Spring 2015

Effect of Nanofiber Morphology on PVDF Air Filter Performance

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Honors Research Project

Submitted to

The Honors College

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Contents

Abstract

Poly(vinylidene fluoride) (PVDF) can be formed into small nanofibers by electrospinning that are useful for a variety of applications. Air filters produced with PVDF are known to capture ionic particles with high efficiency. Existing studies have focused on the effects of electrospinning conditions on nanofiber morphology. In this study fibers were generated with varying morphologies. Air filters were then made from each sample and then characterized by TSI. Air filters were found to have increased resistances relative to their capture efficiencies according to particle diameter. Capture efficiencies did not correlate strongly with particle diameter, and the presence of beads in fiber samples did not have an impact on filter performance. Subsequent studies should focus on the development of statically charged PVDF mats to compare performance with the data generated by this study.

Executive Summary

Air pollution is a growing issue in developed and developing nations worldwide. Disease as a result from exposure to different kinds of air pollution is growing and research into different and more effective methods of preventing exposure to contaminated air has taken on an increased performance. Modern air filters for use in both commercial and industrial applications must be able to effectively remove extremely small quantities of hazardous materials from air, without causing excessive pressure drops or being prohibitively expensive or heavy. Electrospun PVDF nanofibers are a viable material for use in air filtration devices. This study explored the effects of different PVDF nanofiber morphologies and their effect on air filter performance. The study included the production of nanofibers using different electrospinning conditions, the characterization of fiber morphology by SEM imaging, and the assessment of air filter performance using TSI testing.

Fibers were produced via electrospinning using different acetone and DMF solvent ratios, PVDF concentrations, and with and without the addition of an acid to enhance conductivity. All other major electrospinning parameters were held constant for consistency. The produced fibers varied widely in diameter and morphology. Higher PVDF concentrations and higher acetone to DMF ratios (higher viscosity solutions) were found to produce larger diameter nanofibers, in agreement with theory. Lower PVDF concentrations produced smaller diameter nanofibers, but also introduced beads and less smooth fibers. The addition of trifluoroacetic acid (TFA) to enhance conductivity was not found to have a significant impact on fiber morphology, and did not significantly reduce the number or size of beads in low concentration solutions.

The resulting fiber sheets were tested with a TSI Model 8130 Automated Filter Tester. Filter efficiency, characterized by the removal of ions from a stream of air sent across the filter, was

reported along with the associated pressure drop. This data was then plotted against fiber diameter. Significant error existed in filtration testing due to inconsistent thickness of the spun sheets, as demonstrated in the measurements of mass per unit area for each sheet. Each air filter performed at a high level, but a consistent trend between fiber diameter and filter efficiency was not conclusively established. Larger fiber diameters did lead to smaller resistances, but this trend was also statistically weak. More consistent sheets and accurate testing are necessary to effectively quantify the relationship between fiber diameter and filter performance. A method of ensuring consistent sheet thickness or normalizing filter capture efficiency against sheet thickness may provide more accurate and precise data.

Future studies should build on the data generated by performing analysis on additional fiber morphologies. A more thorough analysis of fibers with similar diameters, with and without beads, and the effect of other conductivity additives should be explored. PVDF also has the ability to hold a static piezoelectric charge when properly conditioned. A study comparing identical sheets before and after the application of a charge may show great increases in capture efficiency at reduced pressure drops.

This project helped build understanding of electrospinning techniques, the characterization of nanofibers using SEM imaging, statistical analysis, and air filter performance. Additional skills gained include experimental design, and image analysis software proficiency. The results of this study should assist further studies into the use of PVDF in air filters, and provide a good basis for more detailed examination of specific performance characteristics or relationships between other morphologies and filter performance. In particular, future studies related to electret PVDF filters may use data from this study as a basis. Enhanced air filtration may lead to a reduction in disease related to air pollution and exposure to contaminated air, providing a positive benefit to society.

Introduction

Air pollution is a growing issue worldwide. The World Health Organization estimates that in 2012 alone 7 million people died prematurely as a direct result of exposure to air pollution (more than 1 in 8 global deaths) [1]. Industrial development, auto exhaust, and even dust storms are all potential sources of human health hazards [Na Wang]. New medical research has linked exposure to significant amounts of air pollution to cardiovascular disease and stroke [1]. Research and development into air filtration systems has taken on an increased importance with the rise of global air pollution, both for general indoor air filtration devices as well as protective equipment such as masks used in industrial settings [1, 2].

Traditional air filtration devices have relied on a variety of materials, ranging from cellulose to more advanced glass microfibers. Air filtration devices are characterized by their ability to remove particles from air (collection efficiency) and the associated pressure drop (resistance) [3]. Electrospun polymer fibers are widely used as air filters, and hold a number of potential advantages over other materials. First, electrospinning is capable of producing fibers of very small nanoscale diameter, which correlates with greater capture efficiency of small particles and ions, at the expense of higher pressure drops [4]. Second, different conditions may be applied during which affect fiber morphology (diameter, porosity, presence of beads, orientation, etc.) that may affect filter performance [5, 6].

Polymers with different characteristics may be chosen depending on the desired properties of the resulting filter media application [4, 7]. Poly(vinylidene fluoride) (PVDF) may be spun into nanofibers which have a number of attractive properties for air filtration devices. PVDF is lightweight and flexible, and also has the potential to hold a piezoelectric static charge due to its molecular structure [5, 8, 9]. Electrically charged polymers have the potential to capture ionic particles in air with lower pressure drops and higher efficiencies.

Existing studies have been performed relating the effects of different electrospinning conditions on the morphology of spun PVDF nanofibers. This study produced PVDF nanofibers under different conditions and assess their morphology with SEM imaging. The fibers were formed into large mats and tested as air filters using TSI testing to assess performance. The goal of the study is to relate how fiber morphology (namely diameter and presence of beads) affects filter performance, and provide a background for future studies which may apply electrical charges to PVDF filters for comparison.

Background

Several studies have already explored the electrospinning of PVDF and the general effects of working parameters on electrospinning [5-7]. These studies were reviewed to generate a set of fixed parameters to produce fibers and identify ways to easily manipulate fiber morphology. PVDF fibers are very sensitive to solution conductivity, concentration, and viscosity. At a key concentration, smooth fibers are likely to occur, while at incorrect concentrations, solutions will fail to spin or form beads and other undesirable structures [6, 10]. Conductivity also has a significant impact on fiber morphology, and increasing conductivity is expected to reduce the size and incidence of beads in nanofibers [5, 10-11]. To create solutions with varying viscosities and conductivities, the ratio of two solvents, DMF and acetone, was chosen as one manipulated variable for this study. In addition, some samples received an additive, trifluoroacetic acid, to increase conductivity in the hopes of producing a morphological difference. The fibers generated in this study were compared to those from researched literature to see if similar data results.

After producing fibers of varying morphology air filtration testing will proceed. Air filters are generally rated by their ability to capture small particles from air. In this case, an aerosol of an ionic compound, NaCl will be produced and sent across the filters. Concentration measurements taken upstream and downstream will be used to define penetration: $P = \frac{c_{down}}{c_{up}}$, which in turn defines efficiency: $\eta = 1 - P$ [3]. Another major consideration is the pressure drop caused by the air filter. In real-world applications, lower pressure drops are desirable, and may be required [2, 4]. From research, smaller and smoother fibers are expected to have higher capture efficiencies, but also larger associated pressure drops [2, 5, 12].

This study has generated new data regarding the relationship between fiber morphology and air filter performance specific to PVDF. The filter performance results of each sample and its morphology are presented and discussed. Results are compared to the trends established in literature.

Experimental Methods

Experimental Design and Materials

Six solutions were used to generate fibers according to different parameters. Dimethyl formamide (DMF) and acetone were chosen as solvents for powdered PVDF, sold under the trade name KYNAR 741 by Sigma Aldrich. The ratio of solvents, percentage PVDF by mass, and addition of trifluoroacetic acid (TFA) to solutions were used to vary solution concentration, viscosity, and conductivity to achieve different nanofiber morphology.

Table 1: Summary of sample solutions

Sample	Acetone:DMF Ratio	wt% PVDF	Addition of TFA
1	50:50	20	No
2	50:50	20	Yes
3	50:50	15	No
4	50:50	15	Yes
5	60:40	20	No
6	70:30	16	No

Electrospinning Setup

An existing electrospinning setup was used for generating all tested samples. The setup consists of a syringe pump connected with plastic tubing to an 18 Gauge needle which may be moved parallel to the collection surface to adjust the area of fiber deposition. A rotating collector attached to a belt drive motor covered with a sheet of 12” non-stick aluminum foil. A high voltage DC power supply was used to generate a potential between the needle and collector. The positive hot terminal was connected to the needle, while the negative terminal was connected to the collector, and grounded.

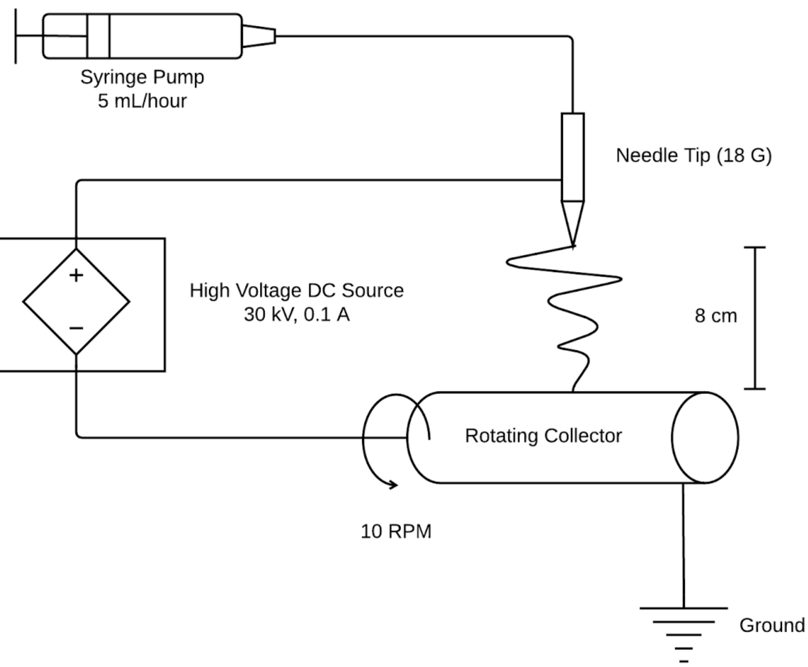

Figure 1: Diagram of electrospinning setup

Through research and initial experimentation, a set of working parameters were established which successfully generated nanofibers. The distance between the needle and collection surface, voltage, flow rate, and ambient temperature were held constant for all samples. All morphological differences in samples arose as a result of solution parameters, described in the materials section above. All constant factors related to electrospinning are tabulated below.

Table 2: Electrospinning parameters

Parameter	Value
Ambient temperature	70 degrees Fahrenheit
Needle to collector distance	8 cm
Voltage	30 kV
Collector rotational speed	10 RPM
Solution feed rate	5 mL/hour

To prevent major variations in thickness across the spun sheets, the needle was moved in fixed positions along the length of the rotating collector, with 5 mL deposited at each position until the entire surface was covered.

To ensure that all solvent evaporated prior to imaging and filtration testing, all samples were placed in an oven at 85 Celsius overnight after spinning.

SEM

A Hitachi TM3000 Tabletop scanning electron microscope was used for fiber characterization. All successful samples were imaged at low magnification to produce images for use in the results section and qualitative observation, as well as three times at high magnifications sampled from different regions of the sheet for software analysis.

The analysis of SEM images was performed by FibraQuant software. Images from each sample were analyzed for fiber diameter. Detailed fiber diameter distributions will be presented for each sample later in this report, along with relevant statistics.

Filter Characterization

Filter characterization was performed using a TSI Model 8130 Automated Filter Tester. A 2 wt% sodium chloride solution was used for testing at a 10 L/min flow rate using a 2.25” orifice. Resistance (pressure drop) and the % penetration were measured using a standard filter test for each sample. All samples were tested three times from different regions of the nanofiber sheet to accommodate possible variations in sheet thickness or fiber morphology.

All fiber sheets were also cut into 100 square centimeter sheets for a large sample, and weighed. This value of mass per unit area was meant to serve as a pseudo thickness measurement, and possibly explain large differences among samples that may have different thicknesses or densities.

Data and Results

Fiber Morphology

Images of nanofibers generated from each solution are shown below for qualitative observations, along with graphs of fiber diameter distribution.

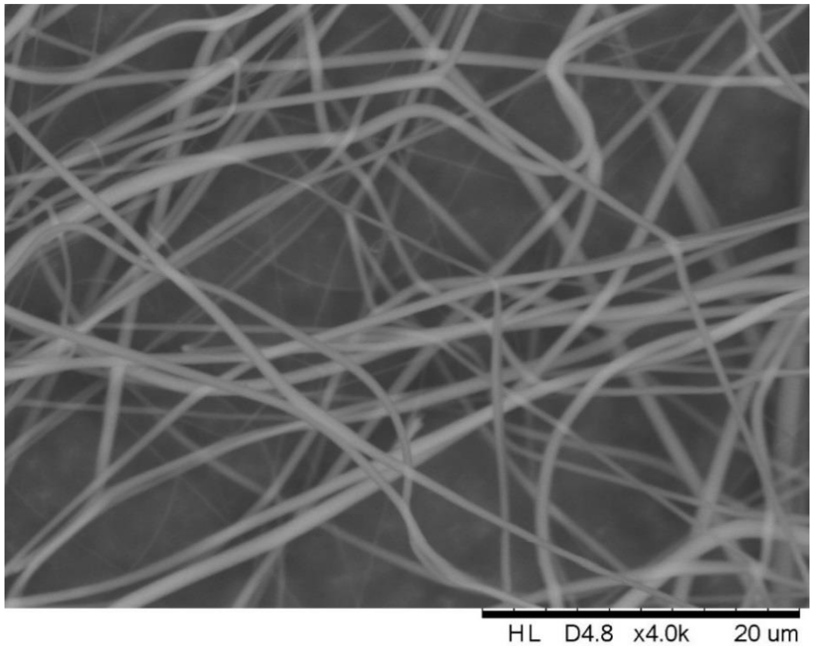

Figure 2, Sample 1: fibers generated from 20 wt.% PVDF in 50:50 acetone:DMF

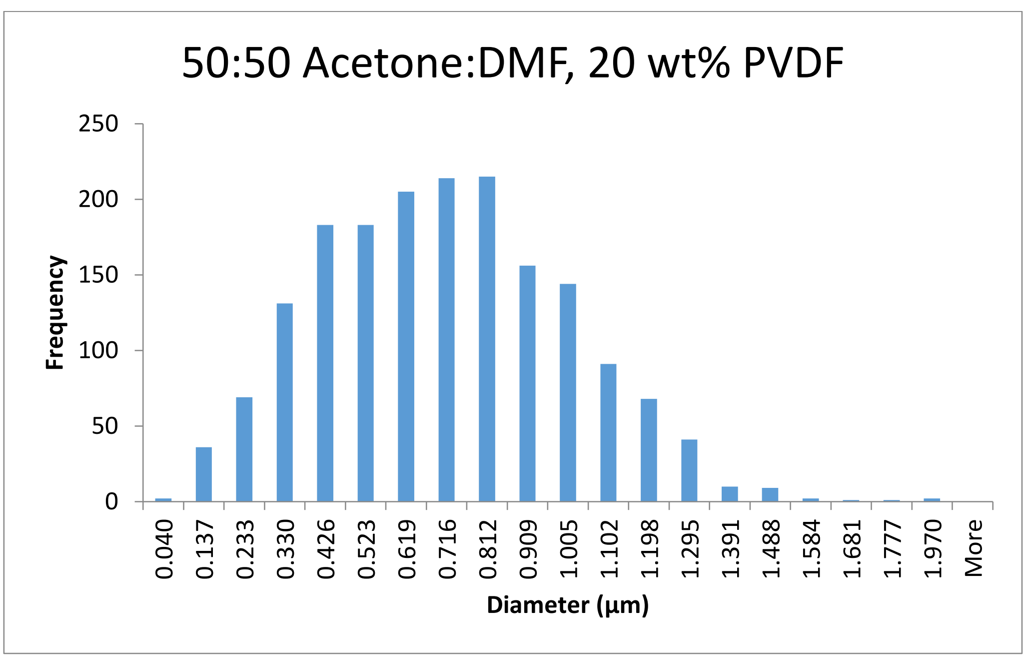

Figure 3: Sample 1 fiber distribution graph

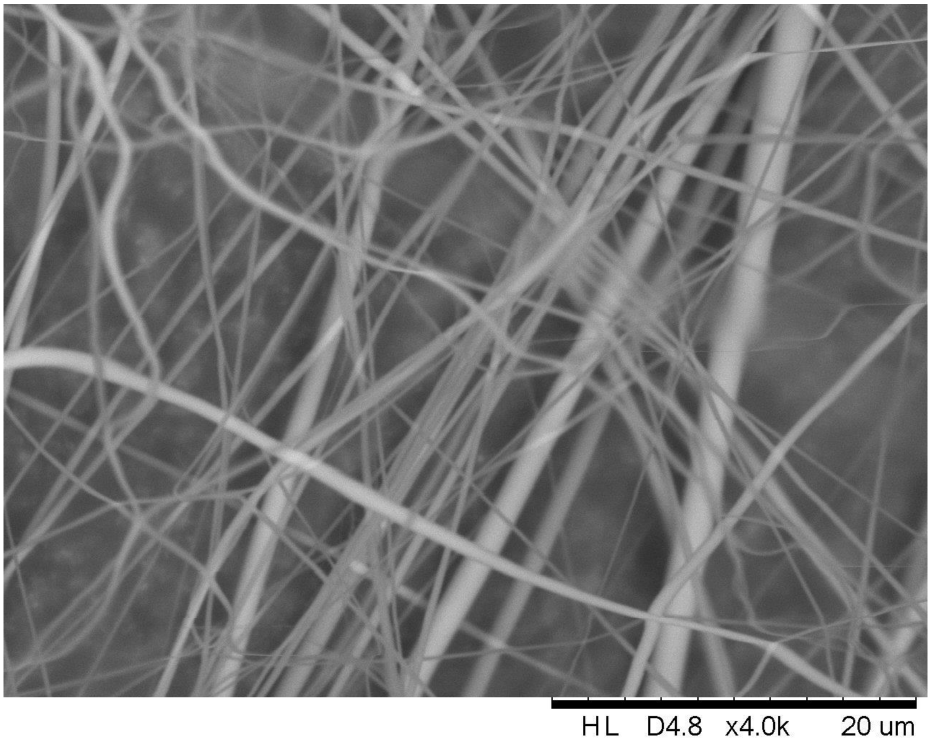

Figure 4, Sample 2: fibers generated from 20 wt.% PVDF in 50:50 acetone:DMF with TFA

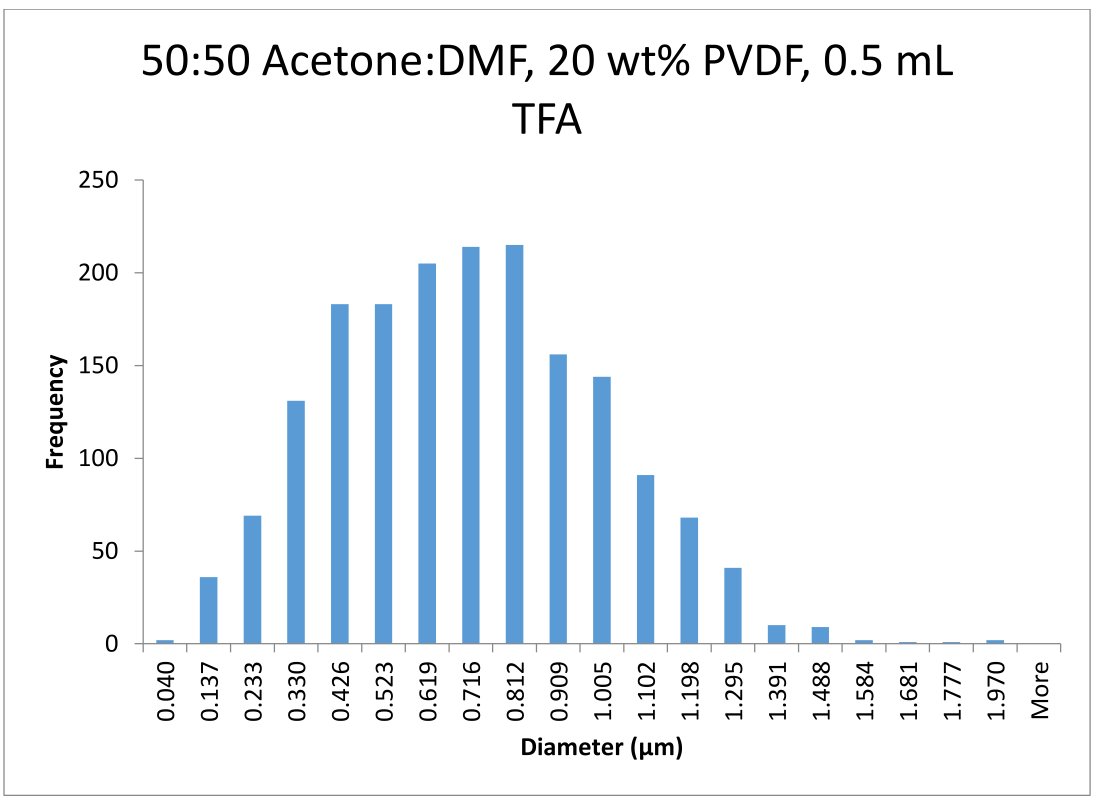

Figure 5: Sample 2 fiber distribution graph

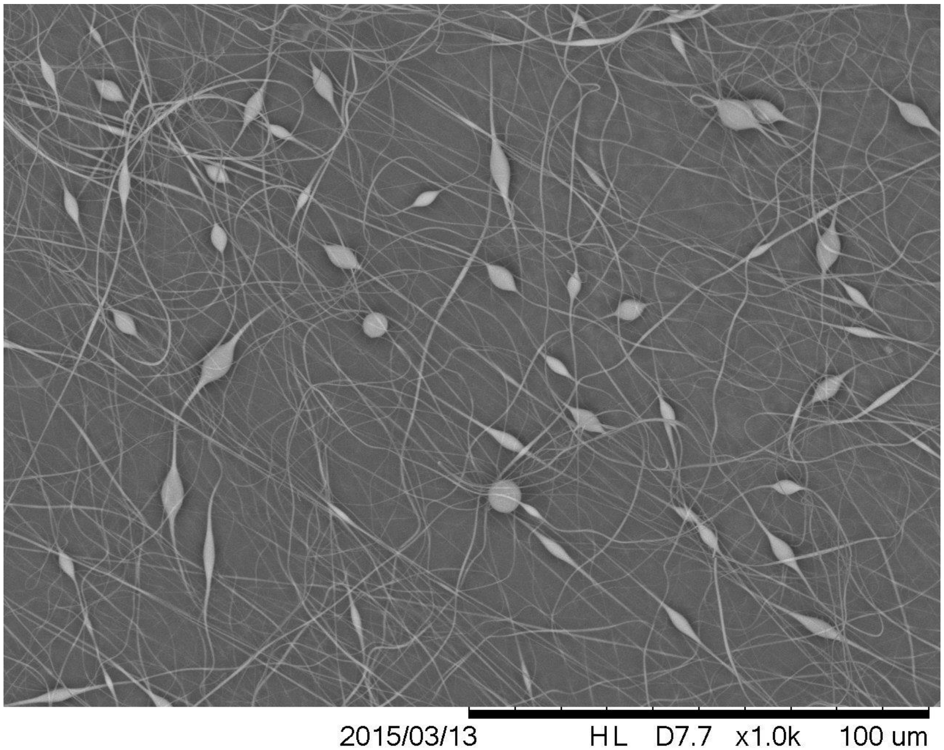

Figure 6, Sample 3: fibers generated from 15 wt.% PVDF in 50:50 acetone:DMF

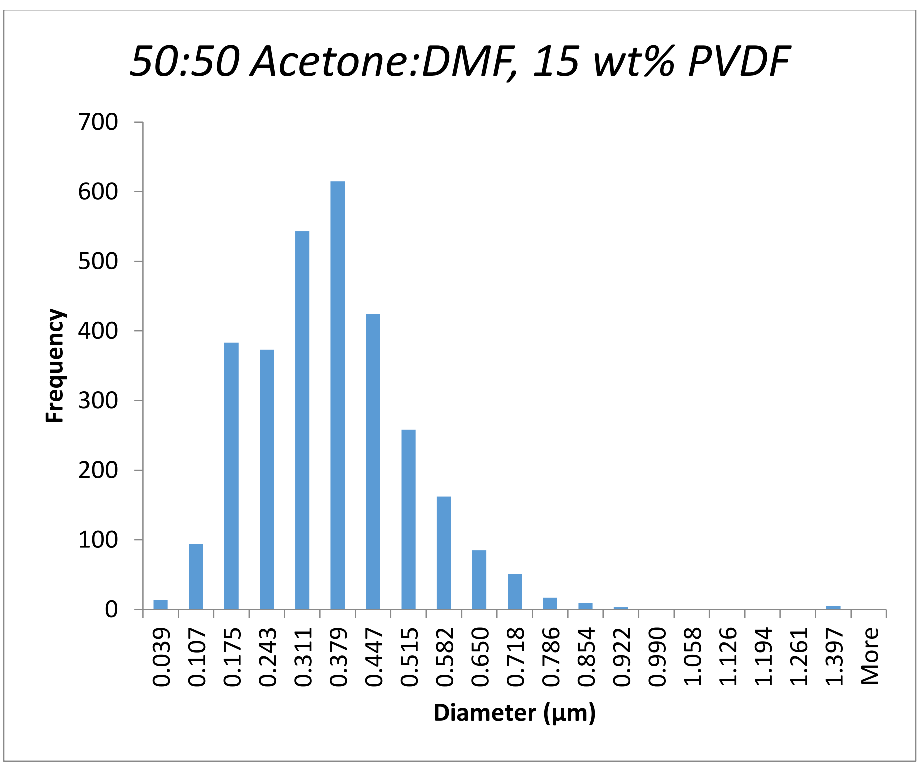

Figure 7, Sample 3: fiber distribution graph

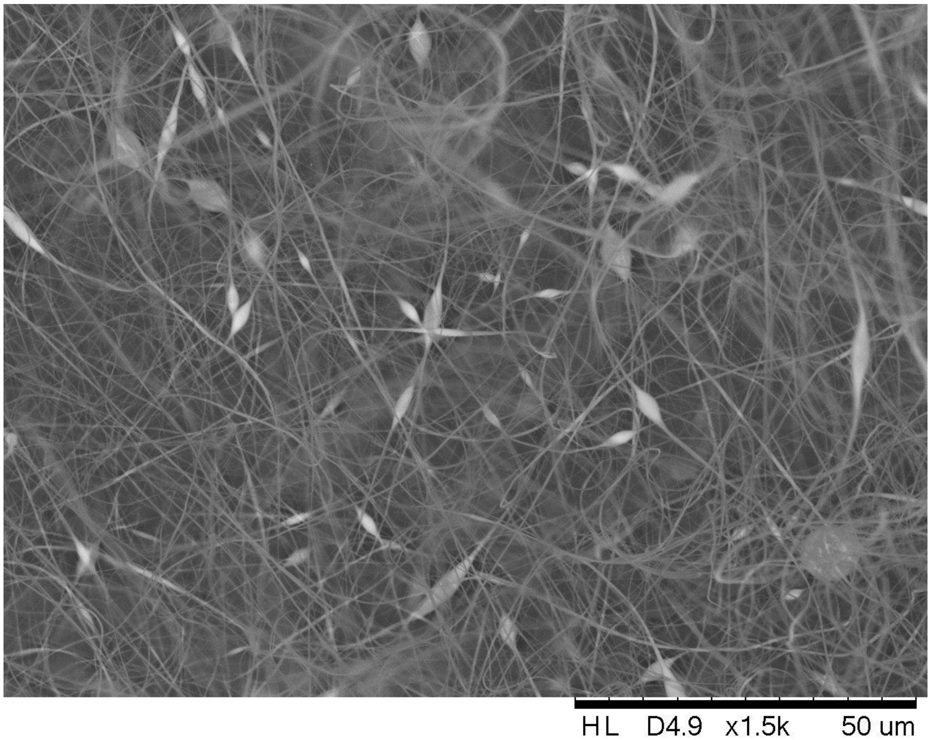

Figure 8, Sample 4: fibers generated from 15 wt.% PVDF in 50:50 acetone:DMF with TFA

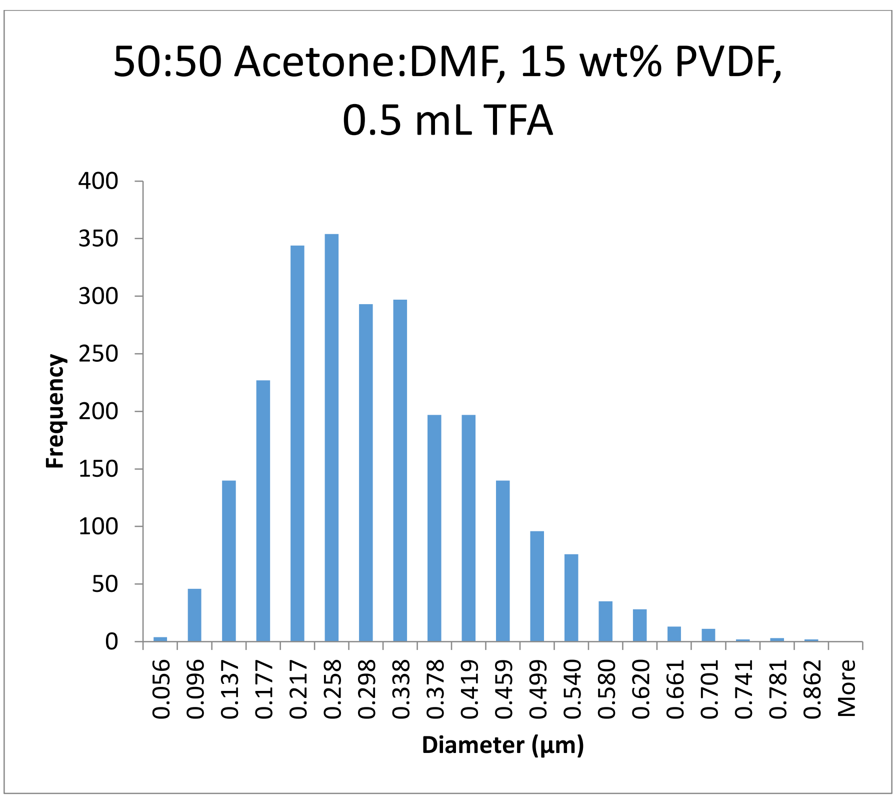

Figure 9, Sample 4: fiber distribution graph

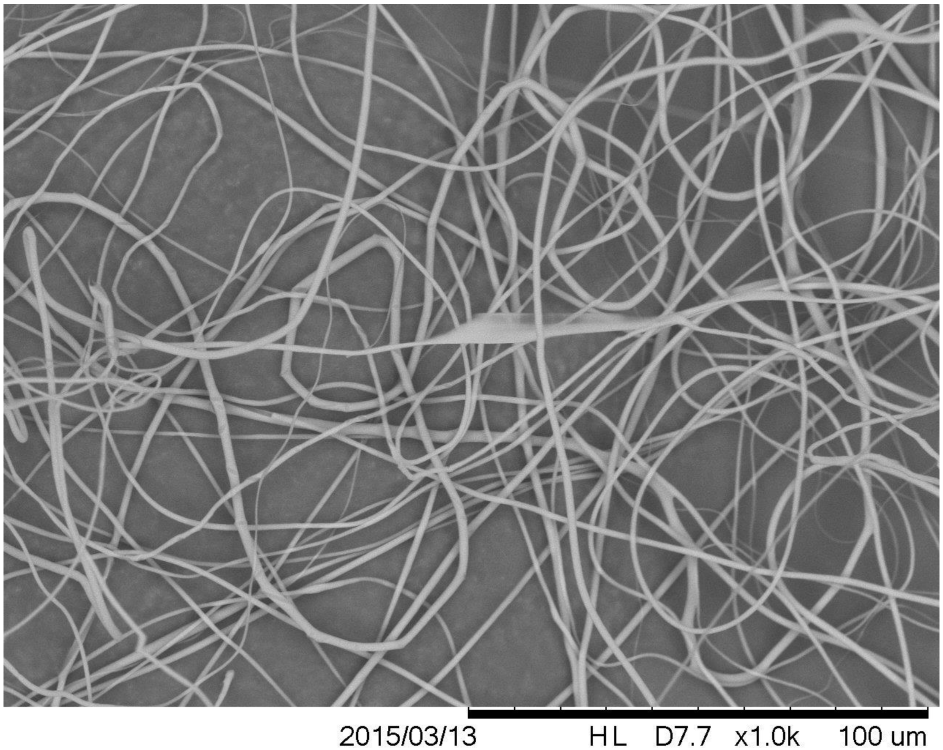

Figure 10, Sample 5: fibers generated from 20 wt.% PVDF in 60:40 acetone:DMF

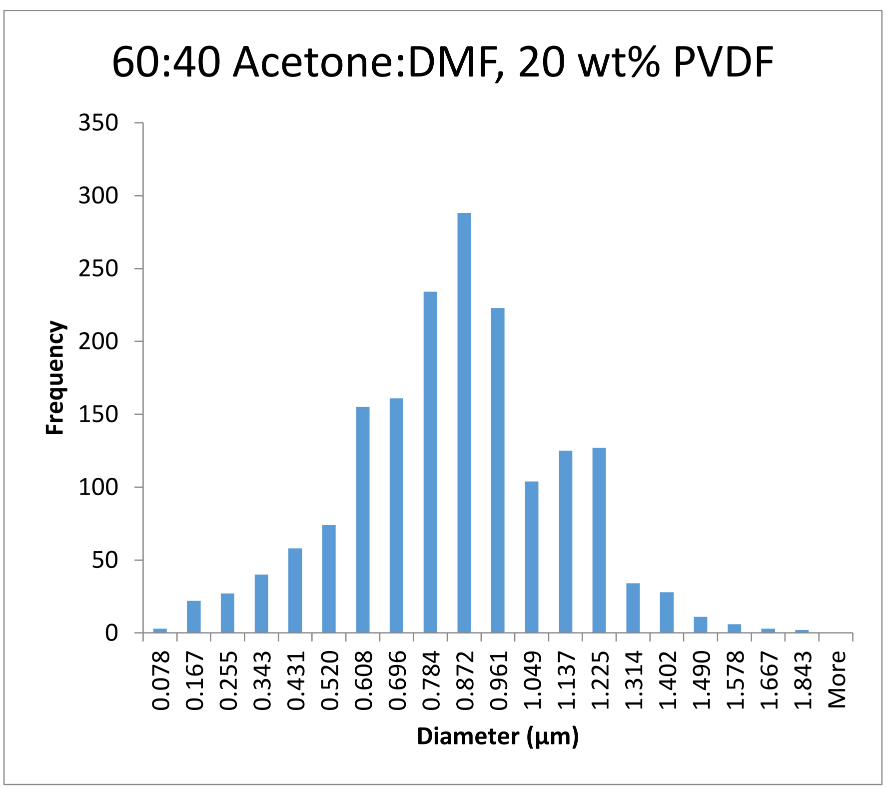

Figure 11, Sample 5: fiber distribution graph

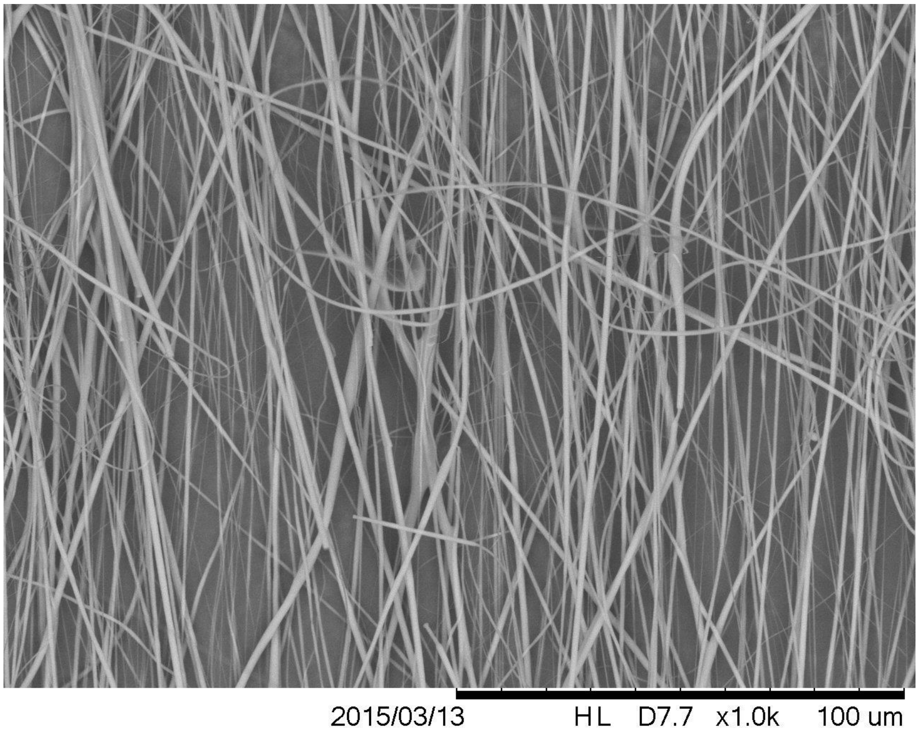

Figure 12, Sample 6: fibers generated from 16 wt.% PVDF in 70:30 acetone:DMF

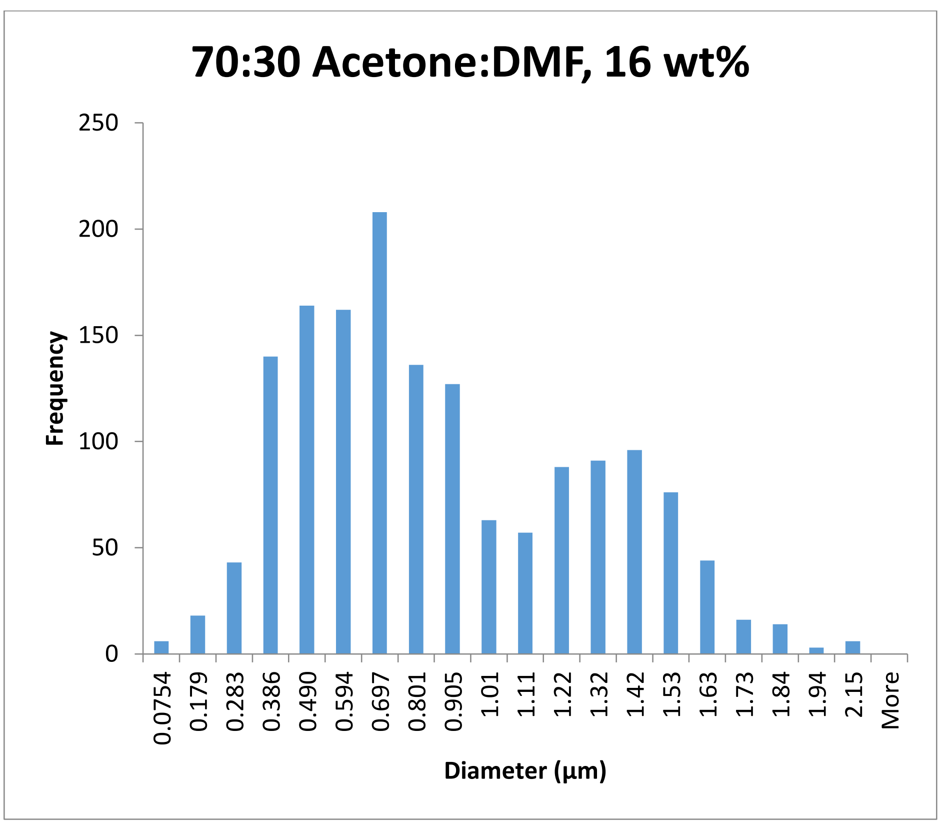

Figure 13, Sample 6: fiber distribution graph

Filter Performance

Data from TSI testing, including resistance, penetration %, and efficiency is tabulated below. All reported values are averages from multiple samples. Standard errors are presented alongside them to reflect sample variation. Data trends are also presented in the form of graphs.

Table 3: Filter performance data

Sample	Fiber Diameter (µm)	Resistance (mmH20)	Penetration %	Efficiency %
1	0.563 ± 0.00462	28.6 ± 1.22	1.31 ± 0.459	98.691 ± 0.459
2	0.653 ± 0.00698	34.3 ± 8.95	1.18 ± 0.636	98.818 ± 0.636
3	0.333 ± 0.00279	47.7 ± 5.42	0.05 ± 0.008	99.945 ± 0.008
4	0.297 ± 0.00248	59.5 ± 7.94	0.10 ± 0.046	99.898 ± 0.046
5	0.810 ± 0.00643	30.8 ± 0.06	0.25 ± 0.010	99.753 ± 0.010
6	0.848 ± 0.0103	50.5 ± 2.66	0.05 ± 0.029	99.945 ± 0.029

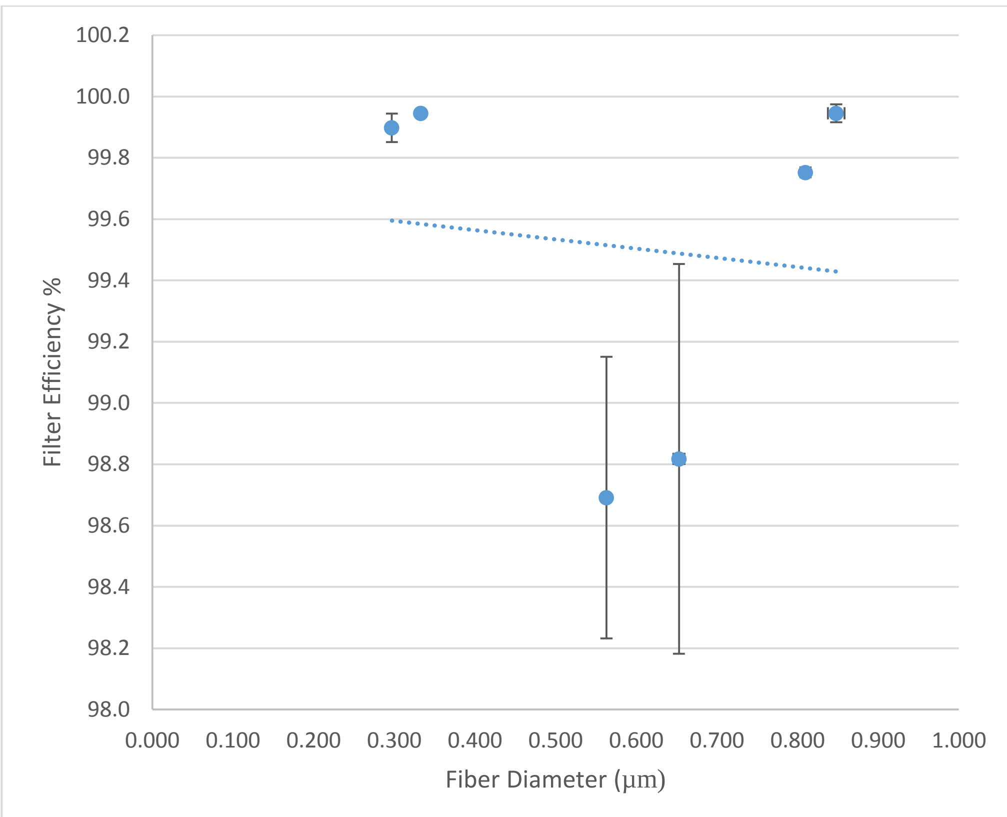

Figure 14: Filter efficiency % versus fiber diameter

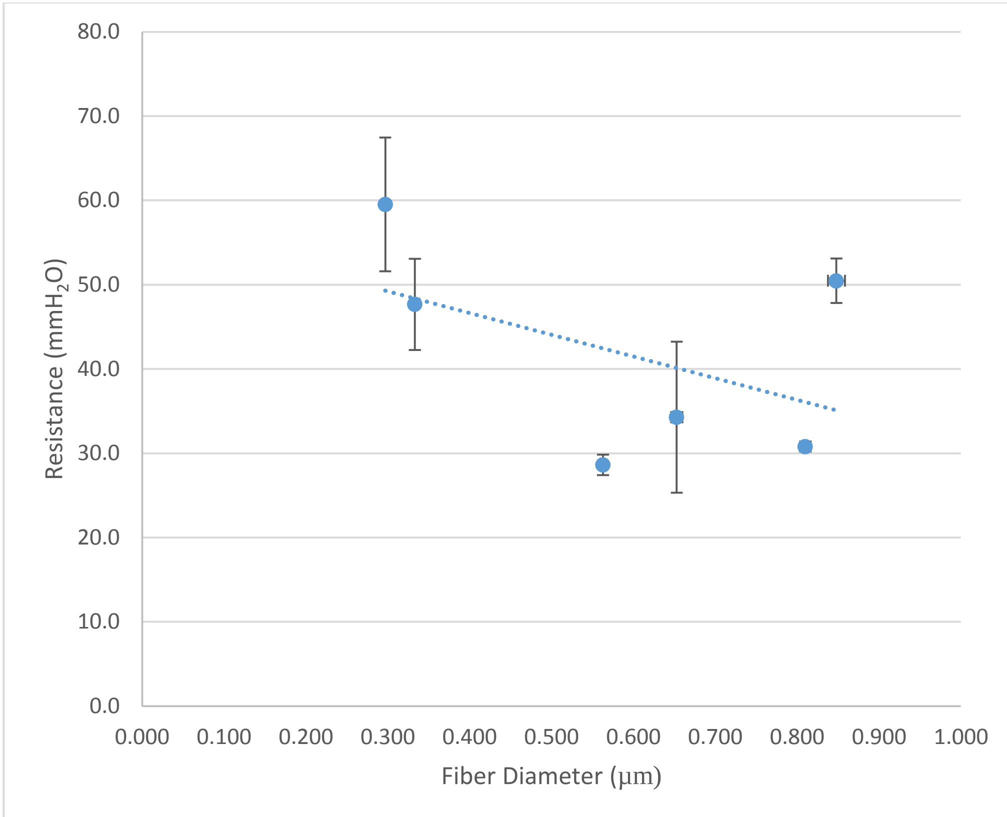

Figure 15: Resistance versus fiber diameter

Each filter was measured for mass per unit area as a way to gauge the relative thickness of the sheet, as shown below:

Table 4: Sample mass per unit area

Sample	Mass/area (g/sq. cm)
1	0.00480
2	0.00407
3	0.00402
4	0.00332
5	0.00451
6	0.00621

Discussion and Analysis

The data presented in the results section has indicated a number of useful facts about PVDF and its effectiveness in air filtration. Fibers produced with higher acetone/DMF solvent ratios and higher PVDF concentrations tended toward larger fiber diameters, in agreement with theory and established research. Both of these factors increase viscosity and reduce conductivity, causing larger fibers. Additionally, at 15 wt% PVDF, beads were found to form in all samples. Treatment with trifluoroacetic acid was found to have a negligible impact on the size and number of beads formed, indicating that further study on other additives may be necessary on increasing solution conductivity and the impact on bead formation.

All filters produced as part of this experiment filtered at high rates of efficiency coming very close to HEPA efficiency compliance (99.95%). The presence of beads in samples in this report was mitigated by the small particle size and filters containing beads performed similarly to non-beaded filters. Trends between filter efficiency and fiber diameter, as well as between resistance and fiber diameter were too weak to be considered conclusive. More data and greater precision may be necessary to fully quantify consistent relationships.

Filtration testing showed significant error when compared with the measurement of fiber diameter. Results varied widely when different regions of a sheet were tested using identical methods. This indicates that the control of sheet thickness was not adequate, and that thin or thick regions forming on each sheet had a significant effect on testing. Measurements made on sheet mass per unit area help explain the more extreme cases of different penetration numbers, in particular sample 6 was much more dense than other sheets, which likely contributed to high capture efficiency. Additional controls or better procedures may be necessary to generate more consistent fiber sheets. A method for normalizing values relative to sheet thickness may also provide more data consistency.

Conclusions

This project was meant to provide additional insight into the performance of PVDF air filtration devices. Fibers were generated using different electrospinning methods and found to conform to the behaviors in established literature. Data gathered on air filtration performance showed showed that smaller fiber diameters produced greater resistances but also that capture efficiency did not have a significant statistical correlation with fiber diameter. Measurements were likely error prone due to variations in local sheet thicknesses, as demonstrated by measurements of mass per unit area for each sheet. Additional work is necessary to generate more data with greater precision, and to evaluate the performance of electrically charged PVDF versus existing filters.

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