

National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No.

M01-MD22

Competency: Materials

Electrostatic Spinning and Properties of Ultrafine Fibers

Project Team:

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Objective:

Our objective is the development of fundamental understanding and technology of electrostatic fiber production ("electrospinning") and the controllable production of materials derived therefrom. In particular, we plan to:

- Extend our current understanding of electrospinning to account for mass transport and polymer viscoelasticity.
- Control fiber diameter through choice of solution properties, operating parameters and equipment design.
- Evaluate methods to introduce electric charge into solutions and to manipulate local electric fields.
- Develop methods for characterizing both fiber and fabric properties.

Progress Statement:

I. Modeling the Stable Jet. The whipping and stretching of the jet is very much determined by its behavior near the nozzle. Our joint effort with M.P. Brenner (School of Applied Sciences, Harvard University) has been focused on modeling the jet profile near the nozzle in the stable regime. We concentrated on the role of viscosity in controlling the stable jet. It was found that in viscous fluids such as glycerol the shape of a rather long segment of the jet is controlled by the balance of viscous friction and electric field pulling on the surface charges. The scaling law describing the shape of the jet in this regime is: $h = \left(\frac{6 \rho Q^2}{\rho I E} \right)^{1/3} z^{\rho}$, where h is the jet radius, z is the distance from the upper electrode, Q is the flow rate, I is the electric current, ρ is the fluid density and ρ is the fluid viscosity.

II. Prediction and Control of the Fiber Diameter. At high fields and flow rates, the whipping instability controls the behavior of the jet and leads to bending and stretching of the jet. The whipping jet thins dramatically, by as much as three orders of magnitude, while traveling the short distance between the electrodes. To determine how thin the jet can become when it bends, we examined the conditions for the whipping instability of the jet. According to the model, thinning of the fluid jet in the whipping regime is a consequence of normal stresses originating from the bending of the centerline of the jet. At the late stages of whipping, the dramatic stretching of the jet due to the whipping instability ceases and the terminal diameter of the jet is reached. We infer that the stretching after the saturation of the whipping mode is minimal and the jet is advected to the collector with essentially constant radius h_t given by the following relation:

$$h_t = \left(\frac{\rho Q^2}{I^2} \frac{2}{\rho (2 \ln \rho \rho 3)} \right)^{1/3} \quad (1)$$

where ρ is the dielectric constant, parameter $\rho \rho R/h$ is the dimensionless wavelength of the whipping instability, ρ_0 is the surface charge density. Equation (1) predicts that the terminal radius of the whipping jet is controlled by the flow rate, electric current and the surface tension of the fluid. The ratio (I/Q) is the net volume density of charge induced in the fluid at the top electrode.

Predictions of equation 1 are in good agreement with experimental data for various polymer solutions as shown at Figures 1&2. The theoretical curve is shifted below the experimental data for polycaprolactone (PCL) by roughly a factor of 2. This suggests that in reality some fraction of the solvent evaporates before the terminal jet diameter is reached. Figure 2 summarizes the level of agreement between experimental data for fiber diameters and the theoretical values predicted by Eqn (1) for several polymers, solution concentrations and processing conditions.

The theory shows a remarkably good agreement for polyethylene oxide (PEO) and polyacrylonitrile (PAN). In the cases of PEO and PAN the main charge carrier is the polymer itself, and the solvent is not so volatile. Thus, most of the charges stay with the jet until it reaches the collector, and the drying takes place after the stretching. PCL on the other hand is non-conducting itself, and the charges are carried by methanol, which is very volatile. In this case,

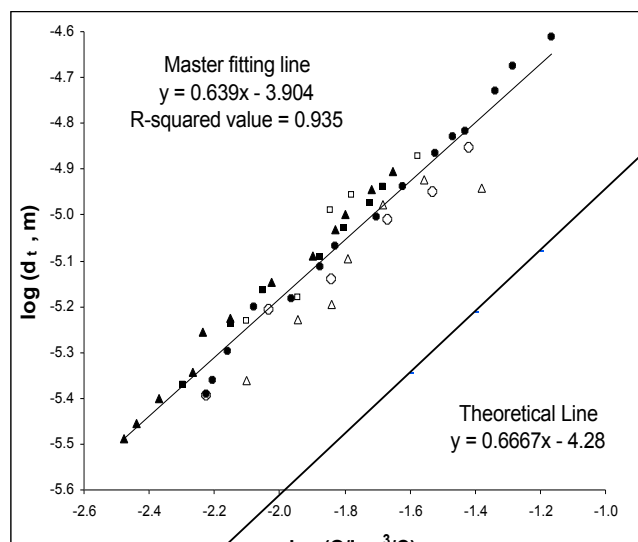


Figure 1. Terminal jet diameter for PCL in methanol: chloroform =1:3 solution: comparison of theory and experiment. The concentrations of PCL are 12% (●), 11% (▲), 10% (■), 9% (□), 8.5% (□) and 8% (□) by weight.

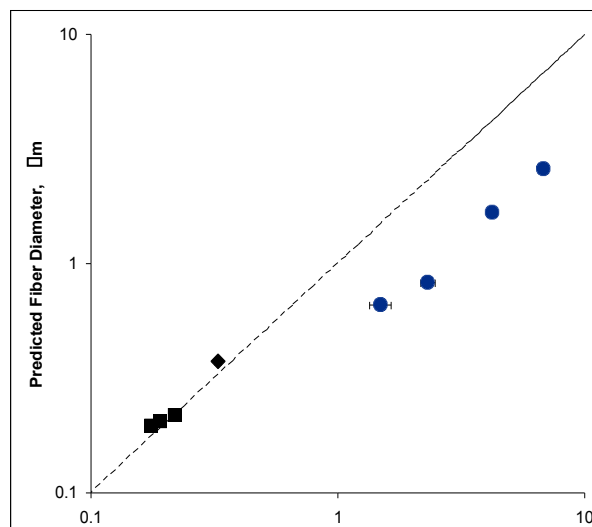


Figure 2. Experimental fiber diameters versus predicted fiber diameters: 12% PCL (●), 10% PAN(○), and 2% PEO(■) at various flow rates and current readings.

the evaporation may also be accompanied by charge loss. Charges carried by evaporated solvent molecules may still reach the collector and contribute to the measured current, I . This would lead to over prediction of surface charge and under prediction of terminal jet diameter for the PCL solutions, as seen in Figure 1.

III. Charge Measurement of Electrospun Fibers. The aim was to understanding the charging process, measuring the charge density of electrospun fibers, and increasing the productivity of the electrospinning process. For this purpose, we control spinning variables such as collection distance, voltage differential, spinning time, selection of polymer systems and feed rate, and evaluate their effects on final morphology and diameter distribution. The polymer systems include PCL in acetone and PAN in dimethylformamide. We have studied positive and negative induction charging and ionized field charging techniques. The charge density was measured using a nanocoulombmeter coupled with a Faraday cup. Corona formation on current has been observed. The charge density of electrospun fabric ranges from 30-60 nC/mg depending on the process conditions and it varies with applied voltage and solution properties. The diameter ranges from 100-600 nm depending on the charging process. Electrospun fibers are bead-like at low concentrations and characteristically high diameter at high concentrations. We have developed a mathematical model for quantification of the charge measurements of the electrospun fibers, which agrees well with our experimental values. The average fiber diameter varies with solution concentration and applied voltage (Figure 7.) As the concentration decreases, the viscosity of the solution decreases and the stretching effect of electric field and induced charges increases. This results in a finer fiber. An increase in applied voltage may give rise to electric field and acceleration of charges in the jet and instability region, this would increase the elongation of the fibers, resulting in a finer fiber.

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Next Year's Goals:

In the coming year we plan to focus our efforts on the theoretical and experimental investigation of nonlinear aspects of the whipping motion. The main goal of this research is to understand the role of solvent evaporation and viscoelasticity of polymer solutions in controlling the whipping motion of electrodriven jets. The use of high-speed camera will allow for direct comparison of the trajectories of the jet with theoretical predictions.

We are also planning to develop a device that will improve the throughput of polymer from a single electrospinning head. We may also begin work directed towards obtaining small fiber diameters from electrospun polymer melts. Finally, some efforts will focus on electrospinning polymer rich mixtures containing a second phase that can impart useful properties, such as strength or modulus, or functionality.

Approach:

Our approach to understand further the electrospinning process, which is the only approach we have space to describe here, entails a combination of mathematical modeling and experimentation. Our mathematical modeling includes both numerical analysis, to solve the exact equations for the jet, and scaling analysis, to determine the leading order terms, which dominate in the several regions of the jet, namely: nozzle, thinning jet and whipping jet. In the experiments we will continue to use not only model fluids such as glycerol and polyethylene oxide/water, but also polycaprolactone/chloroform and polyacrylonitrile/N,N-dimethylformamide solutions to test the mathematical description for validity and generality, varying for example the concentration of polymer to manipulate fluid properties. We will use digital photography to analyze the shape of the whipping jet and to test the theoretical predictions. In order to study solvent evaporation and nonlinear effects in instability, we propose to redesign our equipment to provide a controlled environment and to permit longer spinning distances. The controlled environment chamber will be outfitted with electrodes to permit alterations in the shape of the electric field, for purposes of both focusing and directing the spinning jet. These modifications will allow us to follow the jet behavior further down the spin line, into the region of instability where we believe solidification and determination of fiber diameter are realized. To investigate charge flow, we are testing alternative mechanisms for charge injection (e.g. ion gun), charge polarity, and fluids of different charge-carrying capacity. To characterize the webs, we will continue to use SEM to measure fiber diameter and porometry to measure pore size. DSC and WAXS are used to characterize crystallinity.

Outreach to Industry:

Over the past several years, we have had numerous interactions with several academic institutions and with US Army researchers (Natick Labs). With the founding of the Institute for Soldier Nanotechnologies (ISN) at MIT, funded by the U.S. Army in May 2002, our electrospinning work becomes the primary technology within the ISN for producing nanomaterials in fiber form; we anticipate numerous collaborations arising from our involvement there. Industrial interest in electrospinning has been encouraged, including substantial conversations with, or presentations to, several companies: eSpin Technologies, Charge Injection Corp., Milliken Corp., Physical Sciences Inc., and others. One of the PI's (GCR) is affiliated with the NSF ERC Center for Advanced Engineering Fibers and Films at Clemson, which derives sponsorship from 15 to 20 major fiber and film producers. Our work has been recently presented at several scientific and technical venues, including: Gordon Research Conference on Composites, Meeting of American Physical Society, Annual Meeting of Society of Industrial and Applied Mathematicians, 2nd AUTEX conference, International Conference on Textile Composites TEXCOMP-9, Annual Meeting of the Fiber Society, Annual Meeting of the American Institute of Chemical Engineers.

New Resources Required:

In order to study the effects of equipment design, charge induction/injection to the fluid, and shaped electric fields, resources are needed in the coming year for a new power supply and for fabricated equipment (e.g. a novel spinnerette design). We continue to make use of the Central Facilities of the Center for Materials Science and Engineering at MIT for electron microscopy and other analytical needs. In addition, we anticipate increased costs in the coming year for porometry measurements (outsourced to Porous Materials Inc, Ithaca NY). Staffing for this project will continue at 1 postdoc and 2 graduate students.