

# National Textile Center

## FY 2004 New Project Proposal

**Project No. C04-CD06**

Competency: **Chemistry**

### Nano-Porous Ultra-High Specific Surface Fibers

---

#### Project Team:

Leader: You-Lo Hsieh/UC Davis/Polymer and Fiber Chemistry

Email: ylhsieh@ucdavis.edu Phone: (530) 752-0843

Members: Steve B. Warner/University of Massachusetts, Dartmouth/Fiber Science and Electrospinning  
Heidi Schreuder-Gibson/US Army Natick Materials Science/Polymer Membranes

---

#### Objective:

This research exploits chemical and synthetic strategies to create new nano-porous ultra-fine fibrous materials. The goal is to create ultra high specific surface fibers with diameters in the range of  $10^2$  nm and nanometer-size pores. Natural as well as synthesized polymers are to be employed in combination with chemical reactions and organic syntheses. It is envisioned that the novel fibers with new and unexpected material properties may be discovered. The unique characteristics of these fibrous materials can expand technical capabilities in areas which demand high specific surfaces, controlled porous structure, nano-porosity and target chemical functionality, such as chemical conversion, solid support catalysts, selective separation, membrane supported smart materials, scaffolds for tissue/cell growth, and membranes for immobilizing biological and pharmacologically active agents and molecules. Due to the nanoscale sizes of these fibers and pores, much smaller quantities of these new materials are needed to achieve the targeted functions. These fibrous materials can also be incorporated with conventional textile as well as other structures like coatings, laminates, blends and additives. Another application advantage of these ultra-high specific surface fibers is the miniaturization and/or invisibility of devices and sensors. Furthermore, it is highly probable that unanticipated but other useful properties may be discovered to expand the applications of textiles to areas that currently do not exist.

---

#### Relevance to NTC Mission:

This research is highly relevant to the NTC mission of enhancing the competitiveness of the US industry by building new knowledge on novel fibrous materials. This work exploits fundamental polymer chemistry principles for creating novel fibrous materials with ultra-high specific surface areas, nanometer size pore structures and unique chemical functionalities. Findings from this research contribute to the knowledge base of fiber materials science which is critical to the development of new and improved fibrous materials to meet emerging needs in advanced technical and performance applications such as chemically and biologically protective coatings, recyclable catalysts, reactive and stimuli-responsive materials, selective encapsulation and targeted separation membranes. The long-term impact includes creating new fibrous products for improved quality and better protection of life, expanding high-value markets for fiber and textile products and enhancing the technological leadership of the US industry in the global environment.

---

#### State of the Art:

Fibers are generally considered high specific surface materials, i.e., they have high surface-to-volume or surface-to-mass ratios. Ultra-fine fibers such as nanofibers are typically two to three orders of magnitude smaller than fibers conventionally produced. This translates to two to three order of magnitude higher specific surface areas. These ultra-high specific surface characteristics are of significant scientific and technological interest. Ultra-high specific surface fibers are desirable for applications that rely on materials' surface characteristics, such as separation and filtration, surface-activated and surface-supported chemical reactions, absorbent technology, pharmacological delivery systems, and composite reinforcement.

Current melt and solution spinning technologies are capable of producing fibers with diameters typically in the 20-50  $\mu$ 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 and, upon solidification, fine fibers. Although the concept of electrospinning to form fine fibers was patented in 1934, interest has surged in the last two decades. Most work to date has focused on the formation of fibers from wide varieties of polymers [1].

Electrospinning presents many advantages to fiber formation. It is versatile for forming fine fibers from a wide range of polymers some of which cannot be converted into fibers via conventional fiber spinning processes. It requires very small quantities of polymer, as low as sub-milligram levels, making it possible to transform research-quantity polymer to fibers. The very 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 functioning 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 issues remain, including achieving good dispersion of the additives in the spin dope, these preliminary results illustrate excellent potential for this approach.

Many challenges exist, however, both scientifically and technologically. Most electrospun fibers have diameters in the micrometer to sub-micrometer range. Although fibers as small as 40 nanometers have been reported [2], the generation of polymeric fibers less than 100 nm in diameter remains to be a challenge. To generate fibers of specific uniformity, on a continuous basis, and of commercially viable efficiency is among some of the technological issues to be addressed.

#### **PI's Prior Work and Other NTC Projects:**

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 unique liquid wetting and transport properties [4]. Two previous NTC projects (M01-D22, M98-D01) involving electrospinning have focused on the engineering aspects, such as design of the apparatus (e.g., multiple spinnerets, rotating collector), effects of the charging/ionized field, improving productivity, and characterization of the fiber physical properties. Much of the experimental work of those two projects employs model polymers of polyethylene oxide, polyacrylonitrile, and polycaprolactone. In another active NTC project, M02-05, this project leader investigates the chemical strategies to chemically bond biomolecules, specifically enzymes, to fiber surfaces. None of the above mentioned work deals close to the concept of this research.

---

#### **Approach:**

This research incorporates polymer physics and chemistry principles with the electrospinning process to generate ultra-fine fibers with nanometer size pores. The main goal is to develop a range of capabilities among the strategies in generating these new ultra-fine and nano-porous fibers from natural and synthesized polymers. These approaches should result in fibers with surface areas that are 3 to 4 orders of magnitude higher than conventional high specific surface materials. This proposed research significantly deviates from all previous research (including NTC projects), in that it focuses on chemical and synthetic strategies in forming nanoporous fibers, thus expanding far beyond the range of conventional polymers. Chemical reactions and polymer synthesis are incorporated in the pre-, in-situ, or post- fiber forming processes. This research builds on the logical links among the researchers and the complementary expertise in polymer chemistry, fiber physics and engineering. Excellent synergism is expected from this NTC project.

The PI's lab has an established electrospinning apparatus which consists of a high voltage power supply (ES30P/100, Gamma High Voltage Research Inc.), capable of processing polymer solutions [5-7]. A proposal first submitted in Fall 2002 is currently funded with one-year seed funding (C03-CD01). To date, in the first four months, the concept of phase separation has been explored using two organic-soluble fiber-forming polymers, A and B, one of which (polymer B) is also water-soluble. Electrospinning of organic solutions of these two polymers at varying polymer B contents yields fine fibers with decreasing diameters of ~500 nm to ~100 nm with increasing amounts of polymer B (Figure 1). The DSC shows distinct thermal behavior of the individual polymers, confirming phase separation of the two, in the form of cast films as well as electrospun fibers. Removal of the aqueous-soluble polymer B results in mass losses of 17%, 31% and 49%, very close to the masses of polymer B in the original solutions. The membranes remain fibrous. FTIR confirms qualitatively that differential solubility is a viable way to remove the phase-separated domains of polymer B. Preliminary experiments using liquid inclusion methods shows that porosity in the fibers increases with the removal of polymer B. Additional experimental evidence will be collected to further explore this approach and to expand to other polymer-polymer and polymer-nonpolymer systems, thus widening chemical and physical potentials of these nano-porous fibers.

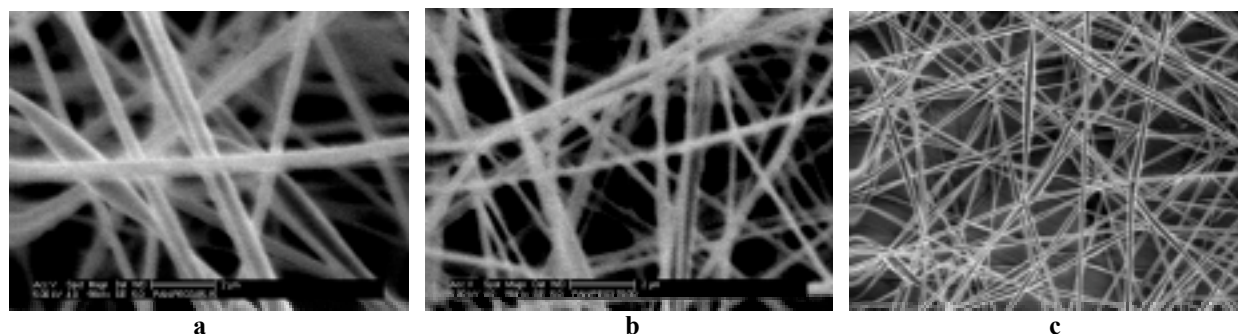


Figure 1. SEM of electrospun fibers from 8% organic solutions of polymers A and B: (a) 15% B, (b) 30% B; (c) 50% B (bar=2  $\mu$ m); viscosities of 8% polymer solutions are 31.2 and 2.7 cP, for polymers A and B, respectively.

Our results thus far indicate that (a) electrospinning of solvent-compatible yet phase-separated polymers is highly efficient; (b) fiber sizes and morphology are easily controlled by polymer compositions; (c) differential solubility removes phase-separated domains. These promising findings strongly support the notion and the scope of this research on nano-porous fibers. Further details are at the website <http://trc.ucdavis.edu/textiles/ntc%20projects/C03-CD01.HTML>.

The approaches to the two major directions of this research are:

### ***I. Fundamental understanding of nano-porosity formation and nano-structure in ultra-fine fibers***

The nano-domain phase-separation phenomena in fibers, i.e., sizes, size distributions and solvent accessibility of these phase-separated domains, the polymer physics on controlling these characteristics, and most importantly, the characterization of the nano-porosity in and on the fibers. Several analytical methods, including BET (surface area, pore size and volume), X-ray diffraction (wide and small angles), TEM and solid-state NMR, will be explored for such investigations.

### ***II. Exploitation of chemical strategies for creation of nano-pores in fibers***

Concepts of interpenetrating network, polymerization, copolymerization, crosslinking, chemical and thermal decomposition will be incorporated as in-situ or post-process with electrospinning to generate nano-scale pores, inside, as well as on the surface of the already fine fibers. Several chemical reactions and polymer syntheses that have been demonstrated to form porous polymers in the PI's lab [8-12] will be explored in combination with electrospinning for fiber formation. Crosslinking, reactive additives, and solvent diffusion/evaporation approaches will also be incorporated with the electrospinning process to form nano-porous fibers. Further details on these approaches to ultra-fine porous fibers may be obtained from the invention disclosure by contacting the Technology Transfer Center (TTC) at the University of California at Davis (<http://ovcr.ucdavis.edu/TTC>).

### **This Year's Goal:**

This focus of our first year is to explore and assess: **1)** the chemical strategies for creating nano-size pores in the fiber formation processes and **2)** the array of analytical techniques to further the fundamental understanding of the nano-porous structure. Several major polymers, including natural (cellulosic and proteinaceous) and synthetics, will be used as models to determine the feasibility of approaches.

---

### **Outreach to Industry:**

These PIs seek collaboration with researchers from academia as well as industry to develop novel fibrous supports of various polymer, and to identify new applications. Industrial partners from the fiber/textile industry as well as chemical/polymer/consumer product sectors will be sought for further development of the concept and transferring of the developed technology to all affiliated industries, including those on the West Coast and in California. Furthermore, collaboration with the government is anticipated. Discussions have been on-going with researchers at the US Army Soldier Biological & Chemical and Medical Command Centers that have been developing absorbent and fibrous materials for decontaminating equipment and personnel from toxic chemicals and biological agents.

---

### **New Resources Required:**

A majority of the proposed budget constitutes the supports for researcher stipends, chemicals and supplies, recharge for instrument (SEM, TEM, X-Ray, NMR, etc), and travel to NTC and other scientific meetings. Future needs include new equipment such as a BET surface area measurement instrument, an atomic absorption spectrophotometer, an atomic force microscope, and a Raman FTIR.