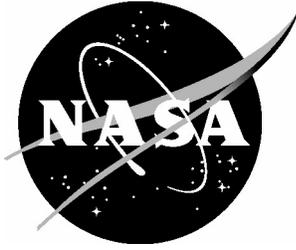


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# Electrospinning of Polyvinylidene Fluoride and Polyetherimide From Mixed Solvents

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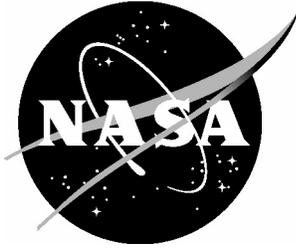
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## Abstract

Polyvinylidene fluoride and Ultem™ polyetherimide were dissolved in 50/50 acetone/N,N dimethylformamide (DMF) and 80/20 tetrahydrofuran/DMF, respectively, and electrospun. Polymer solution concentrations and molecular weights were changed while other spinning parameters (voltage, distance, solution feed rate) were held constant. Fiber diameters in the resulting electrospun mats varied from 0.25 to 4.4 microns, increasing with polymer concentration and molecular weight; trends in diameter were compared with trends in viscosities and surface tensions of the spinning solutions.

## Introduction

In electrospinning, a jet of polymer solution or melt is ejected from the tip of a charged capillary and deposits onto a grounded grid or plate. Electrospun fibers have small diameters (down to tens of nanometers) and high surface areas, suggesting potential applications as tissue scaffolds, filtration media, templates for catalysts, and gossamer structural materials (1,2).

The degree of success obtained when attempting to electrospin a given solution -- as well as the resulting fiber diameter -- may depend on polymer molecular weight and concentration (3), viscosity, surface tension, flow rate, charge density, conductivity, solvent volatility, and tip-to-collector distance (4). The present study narrows the number of variables considered and compares fibers spun from mixed solvents under standardized conditions. Two polymers were chosen: one, polyvinylidene fluoride (PVDF), is of interest because certain crystal forms are ferroelectric; the other, polyetherimide (PEI), is a comparatively thermally-stable, soluble, amorphous thermoplastic.

## Experimental

*Materials* Sources of the polymers and molecular weights specified by the suppliers are given in Tables 1 and 2. Previous experience (5) with spinning these polymers guided the choice of solvents and the concentration ranges. For the concentration study, PVDF530 was dissolved in 50/50 (by weight) acetone/dimethylformamide (DMF) at concentrations  $c=12.5$ , 15, and 16.5 weight percent solids; PEI38 was dissolved in 80/20 (weight) tetrahydrofuran (THF)/DMF at 10, 15, and 20 % solids. For the molecular weight study, the polymers were dissolved in the respective solvents at 15 % (for PVDF) or 10% (for PEI). Solutions were prepared by stirring overnight with warming to 45°C and were used within 8 hours. Upon standing in sealed containers for a day or so, some solutions became cloudy; this was thought to be due to crystallization.

**Table 1: PVDF samples**

Designation	Source	Molecular weight ( $M_w$ ) (kg/mol)
PVDF60	Polysciences	60
PVDF275	Aldrich	275
PVDF530	Aldrich	530

**Table 2: PEI samples (source: GE)**

Designation	Mfr's number	Molecular weight, kg/mol
PEI23	Ultem™ 1040	23.1
PEI33	Ultem™ 1010	33.2
PEI38	Ultem™ 1000	38.3

*Solution characterization* Surface tension was determined via the Du Nouy ring method using a Dynamic Contact Angle Meter and Tensiometer (DCAT) from DataPhysics Corporation. Apparent surface tension increased slightly with time during 200 seconds of measurement, typically by 0.2 mN/m. Data were taken both pushing and pulling the ring and an overall mean value was calculated by the instrument's SCAT software. Measurements taken on two separate days were averaged.

Viscosity measurements were taken in triplicate using oscillatory parallel plate geometry ( $10 \text{ sec}^{-1}$ , 10% strain) in a Rheometric Scientific ARES rheometer. In all cases, apparent viscosity increased fairly steadily with time – by up to a factor of 5 over a period of 10 minutes. This is thought to be due to solvent evaporation from the edge of the sample volume. Tabulated values are therefore average extrapolations to zero time.

In preliminary experiments aimed at the eventual study of conductivity effects, it was found that tetraethylammonium tetrafluoroborate and tetraethylammonium p-toluenesulfonate were soluble in the PVDF and PEI solutions respectively. A YSI 3200 conductivity instrument was employed with a 3256 probe to find solution conductivities in the range of 100-1000 microS/cm. These solutions were not spun, however, so the data were not used in the following.

*Electrospinning* Figure 1 is a photograph of the experimental set-up. It consisted of a syringe pump, a high-voltage dc power supply connected to the blunt syringe needle, and a grounded collection drum that was rotated by a small dc motor about an axis perpendicular to the spinning direction. The collector rotation resulted in some degree of fiber alignment, although alignment was not a subject of this study. A fume hood provided ventilation. Spinning conditions were held constant for each polymer and are given in Table 3. Ambient temperature was 25°C and relative humidity was 50-60%.



Figure 1: Electrospinning apparatus

**Table 3. Experimental parameters**

Setting	PVDF	PEI
DC voltage, kV	15	15
Needle-drum distance, cm	22.9	17.0
Volumetric flow rate, ml/hr	6.00	5.00

*Fiber characterization* Fiber mats were sputter-coated with Au-Pd and imaged using a JEOL JSM-5600 scanning electron microscope. Images (2000x magnification) were analyzed using ImageTool™ software. To minimize size errors resulting from parallax, diameter data from 15 to 20 of the fibers closest to the mat surface were averaged. Results are reported as mean±standard deviation. Wherever possible, diameters were determined in three different places along the length of a fiber in order to account for diameter variations. When beads were present on the fibers, they were not included as part of the fiber diameter.

## Results and Discussion

*Concentration study* PVDF530 and PEI38 were successfully spun at all three concentrations. For both polymers, however, the lowest concentration gave fibers with beads (Figures 2 and 3).

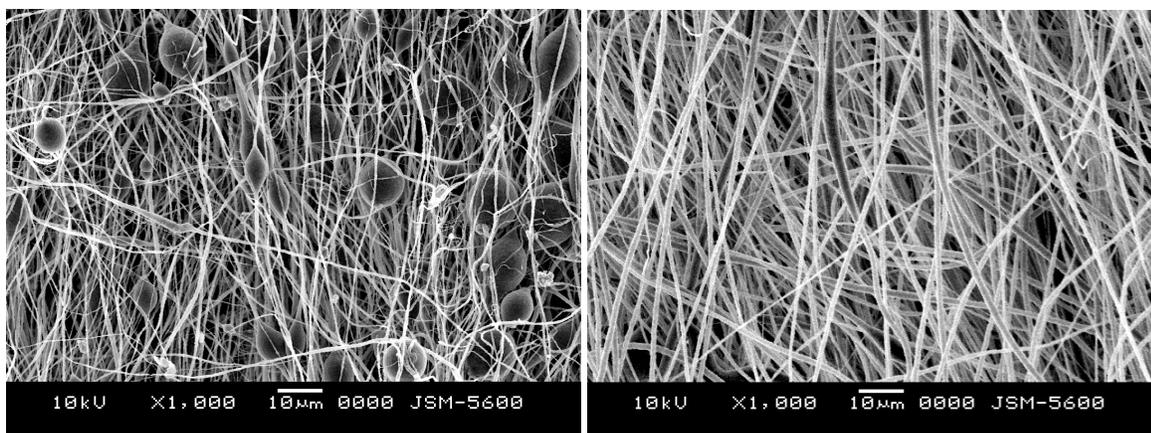


Figure 2 PVDF530 spun from a) 12.5% and b) 15 wt.% solution in 50/50 acetone/DMF.

Transitions from i) electrospinning of droplets to ii) spinning of beaded fibers to iii) spinning of uniform fibers have often been reported in the literature. Recently, attempts have been made to explain such transitions in terms of interchain contacts (3,6). The critical concentration for chain overlap is  $c^*=1/[\eta]$ , where  $[\eta]$  is the polymer intrinsic viscosity. Depending on the polymer molecular weight distribution, Gupta *et. al.* (3) found that  $c/c^*\geq 6-10$  gave uniform fibers. Intrinsic viscosities of our polymers were not measured as a part of this study, but literature data in good solvents (7,8) suggest  $c^*= 1\%$  for PVDF530 and  $c^*=2.3\%$  for PEI38, so Figures 2b and 3b correspond to  $c/c^*= 15$  and 6.5, respectively. The mat appearance is thus very roughly consistent with Gupta's experience.

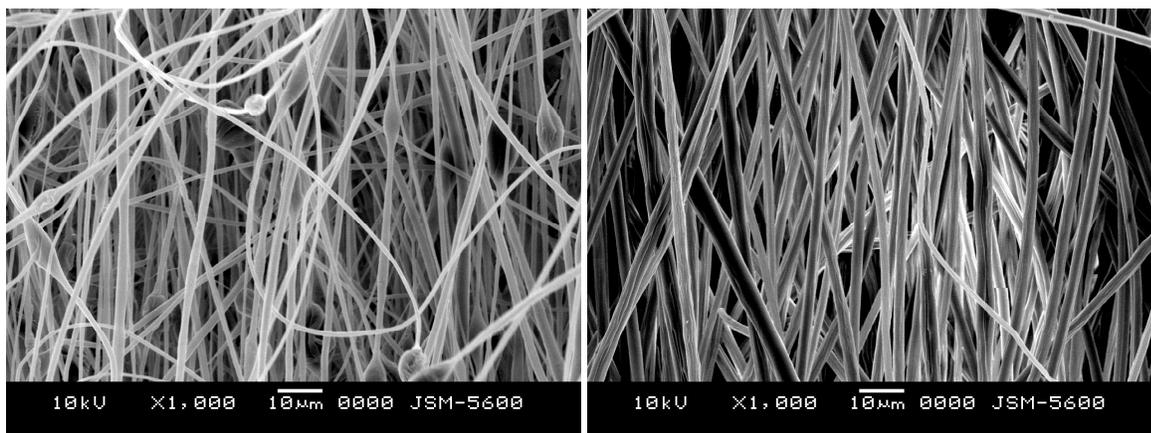


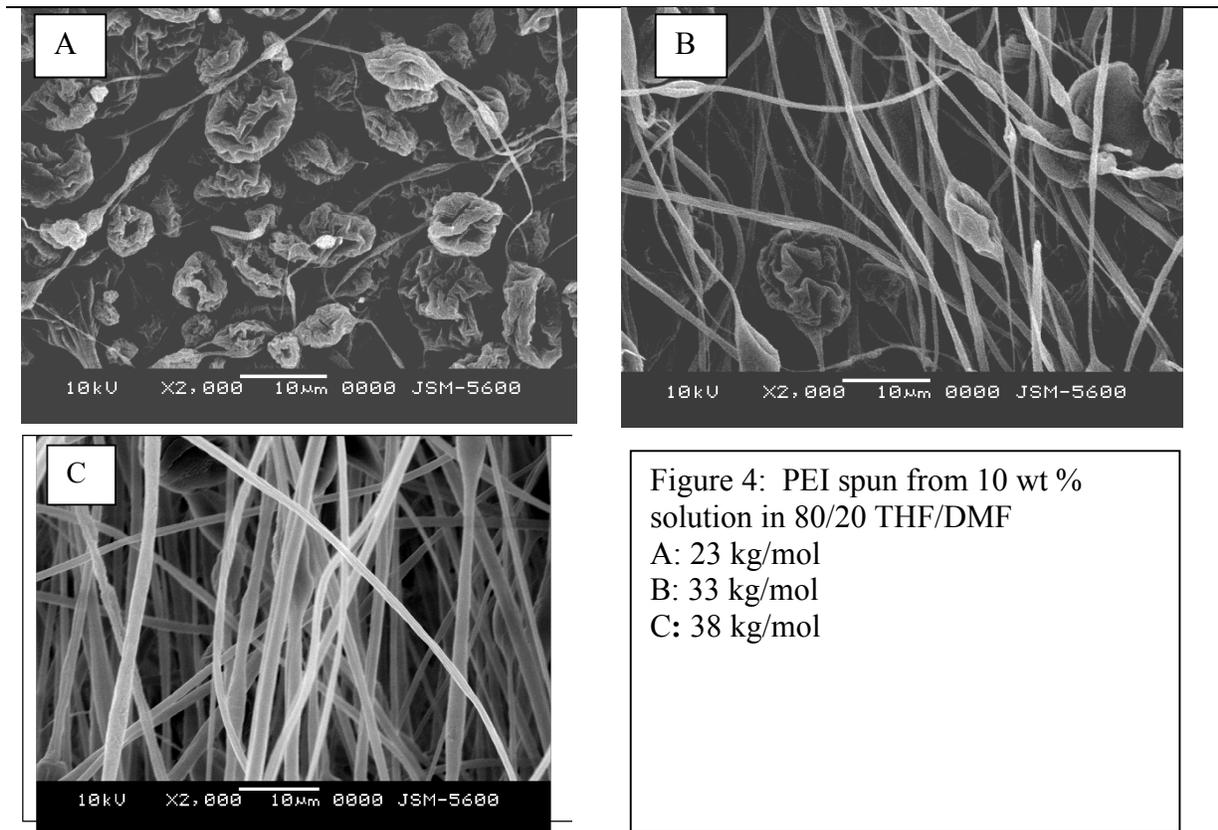
Figure 3. PEI38 spun from a) 10 and b) 15 wt % solution in 80:20 THF/DMF.

As shown in Table 4, surface tensions of the solutions did not vary noticeably with polymer concentration. Viscosity, on the other hand, increased as expected. The effect of concentration on fiber diameter will be discussed in the next section.

**Table 4: Concentration effect**

Solution [Polymer]	Surface tension mN/m	Viscosity (Pa-s)	Mean Fiber Diameter ( $\mu\text{m}$ ) $\pm$ s.d.
12.5 wt.% PVDF530	27.5 $\pm$ 0.5	0.77	0.57 $\pm$ 0.19
15.0 wt.% PVDF530	27.8 $\pm$ 0.3	1.45	1.22 $\pm$ 0.46
16.5 wt.% PVDF530	28.1 $\pm$ 0.1	2.31	1.25 $\pm$ 0.61
10.0 wt.% PEI38	27.8 $\pm$ 0.1	20 $\pm$ 5	1.35 $\pm$ 0.42
15.0 wt.% PEI 38	27.78 $\pm$ .09	112.1	2.42 $\pm$ 0.79
20.0 wt.% PEI 38	28.1 $\pm$ 0.1	213.3	4.35 $\pm$ 1.19

*Molecular weight study* At the lowest molecular weight, 60 kg/mol, PVDF formed beads with trailing fibers. A similar phenomenon was seen with PEI at the two lower molecular weights. The morphology changes are depicted in the SEM images of Figure 4.



Not surprisingly, the mean fiber diameter shows an increase with increasing molecular weight for both polymer series (Table 5).

**Table 5: Molecular Weight Effect**

Solution	Surface tension, mN/m	Viscosity (Pa-s)	Fiber Diam., micrometers $\pm$ s.d.
15.0 wt.% PVDF60	27.57 $\pm$ 0.45	0.12	0.25 $\pm$ 0.16
15.0 wt.% PVDF275	27.53 $\pm$ 0.46	0.26	0.47 $\pm$ 0.17
15.0 wt.% PVDF530	27.84 $\pm$ 0.30	1.45	1.22 $\pm$ 0.46
10.0 wt.% PEI23	27.87	70 $\pm$ 30	0.43 $\pm$ 0.13
10.0 wt.% PEI33	27.91 $\pm$ 0.15	43 $\pm$ 2	0.86 $\pm$ 0.39
10.0 wt.% PEI38	27.76 $\pm$ 0.09	20 $\pm$ 5	1.35 $\pm$ 0.42

When the PVDF data in Table 5 are combined with those in the preceding section, it appears that fiber diameter correlates well with solution viscosity (Figure 4).

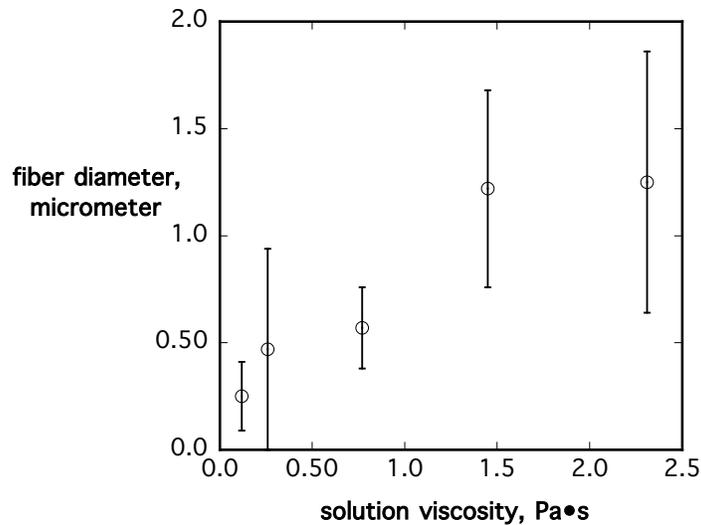


Figure 4. Diameter of electrospun PVDF vs. viscosity of spinning solution (various molecular weights and concentrations).

### Conclusion

It has been shown that the diameters of PVDF and PEI fibers electrospun from mixed solvents increase with increasing solution concentration or molecular weight. For the PVDF, solution viscosity was a good predictor of fiber diameter within the range of concentrations and molecular weights studied. Surface tension did not vary significantly in this range.

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