Electrospun Fiber Mats: Transport Properties

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Electrospinning is a process by which a suspended droplet of polymer solution or melt is charged to high voltage to produce fibers (Baumgarten, 1971; Larronda and St. John Manley, 1981; Doshi and Reneker, 1996). At a voltage sufficient to overcome surface tension forces, fine jets of liquid shoot out toward a grounded target. The jet splays before it reaches the target, dries, and is collected as an interconnected web of small fibers. The technique provides the capacity to lace together a variety of types of polymers and fibers to produce ultrathin layers which are useful for chemical protective clothing. Depending on the specific polymer being used, a range of fabric properties, such as strength, weight, and porosity, can be achieved. Figure 1 shows the electrospinning process used to manufacture these materials and a typical scanning electron microscopy (SEM) micrograph of a nylon electrospun fiber mat. Fiber sizes of 40 nm and smaller were reported (Reneker and Chun, 1996), although we normally produce fibers in the 200 to 500 nm range in our apparatus.

Electrospinning results in submicrometer-size fibers laid down in a layer that has high porosity but very small pore size. One implication is that these materials would provide good resistance to the penetration of chemical warfare agents in aerosol form, while still allowing significant water vapor transport to promote evaporative cooling of the body. Electrospun nonwoven fiber mats may be thought of as a microporous material that behaves like a membrane, as opposed to a more porous, air-permeable fabric. Because of the small fiber/pore sizes in these electrospun membranes, the resistance to convective gas flow is quite large and is comparable to the flow resistance shown by microporous polytetrafluoroethylene (PTFE) membranes, which are often used as a component of protective clothing systems.

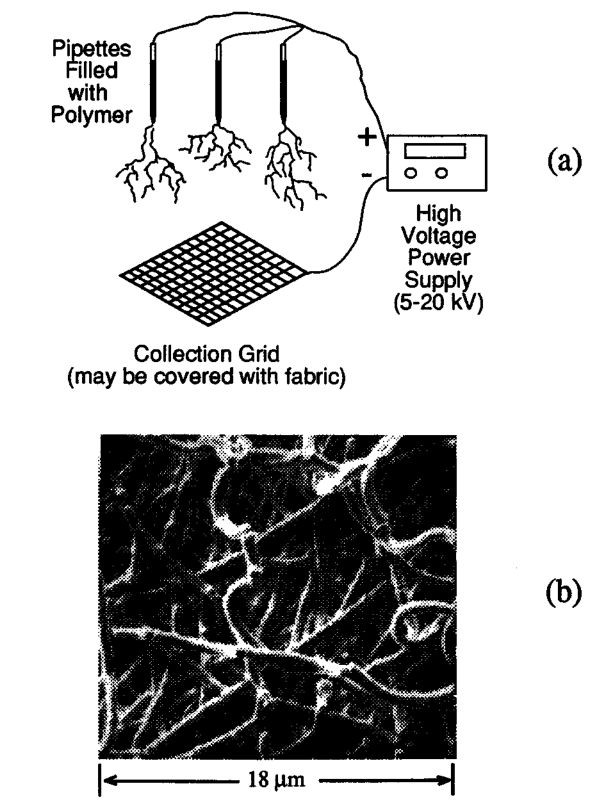

Figure 1. (a) Electrospinning process; (b) SEM image of electrospun nylon membrane.

Experimental Method

Water vapor diffusion and gas convection properties of electrospun fiber mats were determined with an automated dynamic moisture permeation cell (Figure 2) (Gibson et al., 1995, 1997a,b). Gas flows of known temperature and water vapor concentration enter the test cell; by measuring the temperature, water vapor concentration, and flow rates of the gas leaving the cell, one may measure the fluxes of gas and water vapor transported through the test sample. With no pressure difference across the sample, transport of water vapor proceeds by pure diffusion, driven by vapor concentration differences. If a pressure difference across the sample is present, transport of vapor and gas includes convective transport, where the gas flow through the sample carries water vapor with it, which may add to or subtract from the diffusive flux, depending on the direction of the convective gas flow.

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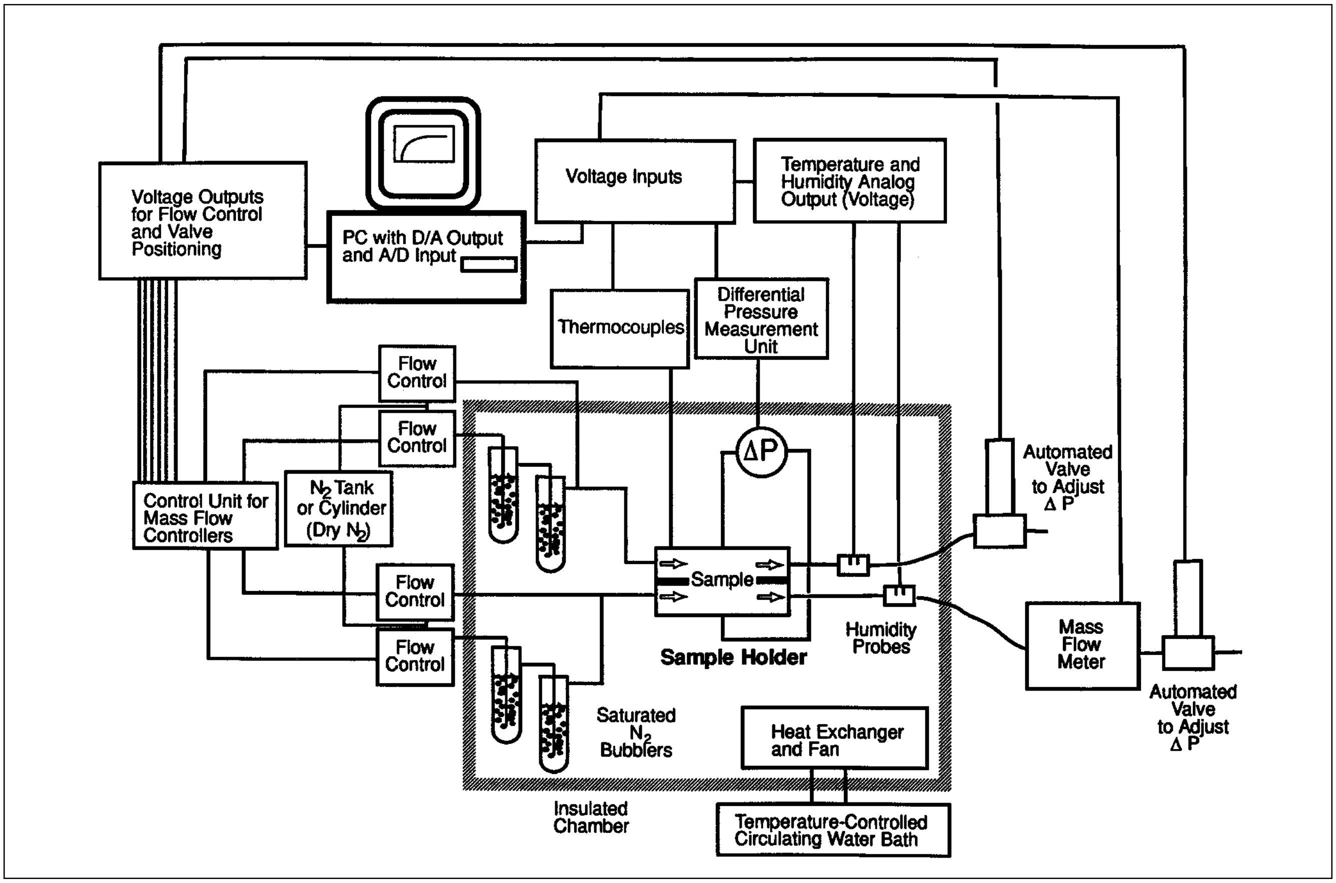

Figure 2. Experimental apparatus to determine water vapor diffusion resistance and convective gas flow resistance of electrospun fiber mats.

Permeability to convective gas flow is given by Darcy's Law (Dullien, 1979) such that

$$k_D = \left(\frac{\mu Q}{A}\right)\left(\frac{\Delta x}{\Delta p}\right) \tag{1}$$

where k_D is the permeability constant (m^2), μ is the gas viscosity (17.85×10^{-6} kg/m·s for N_2 at 20°C), Q is the total volumetric flow rate (m^3/s), A is the area of test sample (m^2), Δx is the thickness (m), and Δp is the pressure drop across sample (N/m^2 or Pa).

Thickness measurements for textiles are often problematic, although they seem simple, and can be a large source of error if they are incorporated into reported measurements of Darcy permeability. It is preferable to present the pressure-drop/flow rate results in terms of an apparent flow resistance defined as:

$$R_D = \left(\frac{A \Delta p}{\mu Q}\right) \tag{2}$$

where R_D represents the apparent Darcy flow resistance (m^{-1}).

We define the resistance to mass transfer by diffusion as the simple addition of an intrinsic diffusion resistance due to the sample (R_i) and the diffusion resistance of the boundary air layers (R_{bl}):

$$(R_i + R_{bl}) = \left[\frac{\Delta \overline{C}}{\left(\frac{\dot{m}}{A}\right)}\right] \tag{3}$$

where R_i is the intrinsic diffusion resistance of sample (s/m), R_{bl} is the diffusion resistance of boundary air layers (s/m), $\dot{m}$ is the mass flux of water vapor across the sample (kg/s), A is the area of test sample (m^2), and $\Delta \overline{C}$ is the log mean water vapor concentration difference between top and bottom nitrogen streams (kg/m^3).

The test material's intrinsic diffusion resistance may be obtained by subtracting off the apparent boundary layer diffusion resistance (Gibson et al., 1997a), but in many cases it is sufficient to leave the results in the form of a total resistance to water vapor diffusion including the boundary layer effects.

Results

The magnitude of the convective flow resistance for two typical electrospun membranes composed of polyacrylonitrile

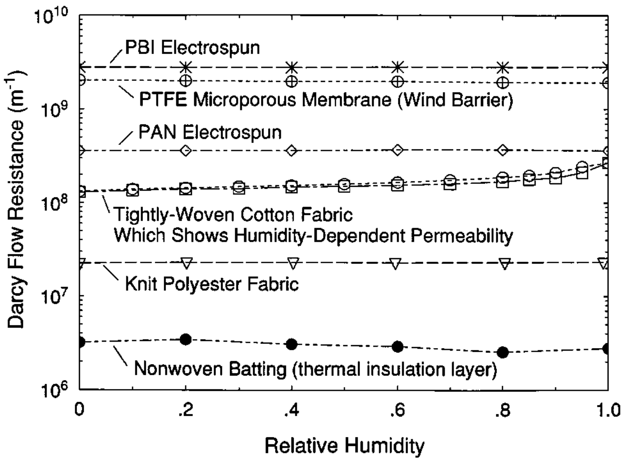

Figure 3. High convective gas flow resistance of microporous membranes and electrospun nonwovens.

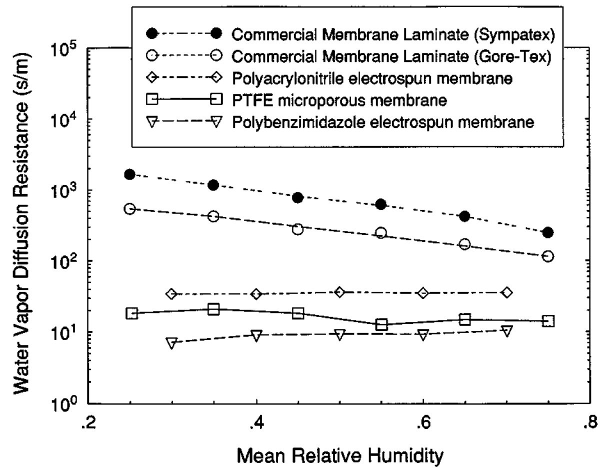

Figure 4. Excellent water vapor transport properties of electrospun nonwovens.

and polybenzimidazole (Kim and Reneker, 1998) is shown in Figure 3 and compared to other common fiber-based materials. Figure 3 shows the gas flow resistance as a function of relative humidity, which is most important in the case of a hydrophilic fiber, such as cotton (Gibson et al., 1997c).

The convective flow resistance of the electrospun fiber mats is much greater than that of normal clothing materials, yet, as will be shown later, the high resistance to air flow does not impede the diffusion of water vapor through the pore structure of the electrospun nonwoven material. In general, materials with high rates of water vapor diffusion and low air permeability are promising candidates for protective clothing applications.

An interesting complicating factor in the analysis of gas flow through porous materials with such small fiber diameters is that the mean free path of gas molecules becomes comparable to the fiber size (Kirsch et al., 1974). There is gas slip at the fiber surface, and the normal linear dependence of flow rate with pressure drop, valid in low Reynolds number laminar flows, becomes less applicable to the flow field in the electrospun nonwoven pores.

Water vapor transport properties of electrospun nonwovens are excellent and indicate that layers based on electrospun fiber technology will be thin, lightweight, and very "breathable" with respect to allowing evaporative cooling to take place through the protective clothing system. Water vapor diffusion measurements for the same materials given in Figure 3 are shown in Figure 4. The electrospun nonwoven resistance to water vapor diffusion is much lower than the commercially available membrane laminates presented in Figure 4, which are often said to be highly "breathable." Figure 4 compares the performance of the materials as a function of the "mean relative humidity," which is useful as an indication of concentration-dependent transport behavior in polymer membranes and membrane laminates (Gibson et al., 1995, 1997a,b).

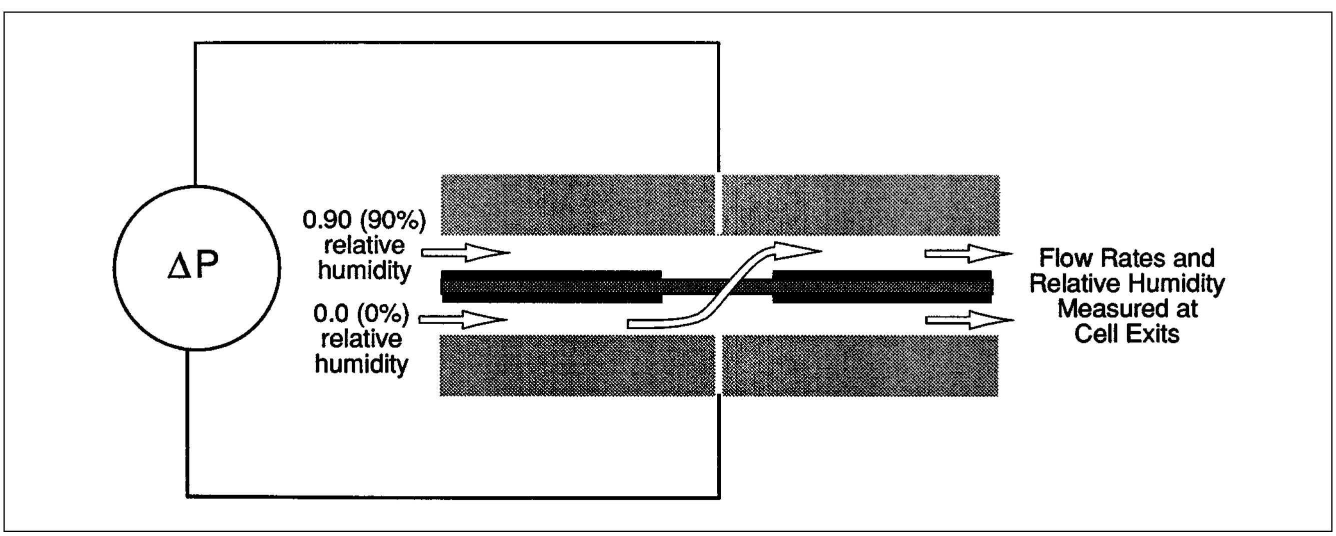

Figure 5. Convection/diffusion experiment in the DMPC.

Example shows bottom outlet flow restricted to force convective flow across sample, which opposes diffusive flux of vapor.

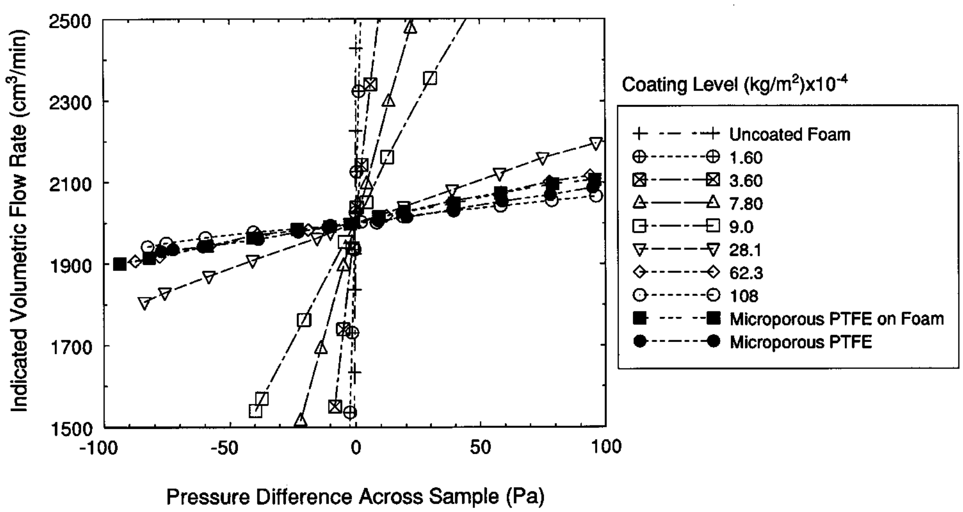

Figure 6. Convective flow through samples as a function of pressure drop.

Electrospinning also lends itself very easily to spraying a fiber coating directly onto other materials. For example, an extremely thin electrospun fiber coating may be sprayed onto the surface of chemical protective garments to improve aerosol particle filtration and capture, or to incorporate additional functionality to the chemical protective garment such as agent-specific enzymes or catalysts.

Water vapor diffusion resistance and air flow resistance properties were determined for an electrospun nonwoven (nylon 6,6) deposited onto an activated-carbon-loaded polyurethane foam, which was an experimental variant of the material used as a chemical protective layer in the U.S. Army Battle Dress Overgarment (BDO). This foam had a nominal thickness of 8.7×10^{-4} m with an areal density of 0.19 kg/m^2; the open foam structure results in very little resistance to convective air flow (flow resistance is 3.2×10^{6} m^{-1}). Foam thickness and areal density may vary as much as 10% from the mean value.

Seven different electrospun coating add-on levels were produced over the range of 1.6×10^{-4} to 1.1×10^{-2} kg/m^2. Three other materials were also tested for comparison purposes: the uncoated foam, the uncoated foam tested in combination with a microporous PTFE membrane, and the microporous PTFE membrane by itself. The test method determines water vapor diffusion properties and air flow resistance under simultaneous diffusion/convection conditions, as shown in Figure 5 (Gibson et al., 1997d, 1998).

The plot of convective flow as a function of pressure drop in Figure 6 shows the expected trends. In this test method, materials with a low slope in Figure 6 have a high flow resistance; the numerical value of the slope can be converted to a flow resistance as given in Eq. 2. The electrospun membranes' air flow resistance correlates well with the electrospun layer coating level, as shown in Figure 7. Figure 7 also shows the results for the microporous PTFE membrane, which has an areal density comparable to the highest electrospun coating level.

The water vapor diffusion resistance as a function of pressure drop (Figure 8) reflects the different air permeability properties of each coating level. Water vapor diffusion resistance is defined as the intersection of each curve with the point where the pressure difference across the sample is equal to zero. Figure 8 contains information about both convective and diffusive transport across the test sample. Those materials with higher flow resistances are affected less by the pressure difference across the sample. Figure 8 includes the boundary layer resistance due to laminar air flow over the sample, which in this case is about 105 s/m. It is known from previous work (Gibson et al., 1997a) that the intrinsic diffusion resistance of the PTFE membrane is 6–8 s/m. All the electrospun coated foam samples, the foam sample tested in combination with the PTFE membrane, and the uncoated foam sample converge to approximately 200 s/m at the zero

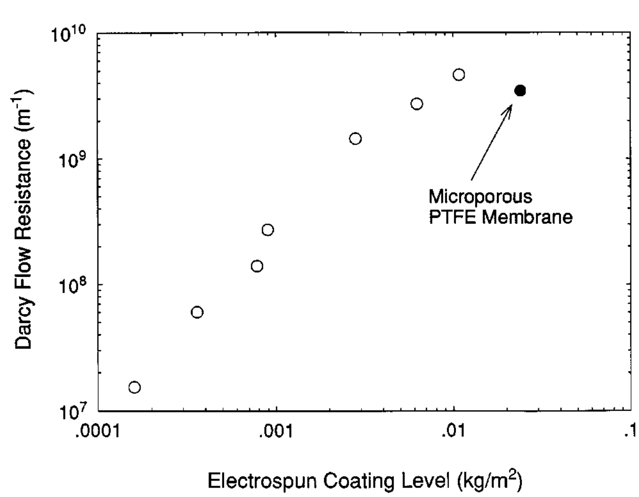

Figure 7. Convective gas flow resistance related to electrospun coating level.

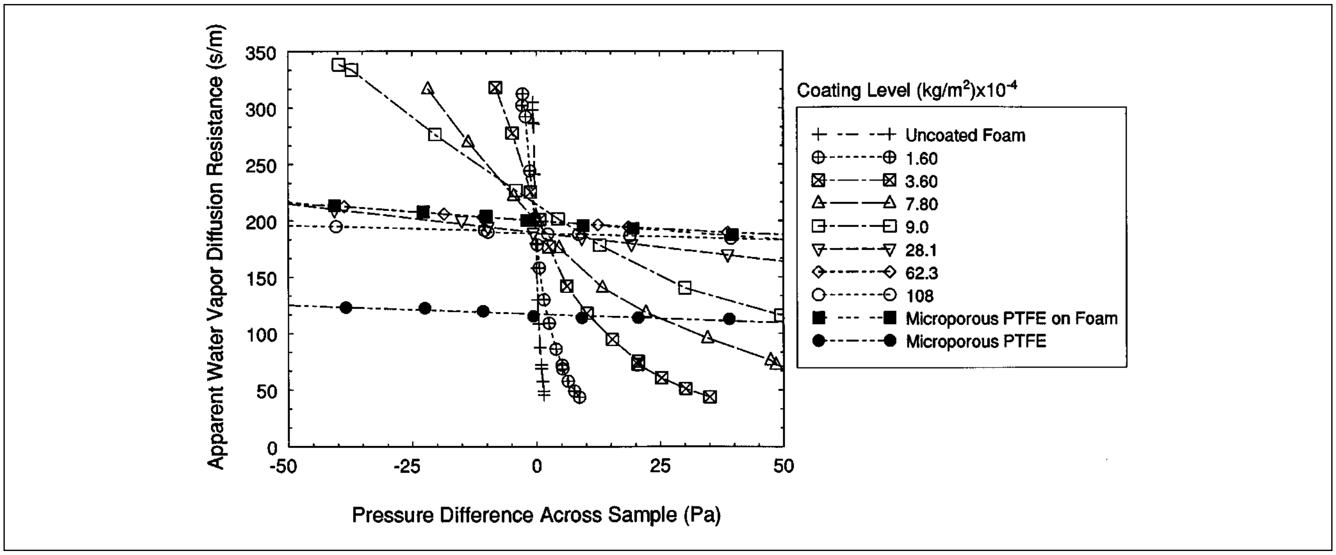

Figure 8. Water vapor diffusion resistance as a function of pressure drop.

pressure difference point. This translates to an intrinsic diffusion resistance for the samples of approximately 95 s/m after subtraction of the boundary layer resistance. The small variations in intrinsic diffusion resistance of the coated and uncoated samples are negligible in the practical sense, since they are within the experimental variation of diffusion resistance caused by the large thickness variations in the foam substrate. It is likely that none of the electrospun layers added more than 10 s/m to the total diffusion resistance of the foam layer. It is worthwhile to refer to Figure 4 where the water vapor diffusion resistances of commercial breathable laminates are shown to be much higher (200–1500 s/m). Other factors in clothing systems, such as stagnant air trapped underneath or between layers, or boundary layer resistances due to air flow over the body surface, also result in water vapor diffusion resistance factors which far outweigh the small contribution of the electrospun membrane layers.

Summary

Early performance measurements on experimental electrospun fiber mats compare favorably with transport 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. Moisture sorption and transport are also important for catalytic hydrolysis of chemical agents in reactive fabric layers. Air flow resistance measurements and electron microscopy suggest that pore size is small enough to exclude aerosol particles. These encouraging results point towards more intriguing questions such as: what is the pore size distribution in these layers, and how will manufacturing processes affect pore size and function? How will the incorporation of reactive solids in the fibers affect transport properties? Can the effect of fiber chemical composition on transport properties be reliably predicted (e.g., hygroscopic fibers will swell and decrease pore size).

Once these fundamental effects are understood, a well-defined and tailorable membrane-processing technique will be available for development. 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 3-D screen forms obtained by 3-D body scanning. Scientists can use a laser-based optical digitizing system to record the surface coordinates of a soldier's body. 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.

Acknowledgments

The authors would like to acknowledge the assistance of Professor Darrell Reneker, Department of Polymer Science, University of Akron, for assistance in setting up our electrospinning facility, and for supplying the polybenzimidazole and polyacrylonitrile electrospun samples.

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LETTERS TO THE EDITOR

To the Editor:

In the article titled "New Approach to Analysis and Design of Smith-Predictor Controllers"by Tan et al. (June 1996, p. 1793), a new approach to the design of Smith-predictor controllers is developed on the basis of an equivalent representation of the Smith-predictor controller given in Figure 2. In the third part of the paper, the authors claim that "... we can actually view the single-loop control system as a particular case of a mismatched Smith system with $L_o = 0$" and that "With this particular representation, every Smith system has an associated 'compensated' process $F(s)$ and all the uncertainty is concentrated in this process. The properties of $F(s)$ will thus directly affect the achievable closed-loop performance of the Smith system." This implies that Figure 1 is always equivalent to Figure 2 and the transfer function from the load disturbance d to the system output y is always $g_p(s)$, even when uncertainty exists. That is impossible. In fact, Figure 1 can be equivalent to Figure 2 only when $g_p(s) = g_{po}(s)$. In addition, why are there two practical processes with different inputs in the equivalent representation of the Smith predictor? If the $g_p(s)$ in $F(s)$ and $C(s)$ is actually the model, then $C(s) = e^{sL_o}$ and $F(s) = g_{ro}(s)$. How can all the uncertainty be concentrated in the $F(s)$ and how can the $F(s)$ affect the achievable closed-loop performance of the Smith system?

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Reply:

Figures 1 and 2 in Tan et al. (1996) are equivalent whether the model is perfect or not. The confusion arises from the use of the notation d for the equivalent disturbance signal in Figure 2, which is not the same as the signal d in Figure 1. Therefore for clarity, we now replace d by $\tilde{d}$ in Figure 2, where

$$\tilde{d} = g_p(1 - g_{yr})d$$

On the question of Zhang and Xu concerning why there are "two practical processes with different inputs in the equivalent representation," we would just like to clarify that the equivalent representation is used only for the purpose of analysis and design of the Smith-predictor controller and in this instance is also used to highlight the possible use of model mismatch to improve control performance.

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