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# **Protective Materials Based on Electrospun Nanofibers**

Heidi Schreuder-Gibson,\* Phillip Gibson, Kris Senecal,  
Michael Sennett, John Walker, Walter Yeomans, and David Ziegler  
U.S. Army Natick Soldier Center  
Natick, Massachusetts, 01760-5020

Peter P. Tsai  
Textiles and Nonwovens Development Center (TANDEC)  
University of Tennessee, Knoxville, TN 37996-1950

Electrospinning is a process for making extremely fine submicron fiber by a process of charging polymer solutions to thousands of volts. This method of manufacturing man-made fibers has been known since 1934, when the first patent on electrospinning was filed by Formhals.<sup>1</sup> Since that time, many patents and publications have been reported on electrospinning.

This paper describes our latest accomplishments to produce useful fabric membranes from electrospun fibers and characterize the final properties of these membranes with respect to their strength and performance as protective layers. This paper reviews the electrospinning process, it's current status as a manufacturing method, and the performance of electrospun membranes as potential laminates for specialty textiles.

## **Introduction to Electrospinning**

Electrospinning occurs when a polymer solution or melt is charged to high voltage to produce fibers. Voltages of 5kV to 30kV are sufficient to overcome surface tension forces of the polymer, and a free surface of charged polymer will produce fine jets of liquid that are rapidly drawn toward a grounded target. The jet splits a few times near the liquid surface, but before it reaches the target, substantial drawing is observed in a series of looping actions of the rapidly solidifying fiber.<sup>2</sup> The fiber is collected as an interconnected web of small filaments on the surface of a grounded target. The technique has been used for over a decade to produce ultra high efficiency filtration webs.<sup>3-5</sup> It is important to recognize that electrospinning can be used in many other products as well. For example, electrospinning provides the capacity to lace together a variety of types of polymers and fibers to produce ultrathin layers which are useful for protective clothing.<sup>6</sup> Depending on the specific polymer being used, a range of fabric properties, such as strength, weight and porosity, can be achieved. Fiber sizes of 10 nm and smaller have been reported, although lab scale apparatus normally produces fibers from 100nm to 500 to 1.0  $\mu\text{m}$  in diameter. Commercial production size equipment produces fibers in the 0.5 to 10  $\mu\text{m}$  diameter range. Fiber size depends upon solution viscosity, field strength, and field uniformity.<sup>7</sup>

\*Author contact: [Heidi.Gibson@natick.army.mil](mailto:Heidi.Gibson@natick.army.mil)

## Current Status of Electrospinning Manufacturing

There have been a number of patents of the electrospinning process for the production of fibers, of filter media, and of medical materials.<sup>8-12</sup> There is one major producer of electrospun products in Europe and the United States. Freudenberg Nonwovens has been electrospinning for over 20 years, producing electrospun filter media from a continuous web feed for ultra high efficiency filtration markets.<sup>9</sup> Smaller companies are now beginning to electrospin, including eSpin Technologies in Chattanooga, Tennessee and Foster Miller, Inc. in Waltham, Massachusetts.

Despite the long history of electrospinning technology, it has never been applied to fabrics as a protective membrane layer. This new application has been under development at the U.S. Army Natick Soldier Center for the purpose of providing protection from extreme weather conditions, enhancing fabric breathability, increasing wind resistance, and improving the chemical resistance of clothing to toxic chemical exposure. Papers published to date have described our measurements of moisture vapor transport and air convection across electrospun membranes to characterize their “breathability” and “wind resistance.”<sup>13,14</sup> These properties and new membrane characterization data are discussed below as we describe our latest material: the first reactive, tough, elastic electrospun membranes evaluated for protective clothing applications.

## Transport Properties of Electrospun Membranes

Various electrospun membranes have been prepared by charge induction of polymer solutions. A positively charged electrode is submerged in a pipette filled with a solution of polymer. In this configuration, shown in Figure 1, charged fibers are easily collected over a period of 3-4 hours on a grounded screen. Microstructure of electrospun fiber mats are shown in Figure 2, exhibiting a range of fiber sizes and porosities produced by different electrospun systems. Fiber production rates by inducted charge are on the order of 1g fiber per nozzle per hour, depending upon the polymer/solvent combination used.

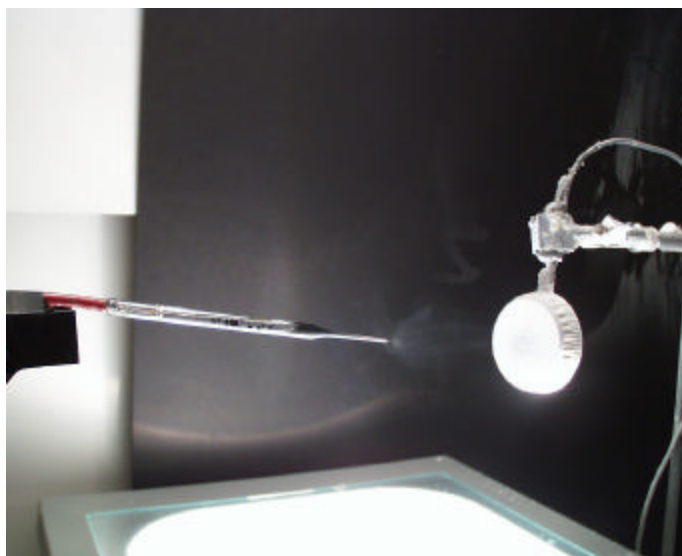
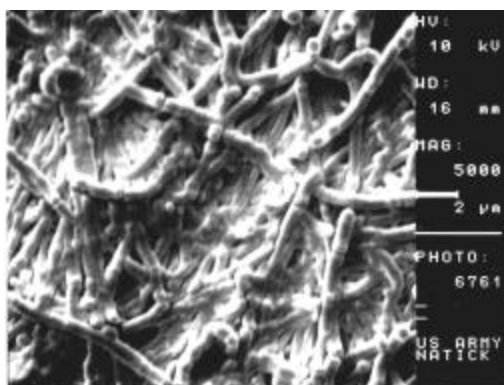
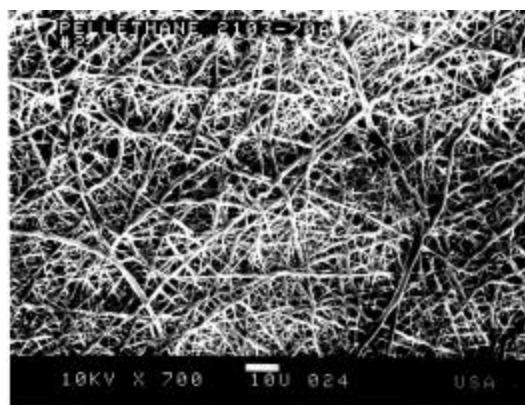


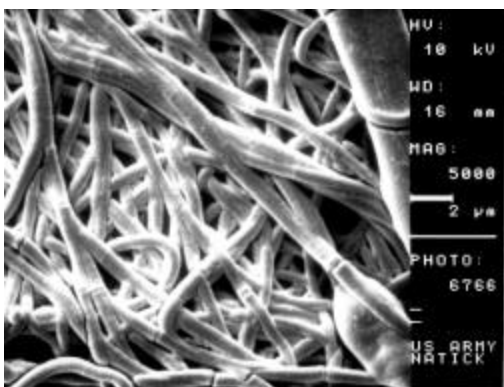
Figure 1. Laboratory scale apparatus for electrospinning  
Charged polymer solutions from pipette.



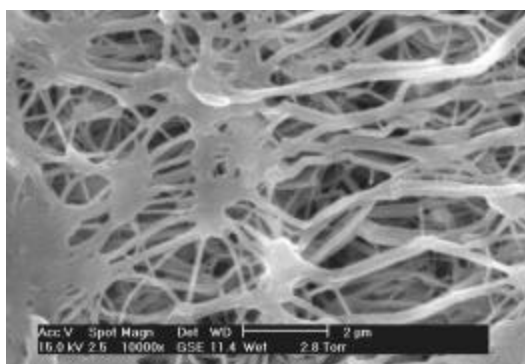
Nylon 6,6



Pellethane®



Poly(benzimidazole), PBI



Poly(tetrafluoroethylene), PTFE

Figure 2. SEM micrographs of electrospun polymers.  
The microstructure of expanded PTFE membrane is shown for comparison.

These electrospun membranes have been characterized with regard to breathability and air flow resistance, and compared to commercial membranes, films and fabrics which are in use, or under evaluation for use, in fabric laminate systems for military and sport clothing.

Moisture vapor diffusion measurements, and air flow-through capacity of textile materials can be conveniently tested using an apparatus developed at the Natick Soldier Center. This device, called the Dynamic Moisture Vapor Permeation Cell (DMPC), is designed to measure both the moisture vapor transport and the air permeability (convective gas flow) of continuous films, fabrics, coated textiles and open foams and battings. Both transport properties can be measured simultaneously as well as separately on samples as small as 5 cm<sup>2</sup>. The testing method used to determine water vapor diffusion properties and air flow resistance under simultaneous diffusion/convection conditions is shown in Figure 3. A gas stream enters the DMPC at a relative humidity of 90% at the top of the cell. The relative humidity is 0% at the bottom of the cell, producing a gradient of humidity across the sample. Automated valves are used to restrict the flow on one side of the cell, causing the pressure on one side to be higher than the other. This restriction produces convective gas flow through air-permeable samples, in addition to the diffusion flux taking place across the sample from the humidity

differences. Measurements are taken as a function of pressure drop across the sample, while the convective flow and pressure drop are gradually increased in stepwise increments. Pressure drop and mass flow rate across the sample are recorded, and the humidity of the test conditions is taken to be the average humidity across the sample.

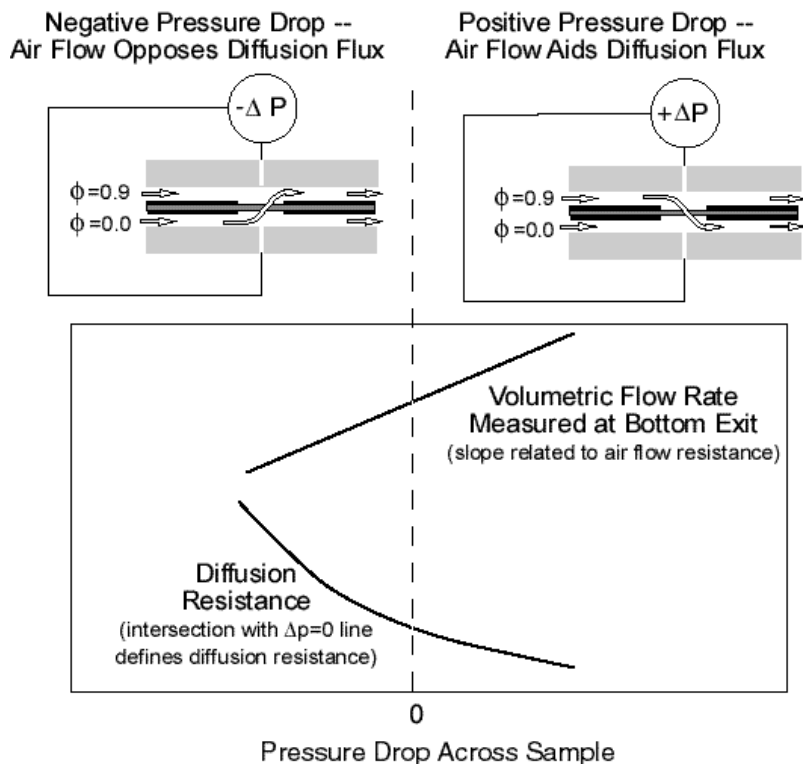


Figure 3. Convection/diffusion experiment in the DMPC.

For pure vapor diffusion measurements (no convective flow present), the DMPC uses a series of setpoints where there is no pressure difference across the sample, and water vapor transport occurs due only to diffusion driven by the water vapor concentration gradient. Testing begins at conditions of 60% relative humidity on one side and 10% relative humidity on the other side (gradient of 50% r.h.). A constant gradient of 50% r.h is maintained for the succeeding setpoints as the humidity on both sides is gradually increased up to the point of 95% r.h and 45% r.h. on the two sides of the sample. Testing according to this method allows one to track the concentration-dependent diffusion behavior of nonporous polymer membranes. At the higher average relative humidities, which corresponds to a higher polymer water content, the water vapor diffusion resistance is usually much lower for hydrophilic polymers than it is for the drier conditions at lower mean relative humidity test conditions. In contrast, porous materials which depend on transport of water vapor through interconnected pore spaces usually show a constant value of water vapor diffusion resistance which is independent of the test conditions.

Shown in Figures 4 and 5 are data collected from separate measurements of moisture vapor diffusion and gas convection in the DMPC. Figure 4 shows the moisture vapor diffusion resistance of a range of materials which vary in their microporosity and hydrophobic character. The materials used in this comparison are expanded polytetrafluoroethylene (e PTFE) unfilled membrane, electrospun Estane®, a

thermoplastic polyurethane manufactured by BF Goodrich, and a two-layer Gore-Tex® membrane laminate by W.L. Gore. Estane® has been electrospun from a solution of dimethyl formamide. The continuous film of Estane® was obtained as the commercial product, Bioclusive®, a breathable barrier material sold by Johnson & Johnson.

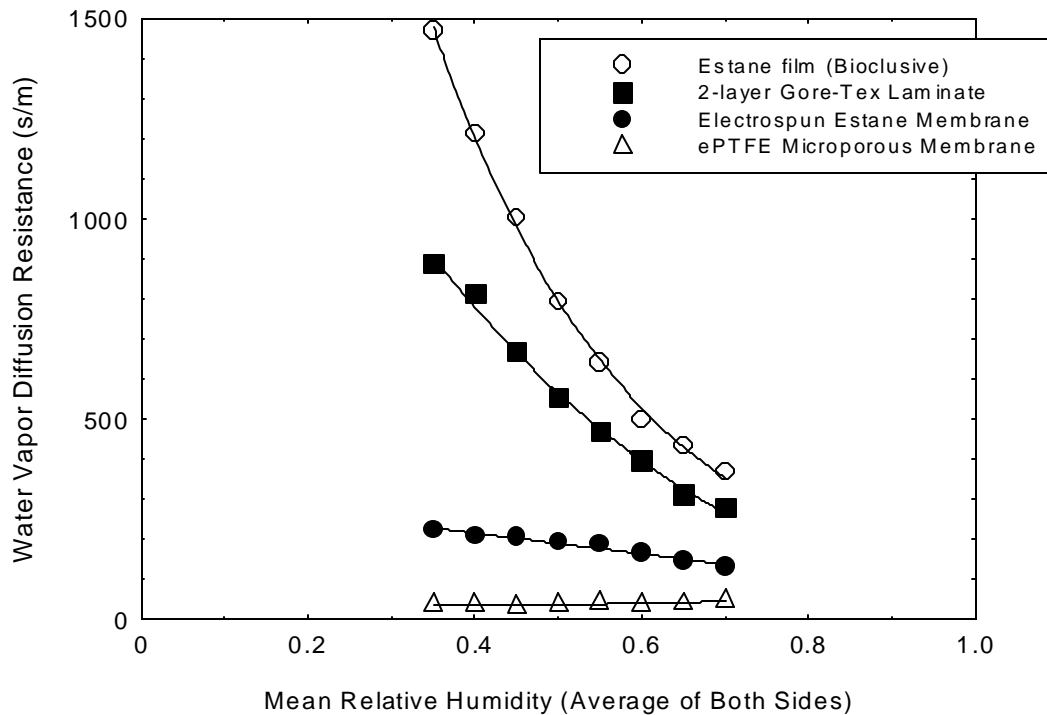


Figure 4. Water vapor transport properties of films, membranes and laminates.

Moisture vapor diffusion resistance is not high for continuous films, as shown by the values for the Bioclusive® film and the film-laminated Gore-Tex®. Very few hydrophilic polymers exhibit good diffusion through a continuous film, although it has been found that moisture vapor diffusion improves at higher relative humidity conditions, due to higher membrane water content, for hydrophilic films.<sup>15,16</sup> Both Bioclusive® and the coated PTFE membrane-laminate Gore-Tex® (in which the porous PTFE is filled with a hydrophilic polymer), show the expected concentration-dependent transport behavior of hydrophilic polymer films. Better transport can be achieved in a microporous structure. Electrospun Estane® is much more transmissive than a film of the same material. When electrospun, Estane® exhibits a comparable resistance to diffusion as uncoated PTFE membrane. Because the electrospun Estane® fibers are themselves quite permeable to water vapor, the water vapor diffusion resistance plot shows a small slope due to concentration-dependent transport of water vapor through the solid polymer fiber matrix, as well as through the pore spaces of the membrane.

Air convection through the membranes can also be determined as a function of humidity in the DMPC. In Figure 5, a series of materials are ranked in terms of their resistance to convective air flow through their structure. Very open structures like nonwoven battings used as thermal insulation layers have very low resistance to air flow. Tighter weaves of polyester and nylon are less permeable, but the greatest resistance to

air flow is exhibited by the microporous membrane materials. Electrospun Estane® is as “wind resistant” as PTFE membrane. High resistance to air flow does not impede the diffusion of water vapor through the pore structure of electrospun membranes, so even very thick layers of electrospun material will not affect a fabric’s breathability. In general, materials with high rates of water vapor diffusion and low air permeability are promising candidates for protective clothing applications.

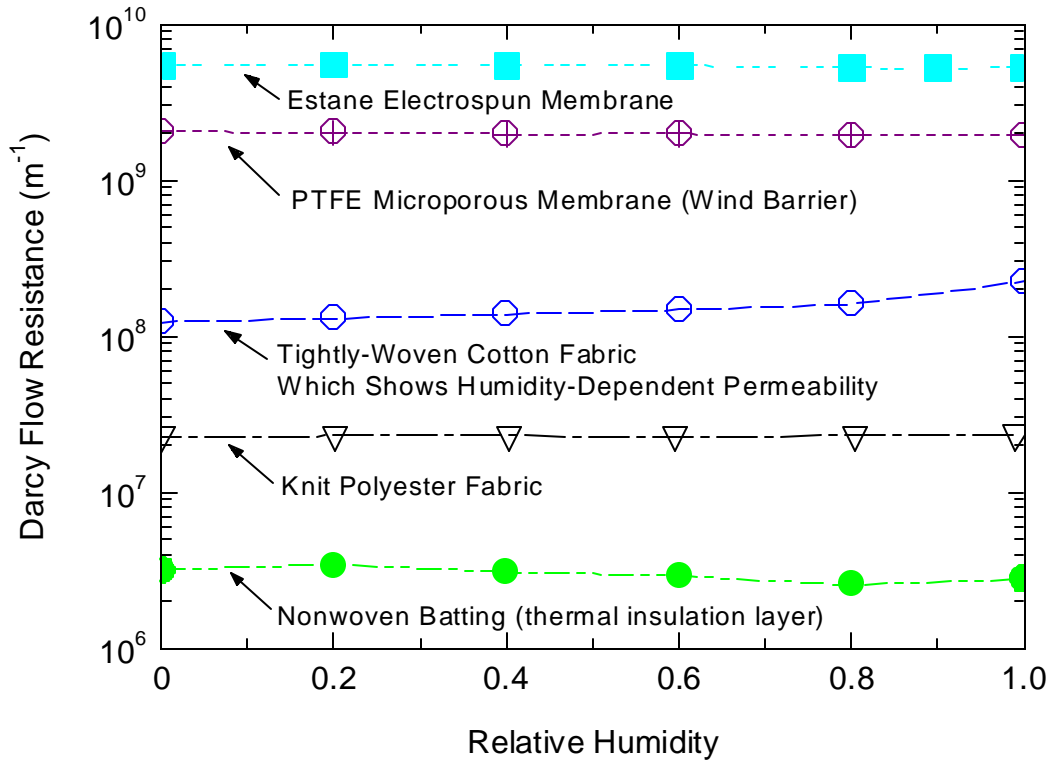


Figure 5. Convective air flow resistance of representative textile materials.

Electrospinning enables control of membrane thickness by direct spray time. In order to determine the membrane thickness necessary to provide protection from wind and air-borne particles, a range of areal densities of electrospun membranes have been compared in an air resistance study. Nylon 6,6 is electrospun from formic acid and deposited onto an a carbon-loaded polyurethane foam in thicknesses controlled by spin time. This foam has a nominal thickness of 0.87  $\mu\text{m}$ . Seven different electrospun coating thicknesses exhibit a range of areal density of 0.16 to 11  $\text{g}/\text{m}^2$ . The uncoated foam, the electrospun Nylon coated foam, and PTFE membrane by itself have been tested for air resistance effects. The open foam structure has very little resistance to convective air flow. Figure 6 shows that air flow resistance correlates well with the electrospun layer coating thickness on the open foam. The miroporous PTFE membrane has an areal density that is comparable to the highest electrospun coating level, and a similar value for flow resistance.

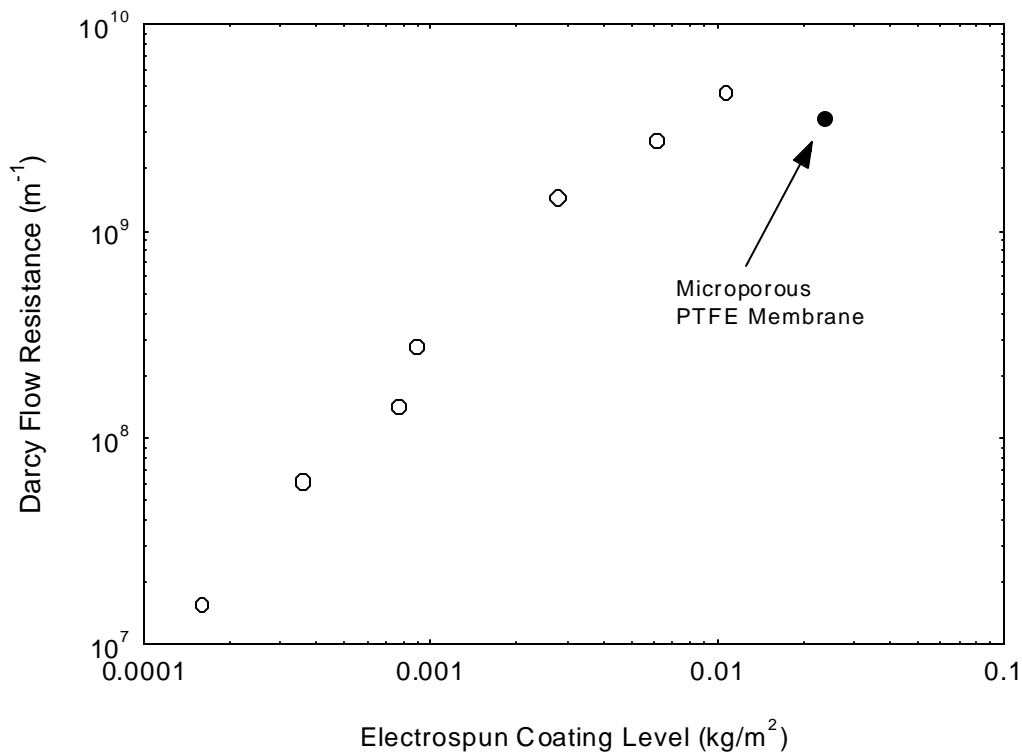


Figure 6. Effect of electrospun layer thickness upon convective air flow resistance.

The excellent air flow resistance of electrospun membranes suggests that they are potentially good barriers to airborne particle penetration. Fine particle filtration, and aerosol, bacterial and viral protection are all desirable properties for protective clothing. Aerosol filtration by these coated foam samples has been determined with a particle filtration test system that impinges a flow of aerosolized potassium bromide of particle size 0.5 to 20  $\mu\text{m}$  at the sample surface with a face velocity of 15.7cm/s. Aerosol filtration efficiency is given by:

$$E = (n_2 - n_1) / n_2$$

Where  $n_2$  is the aerosol particle concentration upstream, and  $n_1$  is the concentration downstream of the sample.

Figure 7 shows the effect of these coating thicknesses on aerosol particle filtration of the carbon-loaded foam, and demonstrates the deviation of filtration performance from air flow resistance in these materials. For microfiber filters, particle filtration by impaction with the web is not the only mechanism responsible for filtration capacity; particle diffusion by Brownian motion and a combination of diffusion and impact contribute to overall filtration efficiency.<sup>17</sup> An additional consideration needs to be included when accounting for air flow characteristics in nanofiber webs. Because the electrospun fiber diameters are comparable to the mean free path of air molecules, the high pressure drop penalty incurred by small-fiber filter materials which operate in the continuum flow regime is much reduced.



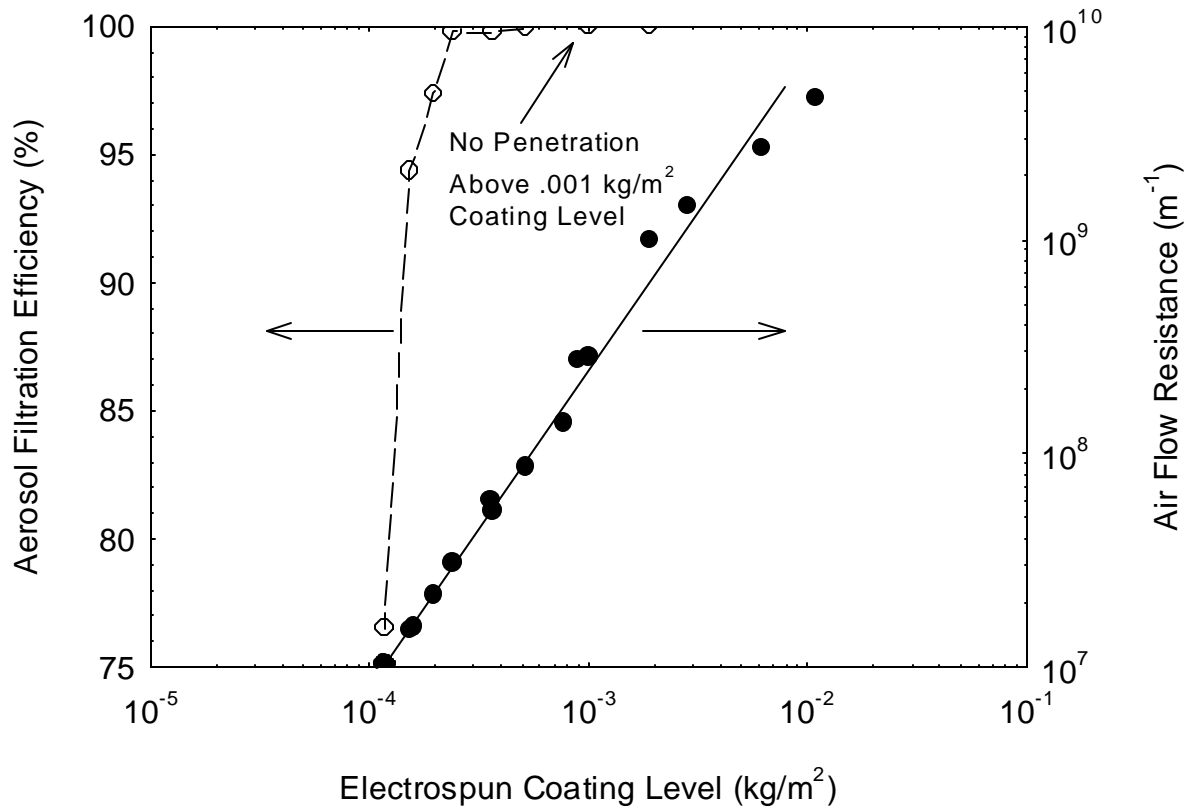


Figure 7. Aerosol filtration and air flow resistance as a function of coating level.

Fibrous materials used for filter media possesses both high filtration efficiency (FE) and low air resistance. Certain treatments can be applied to fibers to improve filtration efficiencies even further, such as electrostatic charging of the fibers in the final fiber mat. Electrostatic post treatments of filter media include corona charging,<sup>18</sup> and triboelectrification charging<sup>19</sup> of fabrics consisting of a two-component blend of fibers of dissimilar electronegativity. Electrospinning has been investigated as a method to produce charged fibers for filtration media. Results from electrospun membranes were compared to the filtration efficiencies of needle-punched felts that were charged by corona charging of a polypropylene (PP) material in one case, and triboelectrifying a blend of polypropylene and a modacrylic through the process of carding the electrically dissimilar fibers in the other case. Data on the fabric weights, filtration efficiencies and residual surface charges are shown for each material in Table I. Filtration efficiency has been normalized with respect to the fabric weight to take into account basis weight differences.

**TABLE I.****Physical Properties and Filtration Efficiencies (FE) of Electrostatic Media**

| Process | Media          | Normalized FE (%) | Surface Charge Potential (V) |                |
|---------|----------------|-------------------|------------------------------|----------------|
|         |                |                   | Top Surface                  | Bottom Surface |
| Corona  | Needled PP     | 75.7              | 304                          | -221           |
| Tribo   | Needled PP+Acr | 94.7              | 974                          | -556           |
| Espun   | Polycarbonate  | 99.9984           | ----                         | ----           |

Surface charge potential was measured by the surface charge potential scanning system developed at the University of Tennessee.<sup>20</sup> The processes of triboelectrification of the fibers and corona charging of the webs produce “electrets,” or a separation of charges within the webs that produce the significant charge differences seen in Table I. No such charging is evident in the electrospun webs, as the surface charges on the polycarbonate fibers are not retained for long in the grounded web during spinning. However, the filtration efficiency of the electrospun polycarbonate is very high when tested against 0.1  $\mu\text{m}$  NaCl aerosol at 5.3 cm/s face velocity in a TSI 8110 automatic filtration tester. It has been noted in our earlier air permeation studies that electrospun materials achieve high filtration efficiencies at very low basis weights (Figure 7), but this comes with a high air resistance penalty. The needled melt blown webs of polypropylene exhibited lower filtration efficiencies on a basis weight, but also produced lower pressure drops during filtration than the electrospun material.<sup>21</sup> The outstanding protection levels of electrospun membranes against aerosol penetration are due to high fiber surface area and not charge attraction. The mode of filtration in electrospun media suggests the best use of this material against aerosol threats is in a low pressure drop application, such as aerosol protection in clothing, rather than in filters, unless a very low quantity of these nanofibers can be incorporated into high flow capacity filter media.

**Physical Properties of Electrospun Membranes**

Electrospun membranes are highly porous, which contributes to their excellent moisture vapor transport properties. A few representative electrospun membranes have been measured by bubble point porometry by Porous Materials Inc. Analytical Services Division using a PMI 4090 capillary flow analysis method. Membranes prepared from Nylon, Pellethane, and Poly(benzimidazole), PBI, were evaluated and compared to the porosity of expanded PTFE. SEM images of these samples are shown in Figure 2. Results from the bubble point capillary porometry are shown in Table II. Nylon can be electrospun into a very fine membrane with extremely small pore throat sizes that are much smaller than the average fiber diameters. PBI also exhibits pore sizes that are smaller than the electrospun fiber sizes. On the other hand, Pellethane® exhibits mean pore sizes that are significantly higher than the other electrospun membranes. The fiber size of Pellethane® is larger than the Nylon and the PBI. Pellethane® is also highly deformable, while Nylon and PBI are not, and it is not certain whether the Pellethane® sample deforms during the pressurization required for bubble point testing, and whether this deformation might increase the measured pore throat diameters.

**TABLE II.**

| <b>SAMPLE</b> | <b>Mean Flow Pore Diameter (<math>\mu\text{m}</math>)</b> |
|---------------|---|
| Nylon 6,6     | 0.121   |
| PBI           | 0.198   |
| Pellethane    | 0.807   |
| PTFE          | 0.210   |

Due to the high porosity of the membranes and the random orientation of the fibers, the source of electrospun membrane tensile strength is not well understood. A study of structural effects upon tensile properties of our new elastic electrospun membranes has been initiated to determine the effect of electrospinning upon tensile strength of the material. To date, tensile data for our elastomeric, unoriented fiber mats have been measured and compared to the tensile properties of continuous films prepared by solvent casting from the same solutions used in electrospinning. Tensile data in Table III show that as-collected electrospun Pellethane® thermoplastic elastomer material does suffer a drop in tensile strength and elongation compared to a solid film of the same material. Stress and modulus were automatically calculated by an Instron 4201 tester during measurement at a crosshead speed of 2.5cm/min, but these data were corrected to take into account the reduced material mass in the electrospun mat cross section in the tensile specimens. This fiber density correction factor and the corrected average tensile values for electrospun materials are shown below.

**TABLE III.**

| <b>SAMPLE</b> | <b>Density<br/>Correction<br/>Factor<br/>(% Fiber)</b> | <b>Young's<br/>Modulus<br/>(MPa)</b> | <b>Peak<br/>Stress<br/>(MPa)</b> | <b>Peak<br/>Strain<br/>(%)</b> |
|---------------|--|--------------------------------------|----------------------------------|--------------------------------|
| Cast Films    |  |                                      |                                  |                                |
| Pellethane®   | ---  | 2.9 +/- 0.2                          | 15.8 +/- 1.7                     | 979 +/- 53                     |
| Electrospun   |  |                                      |                                  |                                |
| Pellethane®   | 27.7   | 3.3 +/- 0.1                          | 9.6 +/- 0.4                      | 360 +/- 13                     |

In general, there is no significant change in Young's modulus with electrospinning, while there is a 40% reduction in tensile breaking strength and a 60% reduction in elongation at break for elastomeric electrospun membranes, compared to the corresponding cast films. It will be important to be able to retain more strength in electrospun materials, so further study of tensile properties and membrane modifications is underway to assess effects of post treatments to improve membrane toughness.

## Use of Additives in Electrospun Membranes

We have shown that electrospinning results in submicrometer size fibers that are laid down in a microporous membrane of extremely fine average pore size. Theoretically, electrospun membranes also possess exceptionally large surface area, as shown by the linear relationship between fiber diameter and surface area in Figure 8. Due to the large expected surface area, calculated by estimating fiber surface based upon the surface area of a perfect cylinder, electrospun mats possess the features desirable for catalyst immobilization substrates, absorbant media and encapsulated active ingredients, such as activated carbon and various biocides.

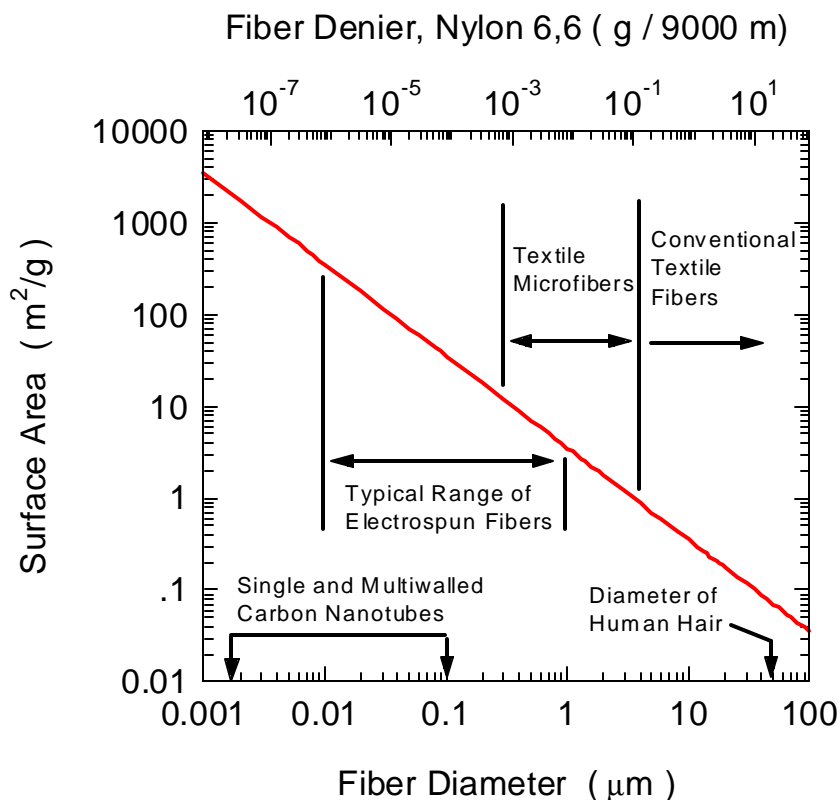


Figure 8. Expected surface areas of man-made and natural fibers.

Electrospun membranes are under investigation as substrates that could provide a sufficient surface for the absorption and detoxification of hazardous liquids and chemical vapors, while still allowing significant water vapor transport to promote evaporative cooling of the body. Additives within the fibers have been investigated to determine whether the unique microstructure of electrospun membranes enable reactivity at the fiber level to chemically break down toxic chemicals. There is growing interest in adding reactive functionality to textiles in protective clothing applications to remove odorous compounds and detoxify industrial contaminants such as aldehydes and ketones, and remove sulfurous by-products from surfaces. It has been reported that a family of relatively new inorganic catalysts, polyoxometalates (POM), are extremely efficient in oxidizing toxic sulfur ethers to non-toxic sulfoxides.

Extending the work of Gall, Hill and Walker,<sup>22</sup> we have suspended a polyoxometalate of composition  $\text{Na}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  in a solution of Pellethane® with the co-oxidant benzoyl peroxide in the solvent tetrahydrofuran. This mixture has been both cast into film form and electrospun into membrane form. A time-dependent study of the reaction of the POM/peroxide system with a target compound, chloroethylethylsulfide (CEES) dissolved in acetonitrile, has been performed by following the disappearance of the sulfide and the appearance of the sulfoxide peak in the reaction products by GasChromatography-Mass Spectrometry (GC-MS). Shown in the plots in Figure 9, the retention time of the chlorosulfide target compound appears at 7 minutes, while the sulfoxide products present a collection of peaks from approximately 20 minutes to 24 minutes into the GC run. We find that after one hour of exposure, the electrospun-supported POM has started breaking down CEES, and after 2 hours, the electrospun POM has oxidized more CEES than the unsupported, solution catalyst system.

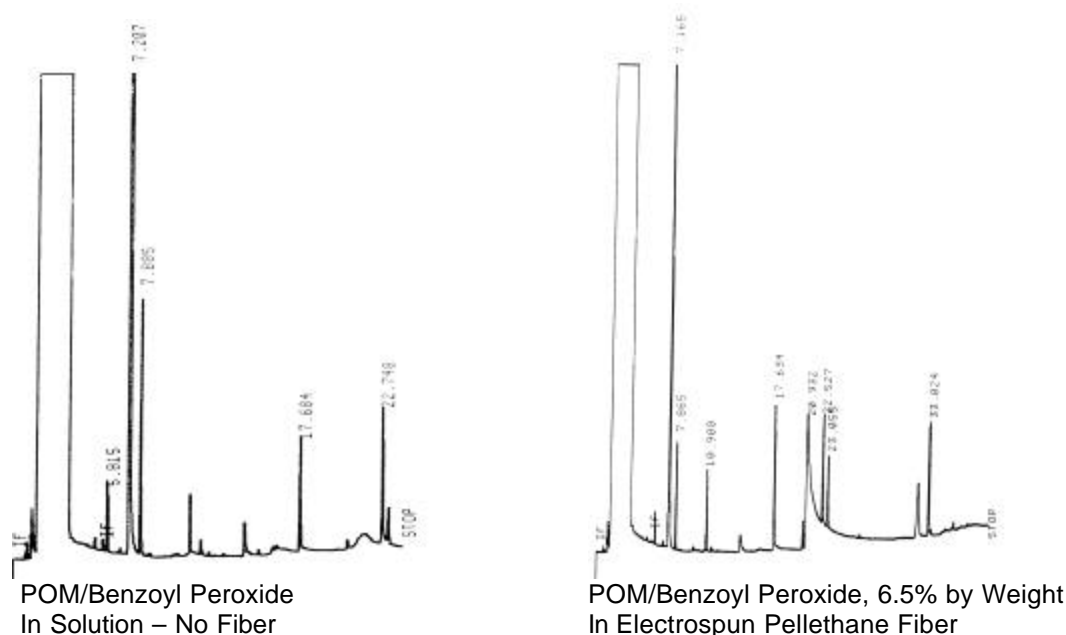


Figure 9. Effect of electrospun membrane support on POM reactivity after 2 hours against CEES.

Integration of these peaks shows that after two hours, the POM catalyst has produced 1% sulfoxide oxidation product without the electrospun support, and has oxidized the CEES to 12% sulfoxide product when the POM is encapsulated within the electrospun Pellethane® fiber mat. Currently, other POM compounds, co-oxidants and aerobic reaction are under investigation to increase reaction rates and catalyst turnover.

There is emerging information about the apparent increase in absorption and activity of other active compounds within electrospun fibers. Recently, it has been reported by Norris et al that conductive polyaniline within electrospun fiber absorbed sulfuric acid vapor twenty times faster than the same polymer cast in film form.<sup>23</sup> This property can be a great advantage for polyaniline, which is a conductive polymer that is doped to the conductive emeraldine salt form at low pH by acid vapor exposure, and dedoped to the nonconductive emeraldine base upon treatment to base.

Our research group has begun studying the conductive properties of electrospun polyaniline which is spun in its conductive form. Normally, conductive polyaniline is unprocessable and intractable. However, recently, it has been shown that polyaniline when prepared by template polymerization remains processable and fully soluble even in the doped conductive state.<sup>24</sup> This soluble conductive polymer can be blended with non-conductive fiber-forming polymers such as Pellethane® or Estane® and electrospun to produce a mildly conductive membrane. This conductivity can be boosted substantially by the use of additives to the conductive polymer blend. We have examined the effect of adding carbon nanotubes to the polymer solution, followed by electrospinning.<sup>25</sup> Carbon nanotubes are reported to be highly conductive, and are of an appropriate size for incorporation into electrospun fibers. The ability to align carbon nanotubes in a head-to-tail orientation along the length of the electrospun fiber would also be expected to increase the effectiveness of the carbon nanotube conductivity in boosting the overall conductivity of polymer blends. It has been found that addition of just 10% by weight to a blend of Estane® containing 20% polyaniline significantly increases the original conductivity of the blend. This is shown in Figure 10, where increasing the content of polyaniline increases ionic conductivity by a factor of 70. Addition of the carbon nanotubes increases conductivity by a factor of 200.

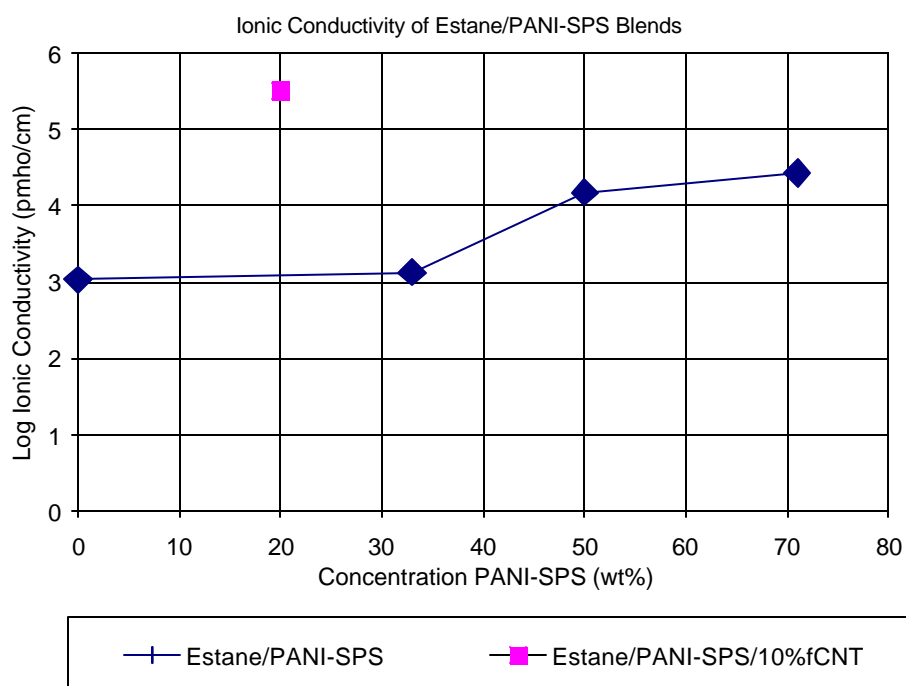


Figure 10. Plot of log ionic conductivity of electrospun fiber mats of Estane/Polyaniline-sulphonated polystyrene blend compositions at 55°C.

One of the biggest challenges in formulating additives into polymer solutions is achieving good dispersion of the additive in the spin dope. We are continuing our studies with conductive polymers and conductive particles to ensure good dispersion and increase conductivity another order of magnitude.

## **Future Concepts for Electrospun Clothing Manufacture**

Potential future applications of electrospun layers include direct application of membranes to garment systems, eliminating such costly manufacturing steps as laminating and curing. It may be possible to electrospin fibers directly onto three-dimensional (3-D) screen forms obtained by 3-D body scanning. In the future, clothing manufacturers will be able to use a laser-based optical digitizing system to record the surface coordinates of a wearer's body.<sup>26</sup> This information could be integrated with computer aided design and manufacturing processes to allow electrospun garments to be sprayed onto the digitized form, resulting in custom-fit, seamless clothing. This concept has all ready been in practice for new racing swimwear produced in solid elastic film form, rather than utilizing fibrous structures. The MACH1 swimwear design by Dianaspport in Italy uses an elastic silicone molded into just two sizes on a computer desined steel mold to obtain desired surface shapes and symmetry for reduced drag in water. Other custom, elastic, skin-tight racing swimwear include Arena's "X-Flat" material, Speedo "Aquablade", and "Fastskin" by Speedo Australia. Clearly, the manufacturing capability to produce head-to-toe body suits for sport clothing and protective clothing utilizing computer generated molds is making strides, and may soon be ready for elastic, microfiber spinning using a method like electrospinning.

### **Summary**

Electrospun fibrous membranes are highly porous structures that can be produced from a number of polymer/solvent combinations. Porosities ranging from 0.1 to 0.8  $\mu\text{m}$  in diameter can be produced from solvent electrospinning. Air and moisture transport measurements on experimental electrospun fiber mats compare favorably with properties of textiles and membranes currently used in protective clothing systems. The electrospun layers present minimal impedance to moisture vapor diffusion required for evaporative cooling. Experimental measurements show that electrospun fiber mats are extremely efficient at trapping airborne particles. The high filtration efficiency is a direct result of the submicron-size fibers generated by the electrospinning process. Electrospun nanofiber coatings have been applied directly to a spunbonded fabric and an open cell foam. The air flow resistance and aerosol filtration properties correlates with the electrospun coating add-on weight. Particle penetration through the foam layer, which is normally very high, is eliminated by extremely thin layers of electrospun nanofibers sprayed on to the surface of the foam. Electrospun media possess filtration efficiencies as high as electrostatically charged olefin fibers. In addition to providing outstanding aerosol protection, electrospun membranes also appear to enhance the activity of reactive additives for chemical protection. New elastomeric membranes prepared from thermoplastic polyurethanes are about half the strength and elongation of a continuous film of the same material, so there is work to be done to improve the tensile properties of these nanofiber membranes. Recent work has begun to show that the electrical conductivity of polymer blends can be significantly impacted by the combination of conductive polymers and carbon nanotubes in electrospun fibers which orient the nanotubes along their axes. Finally, current manufacturing techniques are already being developed which may some day enable us to produce these multifunctional liner materials of man made fibers.

## Acknowledgements

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