Enhancing the Properties of Nanoscale Electrospun Polymer Fibers Through Chemical Architecture, Surface Texturing and Optimization of Processing Protocols

NSF NIRT Grant 0210223

PIs: John Rabolt, Mary Galvin, Kristi Kiick, Darrin Pochan, Jian Sun, Norm Wagner
University of Delaware

Adding submicron texture while simultaneously shaping a polymer saves energy, reduces manufacturing costs and adds "value" to a material. The University of Delaware's NIRT is using a simple method to induce a nanoporous texture on polymer fibers as they are formed using an electrostatic spinning technique (electrospinning). Towards this goal, an integrative system that utilizes electroactive polymer/biopolymer synthesis to produce advanced materials for investigation has been developed. The integrative system then uses a unique processing protocol that involves the electrospinning of fibers, a technique that requires a small amount of sample, and a characterization protocol including mechanical/electrical analysis (via MEMS), vibrational spectroscopy, small angle neutron scattering, electron microscopy and x-ray diffraction. The goal of this NIRT is to use materials chemistry to place reactive groups at selective locations (1.0-3.0 nm) along an alpha-helical polypeptide backbone, then optimize the electrospinning process using rheological, spectroscopic, diffraction and electron microscopic characterization techniques to insure placement of these reactive groups *on the fiber surface*. Determination of the electrical and mechanical properties of these fibers will then be carried out on an automated MEMS test chip ("process-on-a-chip"), which can be used to simultaneously conduct multiple measurements on many fibers of differing chemical architecture and processing history.

Initially, a helical protein with the sequence $(AAAFAAFAAAF)_x$ is being explored for its potential to display non-natural amino acids that can be modified with electroactive groups. Energy minimization of hybrid proteins of the above sequence, in which phenylalanine (F) residues have been modified with paraphenylenevinylene (PPV) pentamers, demonstrates that the PPV oligomers can be aligned on one face of the helical protein, with interchain distances of approximately 4Å. No such alignment is observed in the energy-minimized structures of random coil proteins with pendant PPV groups. Short peptides of the above sequences, in which F is replaced with an aryl-bromide functionalized amino acid, have been produced and will be chemically modified in model reactions. Expression plasmids encoding the helical protein $(AAAFAAFAAAF)_x$, where x = 2, 4, 6, 8, 10, 12, and 14, have been produced and their DNA sequence confirmed. Expression and purification of protein from bacterial hosts equipped with these plasmids is underway.

Simultaneously, electrospinning studies of a commodity polymer, poly(styrene) (PS), have also been undertaken in order to determine the effect of various processing variables (surrounding atmosphere, solution concentration, molecular weight, field strength (spinning voltage), syringe-to-target distance, etc.) on fiber diameter and surface morphology. Initial results[1] indicated that increasing the spinning voltage decreases the average diameter of the fibers produced. On the other hand, an increase in solution viscosity was shown to increase the diameter of the resulting electrospun fiber. An interesting result was obtained when PS fibers were electrospun from a volatile solvent (e.g., tetrahydrofuran (THF)) in higher than 35%

relative humidity (RH). As shown in Figure 1, a nanoporous surface texture resulted and has been attributed to evaporative cooling, which gives rise to condensation of water droplets on the fiber surface. These droplets eventually evaporate but not before they leave an imprint on the surface. Subsequent atomic force microscopy (AFM) studies[2] have shown that the pore depth is approximately 50 nm lending credence to the idea that the nanopores do not originate in the interior of the fiber.

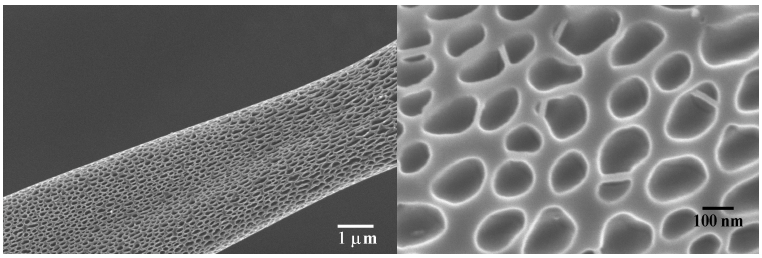

Figure 1. PS fibers electrospun in a humid (>35% RH) environment

In order to prepare the fibers for mechanical measurements a grounded rotating drum was constructed in order to arrange the polymer fibers so that they are parallel to one another. Shown in Figure 2 is an example of a fibrous membrane collected on the rotating drum. The PS fibers are oriented parallel to one another in an approximate straight line direction from the top of the page to the bottom. This anisotropic arrangement of PS fibers will be used for spectroscopic studies and characterization of mechanical properties.

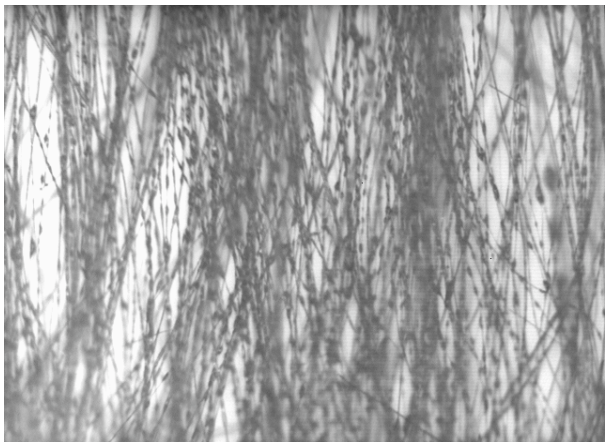

Figure 2. PS fibers aligned by rotating drum.

In addition to the experimental studies described previously, an engineering model is being formulated and validated that will be able to predict the thermodynamic state of the polymer solution in the evolving jet during the electrospinning process. The specific goal is to predict the rates of heat and mass transfer along the jet and their sensitivity to the initial solution conditions (molecular weight, solution concentration, solvent chemistry) and the electrospinning experimental parameters (field strength, surrounding atmosphere). Assuming that the formation of nanotextured surfaces on the fibers, which is desirable for uses in tissue engineering, is a consequence of water condensation, initial calculations can semi-quantitatively explain the

experimental observations made to date. More detailed calculations are in progress to explore the connection between *viscoelastic phase separation* and the electrospinning process as a mechanism to build in nanostructural details during fiber formation, much in the same manner as spinodal decomposition is used to nanostructure polymer blends during processing.

Finally, we are also measuring and modeling the phase behavior of the ternary polymer solutions being electrospun (Fig. 3) to determine if thermodynamic phase separation occurs during spinning. A result for PS in THF/Water is shown below, where the estimated operating line is observed to intersect the miscibility line. This may result in the formation of nanostructures within the context of viscoelastic phase separation and is the subject of an ongoing investigation.

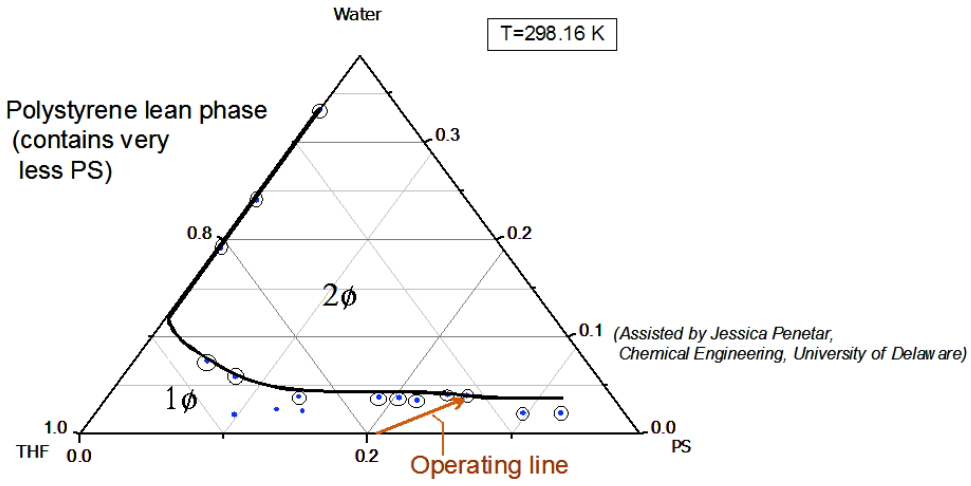

Figure 3. Measured PS/THF/Water miscibility along with estimated operating line during electrospinning. Calculations suggest that thermodynamic phase separation may be occurring at the surface of the spun fiber during electrospinning.

References

[1] Megelski, S.; Stephens, J. S.; Chase, D. B.; Rabolt, J. F., "Arrays of Micro- and Nanopores on Electrospun Polymer Fibers", *Macromolecules* **2002**, *35*, 8456

[2} Casper, c.; Stephens, J. S.; Tassi, N.; Chase, D. B.; Rabolt, J. F.; "Controlling Surface Morphology of Electrospun Polystyrene Fibers: Effect of Humidity and Molecular Weight on the Electrospinning Process", *Macromolecules* **2003** (in press)

[2] For further information about this project link to <www.udel.edu/mse/research.htm>**>**