due to the fact that the distance between any two opposing teeth across the inclined gap was longer than the separation distance between two adjacent teeth on the same side of the gap. The electric energy was likely favoring the release through the shorter distance between serrated teeth. It other words, the residual charges on the fiber surfaces tended to be dissipated through a shorter path between the serrated teeth.

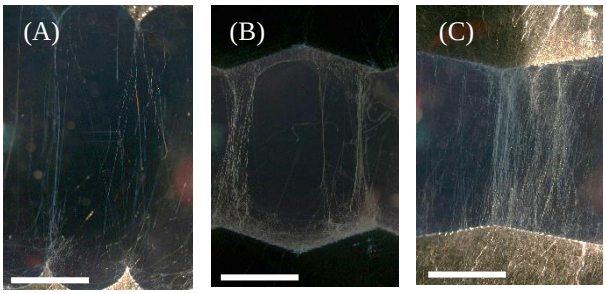

Figure 4. Images of electrospinning results using collectors with (A) petal-shaped teeth, (B) 120° tooth angle, and (C) 143° tooth angle, all with 60s electrospinning duration. Scale bar is 5mm.

To test this hypothesis, we designed a collector with petal-shaped serrated teeth [Fig. 4(A)] and two others with large tooth angles at 143° [Fig. 4(B)] and 161° [Fig. 4C)]. The distance across the inclined gap was reduced to 5 mm. The electrospinning time was set at 60s. From these experimental results, it clearly demonstrated that a more concentrated P(VDF-TrFE) fiber bundles could form across a shorter inclined gap in contrast to those shown in Fig. 3(E). Further, the accumulation of fibers between serrated teeth was significantly reduced.

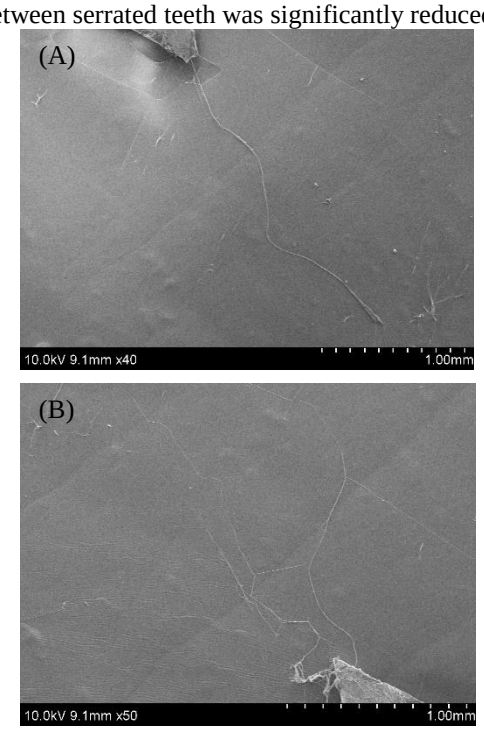

Figure 5. (A & B) SEM images of fibers spanning from the tips of two opposing teeth. Scale bar is 1 mm.

These results suggested that the distance between adjacent teeth and inclined gap played important roles in influencing the directions and alignments of the fiber bundles. Thus, the ratios of the gap between adjacent teeth to the two opposing teeth could be used as design parameters to control the direction of fiber bundle formation. Further, the distance between bundles could be controlled by the separation between serrated teeth.

Figure 5 shows two SEM images of fibers taken from the sample shown in Fig. 4(A). The P(VEF-TrFE) fibers were shown to span the sharp edges between two opposing teeth [Figs. 5(A) and (B)]. Also, a P(VDF-TrFE) fiber bundle was successfully created by using petal-shaped serrated teeth with 5 mm inclined gap. The measured diameter of fiber bundle was 2.81 μm.

4. Conclusions

In this paper, we demonstrated the use of an inclined gap combined with serrated teeth at the edges to create favorable charge dissipation sites to facilitate the alignment of electrospun P(VDF-TrFE) fibers. Fiber bundles could be concentrated around sharp tips, showing evidences that the distances between adjacent serrated teeth and opposing teeth could be used as design parameters to control the direction of fiber alignment. A lower ratio between the teeth separation to inclined gap favored more fiber bundle growth between the opposing teeth across the incline gap than higher ratios. We also demonstrated that a P(VDF-TrFE) fiber bundle with a 2.81-μm diameter was formed using this method. This set of experimental results pointed to the potential of controlling both the alignment and distance of the growth of electrospun P(VDF-TrFE) fiber bundles.

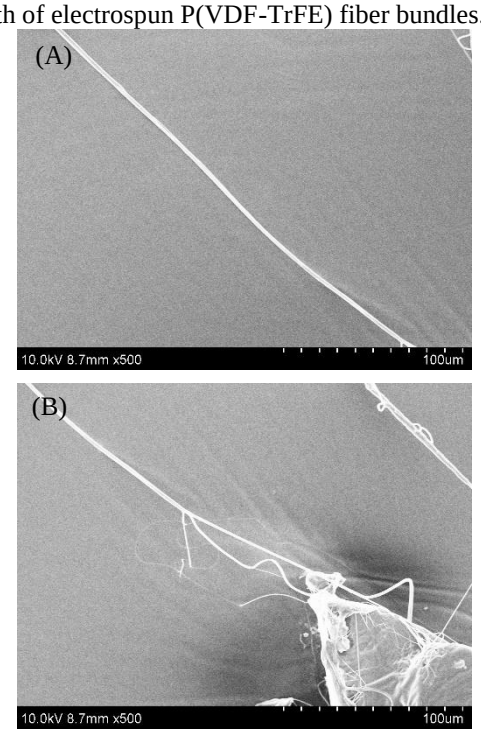

Figure 6. (A & B) SEM images of P(VDF-TrFE) fiber bundles with 2.81 μm diameter. Scale bar is 100 μm.

5. Acknowledgment

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6. References

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