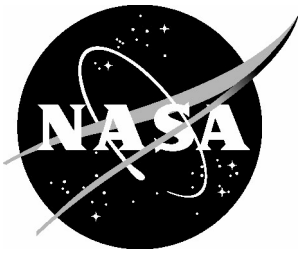
NASA/TM-2005-213786



Electrospinning of Polyvinylidene Fluoride and Polyetherimide From Mixed Solvents

Leslie D. Morgret
University of Colorado, Boulder, Colorado

Kristin J. Pawlowski and Jeffrey A. Hinkley
Langley Research Center, Hampton, Virginia

July 2005

The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the lead center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counterpart of peer-reviewed formal professional papers, but having less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results ... even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at ***http://www.sti.nasa.gov***

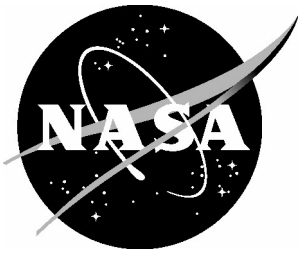
- E-mail your question via the Internet to help@sti.nasa.gov

- Fax your question to the NASA STI Help Desk at (301) 621-0134

- Phone the NASA STI Help Desk at (301) 621-0390

- Write to:
  NASA STI Help Desk
  NASA Center for AeroSpace Information
  7121 Standard Drive
  Hanover, MD 21076-1320

NASA/TM-2005-213786



Electrospinning of Polyvinylidene Fluoride and Polyetherimide From Mixed Solvents

Leslie D. Morgret
University of Colorado, Boulder, Colorado

Kristin J. Pawlowski and Jeffrey A. Hinkley
Langley Research Center, Hampton, Virginia

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23681-2199

July 2005

Available from:

NASA Center for AeroSpace Information (CASI)
7121 Standard Drive
Hanover, MD 21076-1320
(301) 621-0390

National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161-2171
(703) 605-6000

Electrospinning of Polyvinylidene Fluoride and Polyetherimide from Mixed Solvents

Leslie D. Morgret, University of Colorado
Kristin J. Pawlowski and Jeffrey A. Hinkley
NASA Langley Research Center

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 ($10\ sec^{-1}$, 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%.

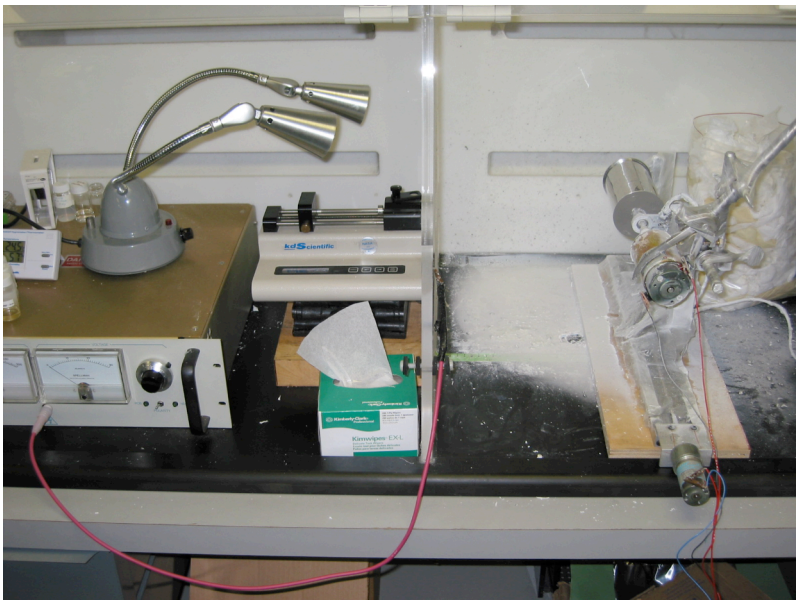


Figure 1: Electrospinning apparatus

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).

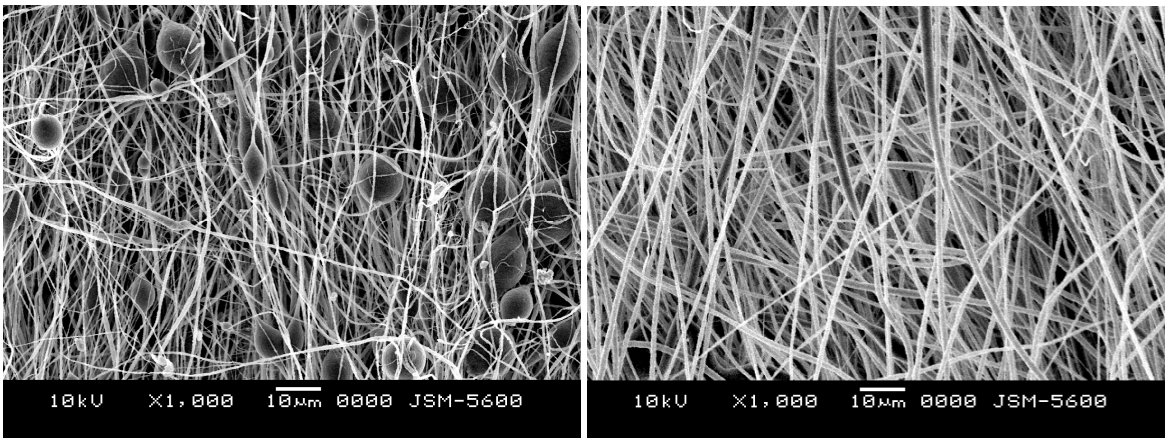


Figure 2 PVDF530 spun from a) 12.5% and b) 15 wt.% solution in 50/50 acetone/DMF.

Transitions from i) electrospraying 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 $c/c^* \geq 6\text{-}10$ 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.

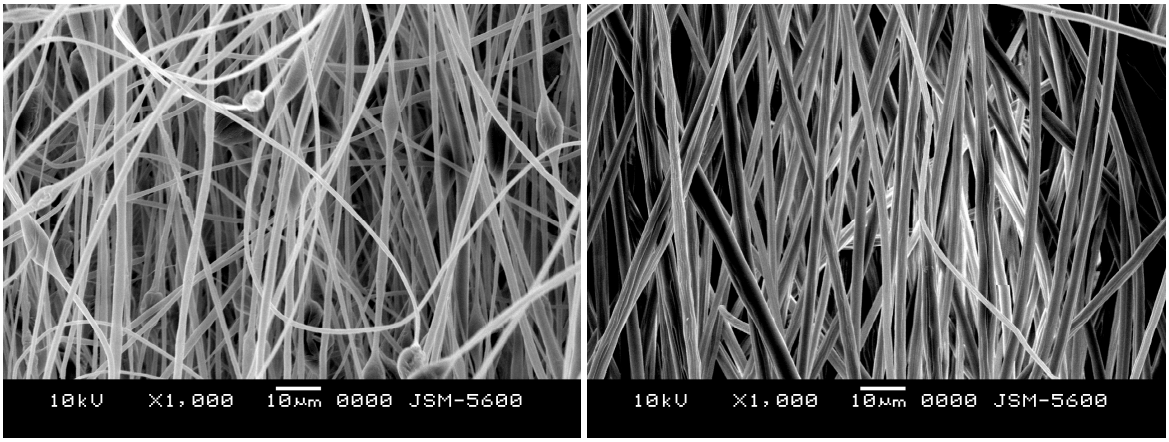


Figure 3. PEI38 spun from a) 10 and b) 15 wt % solution in 80:20 THF/DMF.

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 (μm) ±s.d.
12.5 wt.% PVDF530	27.5±0.5	0.77	0.57±0.19
15.0 wt.% PVDF530	27.8±0.3	1.45	1.22±0.46
16.5 wt.% PVDF530	28.1±0.1	2.31	1.25±0.61
10.0 wt.% PEI38	27.8±0.1	20±5	1.35±0.42
15.0 wt.% PEI 38	27.78±.09	112.1	2.42±0.79
20.0 wt.% PEI 38	28.1±0.1	213.3	4.35±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.

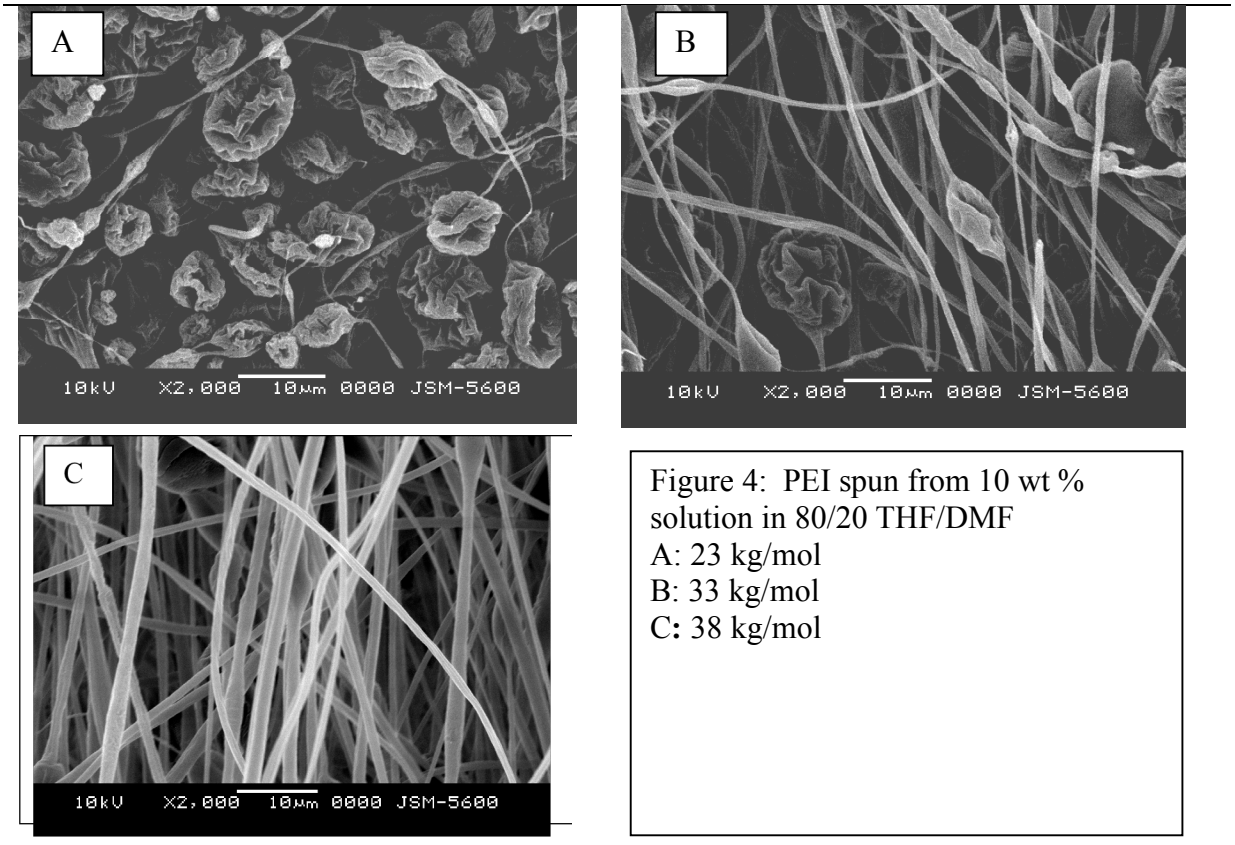


Figure 4: PEI spun from 10 wt % solution in 80/20 THF/DMF
A: 23 kg/mol
B: 33 kg/mol
C**:** 38 kg/mol

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 ± s.d.
15.0 wt.% PVDF60	27.57±0.45	0.12	0.25±0.16
15.0 wt.% PVDF275	27.53±0.46	0.26	0.47±0.17
15.0 wt.% PVDF530	27.84±0.30	1.45	1.22±0.46
10.0 wt.% PEI23	27.87	70±30	0.43±0.13
10.0 wt.% PEI33	27.91±0.15	43±2	0.86±0.39
10.0 wt.% PEI38	27.76±0.09	20±5	1.35±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).

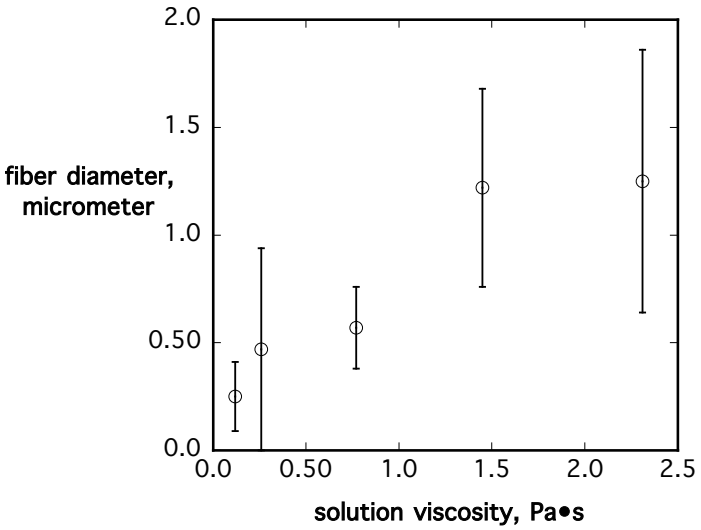


Figure 4. Diameter of electrospun PVDF vs. viscosity of spinning solution (various molecular weights and concentrations).

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.

References

1. White, K.; Lennhoff, J.; and Miller, J.: Application of Electrospinning to the Reinforcement of Gossamer Space Structures, presented at *International Nonwovens Technical Conference 2003* Baltimore, MD, 15-18 September 2003.

2. Pawlowski, K. J.; Belvin, H. L.; Raney, D. L.; Su, J.; Harrison, J. S.; and Siochi, E. J.: Electrospinning of a micro-air vehicle wing skin. *Polymer* 44, 1309-1314 (2003).

3. Gupta, Pankaj; Elkins, Casey; Long, Timothy E.; and Wilkes, Garth L.: Electrospinning of linear homopolymers of poly(methyl methacrylate): exploring relationships between fiber formation, viscosity, molecular weight and concentration in a good solvent. *Polymer* 46(13), 4525-4985 (2005).

4. Theron, S. A.; Zussman, E.; and Yarin; A. L.: Experimental investigation of the governing parameters in the electrospinning of polymer solutions. *Polymer* 45 2017-2030 (2004).

5. Pawlowski, Kristin Joy: Electrospinning as a Processing Method for Electroactive Polymers and Composites. PhD Dissertation, Virginia Commonwealth University, 2004. http://etd.vcu.edu/theses/available/etd-12142004-121132/

6. Shenoy, Suresh L.; Bates, W. Douglas; Frisch, Harry L.; and Wnek, Gary E.: Role of chain entanglements on fiber formation during electrospinning of polymer solutions: good solvent, non-specific polymer–polymer interaction limit. *Polymer* 46(10) 3372-3384 (2005).

7. Welsh, G. J.: Solution properties and unperturbed dimensions of poly(vinylidene fluoride). *Polymer* 15, 429 (1974).

8. Joly, C.; Le Cerf, D.; Chappey, C.; Langevin, D.; and Muller, G.: Solvent effect on the conformation in solution of two polyimides. *Polymer International* 44(4), 497 (1997).

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
01- 07 - 2005	Technical Memorandum	

4. TITLE AND SUBTITLE

Electrospinning of Polyvinylidene Fluoride and Polyetherimide From Mixed Solvents

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Morgret, Leslie D.; Pawlowski, Kristin J.; and Hinkley, Jeffrey A.

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

23-064-50-10

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

NASA Langley Research Center
Hampton, VA 23681-2199

8. PERFORMING ORGANIZATION REPORT NUMBER

L-19153

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546-0001

10. SPONSOR/MONITOR'S ACRONYM(S)

NASA

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

NASA/TM-2005-213786

12. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 27
Availability: NASA CASI (301) 621-0390

13. SUPPLEMENTARY NOTES

Morgret: University of Colorado; Pawlowski and Hinkley: Langley Research Center
An electronic version can be found at http://ntrs.nasa.gov

14. 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.

15. SUBJECT TERMS

Electrospinning; Viscosity; Surface tension; Fiber diameter

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			STI Help Desk (email: help@sti.nasa.gov)
					19b. TELEPHONE NUMBER *(Include area code)*
U	U	U	UU	12	(301) 621-0390