

National Textile Center

FY 2003 (Year 12) Project Proposal

Project No. C03-CD01s

Competency: **Chemistry**

Nano-Porous Ultra-High Surface Area Fibers

Project Team:

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Objective:

This research exploits chemical and synthetic strategies to create novel fibrous materials with nanometer-size pores and ultra-high surface areas. The investigation focuses on creating fibers from both natural and synthesized polymers with diameters in the range of 10^2 nm and nanometer-size pores. It is envisioned that materials with these characteristics are potentially useful in many areas of technical application, such as selective chemical reactivity, solid support catalysts, membrane supported smart materials, and membranes for immobilizing biological and pharmacologically active agents and molecules. Due to the nanoscale sizes of these fibers and pores, much smaller quantity of these new materials is needed to achieve the anticipated functions. Furthermore, it is highly probable that, unanticipated but potentially useful properties may be discovered.

Relevance to NTC Mission:

This research is highly relevant to the NTC mission in that it exploits fundamental polymer chemistry principles for creating novel fibrous materials with ultra-high specific surface areas, nanometer size pore structures and potentially unique chemical functionalities. Findings from this research contribute to the knowledge base of fiber materials science and the development of new fibrous materials to meet emerging needs in advanced technical applications, e.g., chemically and biologically protective coatings, recyclable catalysts, reactive and smart materials, and targeted separation membranes. The long-term impact includes creating new and high-value markets for fiber and textile products and enhancing the technological competitiveness of US industry.

State of the Art:

Fibers have intrinsically high specific surface areas, namely surface-to-volume or surface-to-mass values. Ultra-fine fibers such as nanofibers are typically two to three order of magnitude smaller than fibers conventionally produced. This translates to their two to three order of magnitude higher specific surface areas. These ultra-high specific surface characteristics are of significant scientific interest and highly desirable for applications that rely on materials' surface characteristics, including separation/filtration membranes, composite reinforcement, and surface-activated and surface-supported chemical reactions.

Current melt and solution spinning technologies are capable of producing fibers with diameters in the 20-50 μ m range at relatively high speeds and with good uniformity. Although technological advancement has resulted in efficient production of micrometer diameter fibers, to date, electrospinning remains the only method by which fibers of less-than-micrometer sizes can be generated. Electrospinning of polymer melts or solutions is similar to electrostatic atomization and spraying of liquid jets which have found industrial applications, such as aerosol spraying, atomization in the charged droplets, and formation of particles. When polymer solutions or melts are charged to high voltage under proper conditions, their surface tension forces can be overcome to form fine jets toward a grounded target. Although the concept of electrospinning to form fine fibers was patented in 1934, interest

has surged in the last decades or so. Most work has focused on the formation of fibers from a wider varieties of polymers [1].

Although fibers as small as 40 nanometers have been reported, most electrospun fibers have diameters in the micrometer to sub-micrometer range. In fact, to generate polymeric fibers of nanometer sizes remains a challenge. To put this in perspective, a typical linear polymer has a lateral dimension of a few tenths of a nanometer to the 2.5 nm width of the double helix of DNA molecules [2]. Nanofibers consisting of hundreds of parallel molecules laterally are easier to produce than those with only a few molecules across the lateral dimension. Therefore, forming fibers with lateral dimensions in the nanometer range can be particularly difficult.

Electrospinning presents many advantages to fiber formation. It is versatile in forming continuous nanofibers from many different polymers. It requires very small quantities of polymer, as low as sub-milligram levels, making it possible to transform research-quantity polymer to fibers. The extremely high surface area characteristics of nanofiber membranes make them excellent carriers and supports for reactive compounds. It can be easily understood that catalysts or reagents anchored to recoverable substrates are highly desirable. Recent work has shown that additives in electrospun membranes perform equally well or better than when functioned alone [3]. These effects were demonstrated with an inorganic catalyst polyoxometalate $\text{Na}_2\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ and a conductive polymer, polyaniline additives. Although many challenges remain, including achieving good dispersion of the additives in the spin dope, these preliminary results illustrate excellent potential for this approach.

The PI has collaborated with the Natick Army Material Science Team on microporous chemical protective membranes. The joint project focused on chemical modification of elastomeric polymer membranes for improved chemical resistance as well as with unique liquid wetting and transport properties. Two previous NTC projects (M01-D22, M98-D01) have focused on the engineering aspects of electrospinning, such as the design of apparatus (e.g., multiple spinnerets, rotating collector), the effects of charging/ionized field, improved productivity and the characterization of fiber physical properties. Much of the experimental work has centered on polyethylene oxide (PEO), polyacrylonitrile (PAN), and polycaprolactone (PCL). In another active NTC project, M02-05, the project leader investigates the chemical strategies to link biomolecules, specifically enzymes, to fiber surfaces.

This proposed research significantly deviates from all previous research (including NTC projects), in that it expands not only on the range of polymers but also the chemical and synthetic strategies in the fiber formation process. Chemical reactions and polymer synthesis are incorporated in the pre-, in-situ, or post- fiber forming processes. This proposed research builds upon the logical links of the researchers and expand our complementary expertise in polymer chemistry as well as fiber physics and engineering. Excellent synergism is expected from this NTC project.

References:

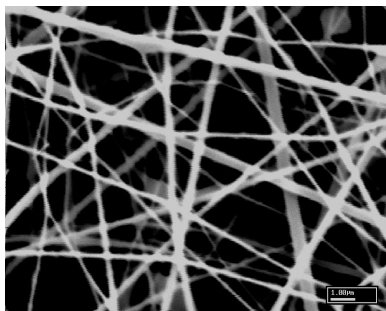
1. a. Fong, H.; Reneker, D.H. Chapter 6 in Structure Formation in Polymeric Fibers, Ed. D.R. Salem and M.V. Sussman, Hanser 225-246.6. b. Fong, H., I. Chun and D.H. Reneker, *Polymer*, 1999, 40(16): 4585.
2. Perkins, T.T., D.E. Smith and S. Chu, *Science*, 1994, 264: 819.
3. Schreuder-Gibson, H., P. Gibson, K. Senecal, M. Sennett, J. Walker, W. Yeomans, D. Ziegler and P.P. Tsai, Protective materials based on electrospun nanofibers (Personal communication).

Approach:

This research incorporates polymer chemistry principles with the electrospinning process to form ultra-fine fibers with nanometer size pores. This approach should result in fibers with surface areas that are 3 to 4 order of magnitude higher than conventional high specific surface materials. Chemical reactions and polymer syntheses, polymer compositions and additives, and solvent systems employed in electrospinning will be expanded and explored to form ultra-fine porous fibers. Concepts of organic synthesis, interpenetrating network, grafting copolymerization and crosslinking, differential etching/dissolution will be incorporated in-situ or post-process with electrospinning to generate nano-scale pores. The main goal is to identify the range of capability among these strategies in generating these new ultra-fine and porous fibers.

Nanofiber Formation. From previous collaboration with the Natick Material Science group, we have devised an electrospinning apparatus, consisting of a high voltage power supply (ES30P/100, Gamma High Voltage Research

Inc.), a polymer solution reservoir, and a target or collector. The solution is fed through a glass tube with capillary opening of approximately 1 mm in diameter. A metal (stainless steel or copper) pin immersed in the solution serves as the electrode and is connected to a high voltage source. With the adjustment of an electrical field, the electrostatic force overcomes the surface tension of the drop, ejecting the jet toward the target. Changes of the polymer jets cause “splaying” or longitudinal splitting of the jet into finer streams. Upon evaporation of the solvent, dried fibers are collected on the counter electrode in a fibrous web. By controlling the solvent systems and solution properties, fibers with diameters of 100-500 nm have been produced from several polymers (bar=1 μm).



Nanopore Formation. Several approaches will be explored to create nanopores in the already fine fibers. Chemical strategies, such as in-situ polymerization and copolymerization, synthesis of interpenetrating networks, and chemical crosslinking as well as physical ones, such as additives, phase separation and selective etching/dissolution, will be explored as part of the electrospinning process. It is envisioned that pores at the order of nanometer size can be formed inside as well as on the surface of these fibers.

Preliminary Results. One of the above mentioned approaches has been tested using two polymers. Scanning electron microscopy of these fibers has shown that fiber diameters are generally <500 nm and surface pores <50 nm.

This Year's Goal:

The goal of the first year is to explore and survey the chemical strategies for creating nano-size pores in the fiber formation processes. Several major polymers, including natural (cellulosic and proteinaceous) and synthesized (chain- and step-polymers) will be investigated for this purpose. Outcome of this year will help to determine which major chemical approaches to be targeted in the following years.

Outreach to Industry:

These investigators seek collaboration with researchers from academia as well as industry to develop fibrous supports of various polymer, to expand existing strategies, and to identify new applications. Industrial partners from the fiber/textile industry as well as chemical/polymer/consumer product sector will be sought for further development of the concept and transferring of the developed technology to all affiliated industries, including those in the West Coast and California.

Furthermore, collaboration with the government is anticipated. Researchers at US Army Soldier Biological & Chemical Command centers and Medical Command have been investigating methods towards the development of absorbent and fibrous materials for decontaminating equipment and personnel upon exposure to toxic chemicals and biological agents. These groups have expressed interest to collaborate for military applications.

New Resources Required:

A major portion of the proposed budget for the first year constitutes the supports for a student, expenses related to chemicals and supplies, recharge for advanced instrument use, and domestic travel. Resources to support these research activities are expected to increase for the following years. Future needs also include new equipment such as Raman FTIR, atomic force microscope, surface area measurement instrument, and atomic absorption spectrophotometer.