ELECTROSPUN ELECTROACTIVE POLYMERS FOR AEROSPACE APPLICATIONS

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Abstract

Electrospun piezoelectric polymers are being developed for use as a component on lightweight wings for micro-air vehicles (MAV). The goal is to incorporate fibers with tailored properties to permit dynamic control and maneuverability during flight. In particular, electrospun fiber mats of two piezoelectric polymers were investigated to ascertain their potential for the MAV application. In the work reported here, the typical experimental set-up for electrospinning was modified to induce fiber orientation in the spun mats. The morphologies of the resulting fibers and fiber mats were evaluated for various experimental conditions, and a comparison between oriented and unoriented fiber mats was carried out.

Introduction

Piezoelectric polymers are materials that exhibit a mechanical displacement in response to an electric field; conversely, a mechanical strain gives rise to an electrical signal. These polymers are therefore of interest for bioinspired micro-air vehicle (MAV) wing designs where sensing and actuating capabilities are required. The polymers of choice for this work were poly(vinylidene fluoride) (PVDF), a semicrystalline piezoelectric polymer, and (β-CN)APB-ODPA, an amorphous piezoelectric polyimide developed at NASA Langley Research Center.[1,2,3,4]

These types of polymers can be processed into fibers using electrospinning.[5,6,7] In this process, a high voltage is applied to a polymer droplet suspended at the tip of a needle or pipette. Charge builds up on this droplet, and, as this charge overcomes the surface tension of the solution, the droplet elongates and forms a Taylor cone.[8,9] The solution is ejected from the tip of the Taylor cone as a jet, whipping as it travels through the air to its target medium. While traveling, the solvent evaporates, leaving fibers that accumulate as a nonwoven mat. The major advantage of this technique over other fiber spinning techniques is the potential of producing nanoscale diameter fibers, resulting in nanostructures with a high surface area to mass ratio.

The MAV was chosen as the platform to demonstrate the concept of a bioinspired wing because of its scale. Our focus has been on the MAV wing, which consists of two main components: a carbon fiber frame and a lightweight membrane designed to cover the frame. The goal is to electrospin a polymer solution into a form that can serve as a strong lightweight covering and double as a means to facilitate fine control of the wing. A group of electrostrictive polymers with actuating capability was investigated for this same purpose in a previous publication.[10] Those results led to the current investigation of piezoelectric polymers, which possess both sensing and actuating capabilities.

Experimental

(β-CN)APB-ODPA and PVDF were electrospun from solution in N,N-dimethylacetamide (DMAc) and dimethylformamide (DMF), respectively. The former was prepared from 2,6-bis(3-aminophenoxy)benzonitrile ((β-CN)APB) and 4,4'-oxidiphthalic anhydride (ODPA) via a poly(amic acid) precursor in DMAc followed by thermal imidization.[11] The latter was purchased in pellet form (Kynar®) (Atofina Chemicals, Inc., Philadelphia, PA) and dissolved in DMF. For each system, fiber morphology results from various processing conditions were determined and compared.

The electrospinning set-up was completely self-contained and mobile. As shown in Figure 1, a benchtop fume hood housed the equipment to ensure protection from hazardous

* Work completed while at Virginia Commonwealth University

solvent fumes as well as electric fields. A high voltage power supply (Spellman High Voltage Electronics Corp., Hauppage, NY) charged a polymer solution contained in a syringe with a voltage in the range of 0-30 kilovolts (kV). At some distance from the needle tip (3-10 inches typically), a grounded collector was suspended so that the two were parallel. The charge on the solution eventually overwhelmed the surface tension of the solution, and a jet was ejected from the needle tip in the direction of the grounded collector. During jet travel, the solvent evaporated and the remaining solid polymer fiber deposited on the collector. Fibers accumulated and spread on the collector, as long as the needle tip was continually supplied with polymer solution via a syringe infusion pump (Fisher Scientific, Suwanee, GA. Eventually, a nonwoven fiber mesh was created.

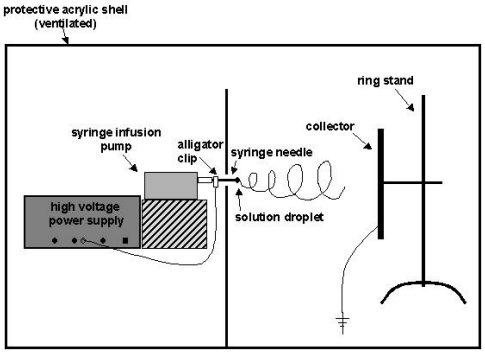

Figure 1. Electrospinning Experimental Set-up

The experimental set-up was modified to have a rotating collector. This device consisted of an assortment of collector geometries that could be attached to the base apparatus. As illustrated in Figure 2, the collector was designed to rotate about its long axis via a motor and shaft coupling or move laterally along a lead screw attached to a second motor to allow for full coverage of the selected collector.

Following spinning, the electrospun mats were dried in a vacuum oven at 60°C overnight or over two days to remove any residual solvent from the fibers. Dried mats were examined by optical microscopy at 100x and 200x magnification using an Olympus BH-2 optical microscope in conjunction with Scion Image, v. 1.62, software. These images clearly demonstrated that fiber characteristics were affected by electrospinning parameters.

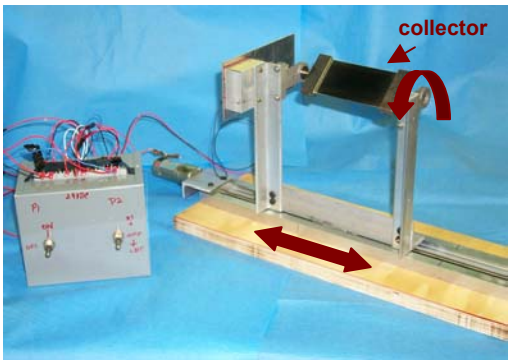

Figure 2. Modified Electrospinning Collector

Results

Modifications to the electrospinning set-up allowed for increased fiber orientation. Figure 3 demonstrates that the rotation speed of the collector affects the orientation of the individual electrospun fibers in the mat. As rotation speed was increased from zero to mid-range to maximum, fibers became increasingly more oriented. It is anticipated that an increase in motor speed range would increase fiber orientation even further.

Solutions of 20 weight percent (wt%) (β-CN)APB-ODPA and 30 wt% PVDF were electrospun. The effect of electrospinning parameters such as applied voltage, distance between syringe needle tip and collector, infusion rate of the solution into the system, and collector surface used on the quality of electrospun fibers are presented in Figures 4 through 7.

Figure 4 shows that, depending on the polymer system of choice, voltage can have very different effects on fiber formation. For (β-CN)APB-ODPA spun at 30 ml/hr at a distance of 8", an increase in voltage from 15 to 20 to 25 kV led to a decrease in fiber diameter, and fibers appeared to be drier and more cylindrical. An increase in applied voltage while maintaining constant distance translates to an increase in electric field. With higher field, the initiated jets experienced greater forces in the direction of the collector leading to the decrease in fiber diameter.

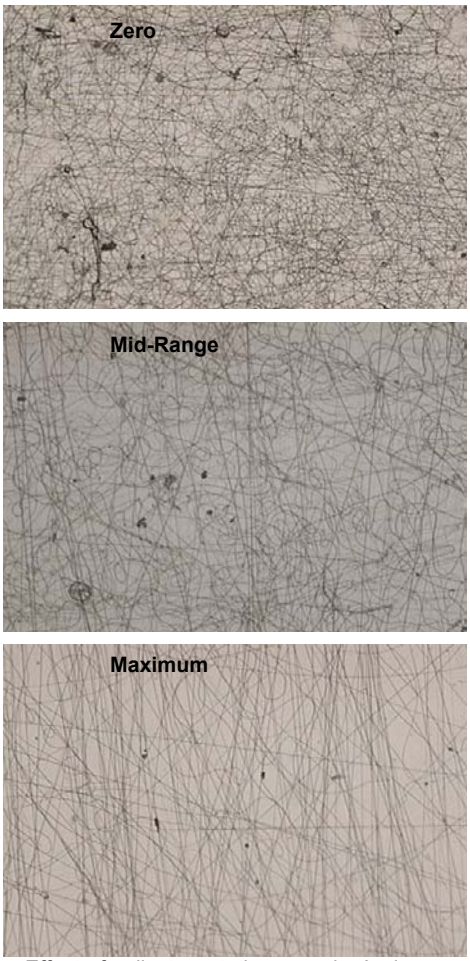

Figure 3. Effect of collector rotation speed. An increase in collector rotation speed causes an increase in fiber orientation in the direction of rotation.

The PVDF solution was more difficult to electrospin. The combination of parameters that yielded acceptable fiber quality was a voltage of 10 kV at a solution dispensing rate of 6 ml/hr with a 9" distance between needle tip and collector. Deviation from this voltage in either direction resulted in wetter, non-uniform fibers. The inherent conductivity of the two polymers and its interaction with the applied voltage may explain these differing results. Values of conductivity at 1 kHz and 25°C for PVDF and (β-CN)APB-ODPA in film form were measured to be 1.07×10^{-10} S/cm and 1.10×10^{-11} S/cm, respectively. Since PVDF is an order of magnitude more conductive than (β-CN)APB-ODPA, it is possible that high conductivity is detrimental to electrospinnability. Work is ongoing to determine the extent that solution properties such as conductivity and viscosity affect electrospinnability.

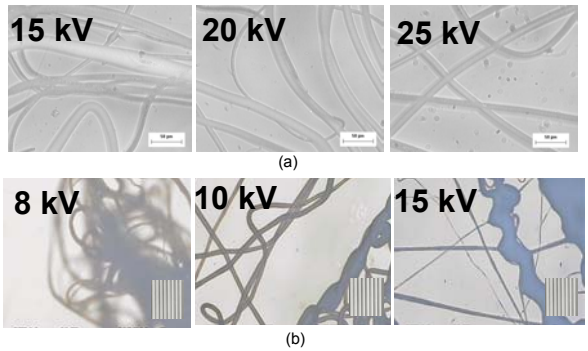

Figure 4. Effects of voltage variation on fiber formation. (a) (β-CN)APB-ODPA (b) PVDF. One division of the bottom scale bar is 10 microns.

In Figure 5, the effects of distance between the needle tip and collector on fiber formation and morphology are illustrated. The top two micrographs show electrospun (β-CN)APB-ODPA samples spun at 30 ml/hr and 25 kV with a 3" and 8" distance between syringe needle tip and collector. These results show that fiber diameter increased with increased distance. An increase in distance with constant voltage results in a decrease in electric field, a smaller driving force on the initiated jets, and, ultimately, larger diameter fibers. PVDF samples were processed with a 6 ml/hr infusion rate at 10 kV. As distance was increased from 6" to 10", a transition from larger diameter, almost sprayed morphologies, to clearly defined and cylindrical fibers with smaller diameter was observed. Again, PVDF seems to have a smaller range of electrospinnability; at 10", favorable conditions were achieved.

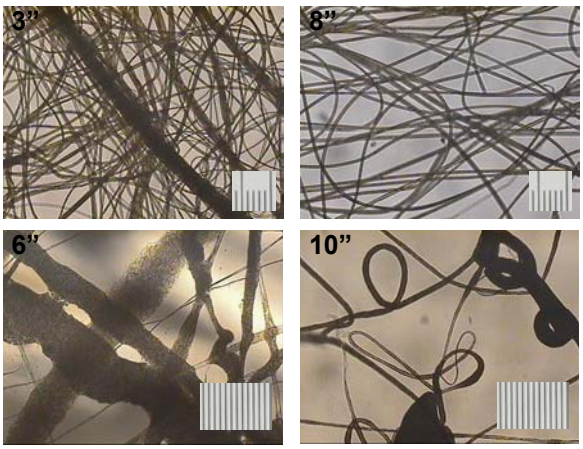

Figure 5. Effects of distance between syringe needle tip and collector. The top two micrographs represent (β-CN)APB-ODPA at 3 and 8 inch distances. The bottom two micrographs represent PVDF at 6 and 10 inch distances. One division is 10 microns.

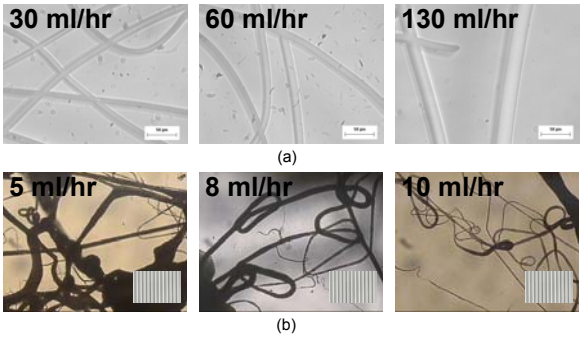

Figure 6. Effects of infusion rate of the polymer into the electrospinning system for (a) (β-CN)APB-ODPA at 30, 60, and 130 ml/hr and (b) PVDF at 5, 8 and 10 ml/hr. One division of the bottom scale bar is 10 microns.

Effects of infusion rate on resulting fiber formation are illustrated in Figure 6. In 6(a), the diameter of (β-CN)APB-ODPA fibers spun at 25 kV with an 8" distance increased as infusion rate was increased from 30 to 130 ml/hr. Results for PVDF spun at 10 kV and a 9" distance in 6(b) were not as clear, as the system appeared to present a range of fiber diameters. Also, these fibers do not appear to be as robust as the former polymer system.

Figure 7 demonstrates the effect of utilizing two different surfaces as fiber collectors. In this case, 20 wt% solutions of both polymers were electrospun. On the left-hand side, an Indium-Tin-Oxide (ITO) conducting plate was used, and, on the right, a typical (nonconducting) glass microscope slide was the substrate. For (β-CN)APB-ODPA spun at 20 kV with an 8" distance and a 30 ml/hr infusion rate, fibers appeared to have a smaller average diameter when spun onto a glass slide. PVDF electrospun at 10 kV with a 9" distance and a 6 ml/hr infusion rate formed beaded fibers on a conductive ITO plate, but fiber formation and deposition on a glass slide while spinning at the same conditions was not apparent. Because the glass plate is nonconductive, the electric field lines are centered between the needle tip and the grounding point on the glass slide, while, for the ITO plate, the entire plate is ground. Electric field lines are aligned and directed differently in the two cases.

Conclusions

The results of this work prove the feasibility of electrospinning piezoelectric polymer compositions. Trends were established for the spinning of both systems, and effective processing conditions were isolated. These trends are presented in Table 1 for the two polymers investigated. It is apparent that each polymer system has its own unique set of optimized electrospinning parameters. At this point, it is not clear whether universal correlations may be found for classes of polymers. Future work will focus on thermal, mechanical, and electrical analyses of these fibers to better identify their niche applications. If electrospun fibers and fiber mats exhibit the same or improved properties compared to the film form, use of this processing technique for applications such as MAVs will be beneficial.

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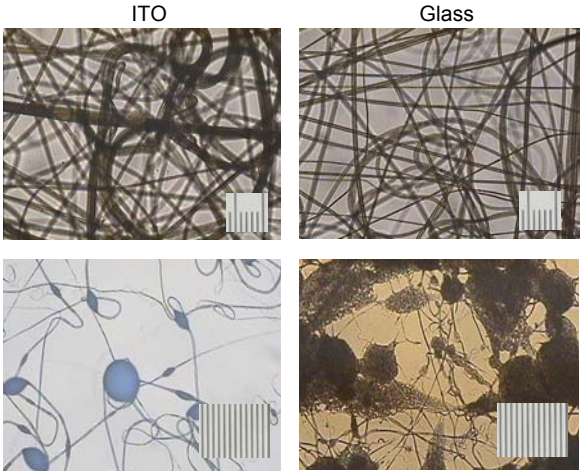

Figure 7. Effects of collector material on fiber formation. At the top, (β-CN)APB-ODPA fibers spun onto an ITO and a glass slide are illustrated. PVDF fibers spun onto the same substrate are illustrated at the bottom of the figure. One division is 10 microns.

Table 1. Trends observed for various parameters.

	20wt% (b-CN)APB-ODPA in DMAc		30wt% PVDF in DMF	
	Diameter	Fiber Morphology	Diameter	Fiber Morphology
Increased Voltage	Decreased	Drier, cylindrical	?	More stable, uniform
Increased Distance	Decreased	Drier, cylindrical	Decreased	More stable, uniform
Increased Infusion Rate	Increased	Same within a range.	Range of sizes.	Same within a range.
ITO vs. Glass Collector	Fibers less defined on glass.		Fibers less defined on glass.	
Optimal Conditions	20 kV, 8", 30 ml/hr		10 kV, 9", 6 ml/hr	

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