

ELECTROSPINNING NONWOVENS FOR COTTON FABRIC COATINGS

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Abstract

Fine nanofibers of polymer can be collected into a microporous membrane by the method of electrospinning. A solution of high molecular weight polymer can be electrospun by inductively charging it to approximately 10,000 volts. Fine jets of charged fiber emit from the solution surface and collect onto a grounded or oppositely charged substrate, such as a cloth-covered electrode. The electrospun layer can be deposited directly onto fabric, and possesses the consistency of typical microporous membranes. Pore sizes are small enough to filter submicron particles. Average fiber size is on the order of 100-500nm. These nanofibers impart high surface area characteristics to the membrane, enabling the immobilization of absorptive and reactive materials within the fibrous structure. Since the spinning solutions may contain liquid or solid additives in addition to the fiber forming component, it is possible to design multifunctional materials that serve as protective fibrous layers in a textile system. Significant improvements in protective characteristics have been achieved with the addition of reactive enzymes to electrospun nanofiber membranes. An enzyme that breaks down highly toxic organophosphorous compounds such as certain pesticides and nerve agents has been covalently attached to cotton surfaced nonwovens and to electrospun cellulose acetate. The success of this cotton functionalization is reported herein.

Introduction

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 (Formals, A. 1934). Since that time, many patents and publications have been reported on electrospinning. This paper reviews the electrospinning process, its current status as a manufacturing method, and the performance of electrospun membranes as potential laminates for textiles such as cotton blends, used for example in the standard military battle dress uniform.

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 (Reneker, et.al., 2000). 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 (Schmidt 1980; Wegmann 1982; Davis 1987; Simm 1976). 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 (Gibson et.al. 1998). 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 0.1 to 1.0 μm in diameter. In contrast, commercial production size melt blowing equipment produces fibers in the 0.5 to 10 μm diameter range. Fiber size depends upon solution viscosity, field strength, and field uniformity (Baumgarten 1971).

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 (Groitzsch and Fahrbach 1986; Bamford and Al-Lamee 1997; Coffee 1997; Martin 1977). 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 (Groitzsch and Fahrbach 1986). 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 (Gibson et.al. 1995; Gibson et.al. 1999; Gibson et.al. 2000). These properties make microporous membranes indispensable for protective clothing applications. Operations involving hazardous chemicals require the use of impermeable hazardous materials suits (HAZMAT) which cause heat buildup when worn for extended periods of time. Military chemical protective suits are semi-permeable versions of HAZMAT suits which rely upon absorption of hazardous vapors within the suit by activated carbon present in the textile. In the future, new protective textiles could be designed to react with specific chemicals on contact, while remaining breathable and lightweight, by use of reactive compounds on the surfaces of the fibers, provided the rates chemical vapor transport are slow enough and the rates of reaction are high enough to provide full protection.

Preparation 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 1-2 hours from a single pipette onto a grounded screen. Cloth can be placed on the grounded surface to enable direct spraying of fabrics with an electrospun coating.

The microstructure of an electrospun coating is shown in the scanning electron micrograph (SEM) in Figure 2, exhibiting a range of fiber size 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.

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 (Gibson et.al. 1998).

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 cm² (Gibson et.al. 2000).

Three samples were examined with respect to transmission of vapor, air resistance, and efficacy of enzymatic bonding and subsequent enzyme activity. Cellulose acetate with an degree of acetyl substitution of 2.5 (Eastman Chemical Co. CA380-30) was dissolved in acetone and electrospun into a microporous membrane structure. Samples of cotton surfaced nonwoven web structures were produced at the University of Tennessee Textiles and Nonwovens Development Center (TANDEC) in the following manner: a 34g/m² polypropylene (PP) spunbond web was thermally bonded on both sides with a 24g/m² surfacing PP web of thermally bonded cotton. PP to cotton ratios in the surfacing web were 40/60 for sample SBPPC60 and 50/50 for sample SBPPC50 (designation referring to Spun-Bonded PolyPropylene-Cotton-50%).

The microstructure of the spunbonded cotton surfaced nonwovens exhibits fiber sizes of over 10 times the fiber diameter of electrospun nonwovens. Seen in the SEM in Figure 3 are 20µm diameter fibers of cotton. Shown on the same scale are 1-5µm electrospun fibers of cellulose acetate in Figure 2.

Shown in Table 1 and in Figures 4 and 5 are data collected from separate measurements of moisture vapor diffusion and gas convection in the DMPC. Moisture vapor and air transport properties of the nonwovens, the electrospun cellulose acetate (ESCA) sample, and a 100% cotton ripstop poplin, were measured for comparison.

Table 1. Water Vapor Transport Properties of Textiles and an Electrospun Membrane.

Sample	Vapor Flux (g/m ² -day)
ESCA	8846
SPPC60	7508
SPPC50	7439
Cotton Fabric	6985

In a practical sense, all samples are very breathable. All are highly porous and water vapor travels easily through each structure. Slight differences are seen when comparing the ripstop cotton fabric to the highly porous electrospun material. There is no significant difference between the two nonwoven samples.

Air convection through the membranes can easily be determined as a function of humidity in the DMPC. In Figure 4, the relatively open structure of the spun-bonded nonwoven has a very low resistance to air flow. Its air resistance is not significantly affected by the quantity of cotton staple within the surfaced web. The nonwoven containing 50% cotton within the bonded surface web is more wind resistant than a 60% cotton web. Both nonwovens have a more open pore structure than a woven cotton fabric. But the most air resistant material is the electrospun microporous cellulose acetate membrane material. It is important to remember that high resistance to air flow does not impede water vapor diffusion through the pore structure of electrospun membranes, so even thick layers of electrospun coatings will not affect a fabric's ability to transmit vapor through its structure. In general, materials with high rates of water vapor diffusion and low air permeability are promising candidates for protective clothing applications.

A final observation regarding the humidity dependence of air flow resistance of textiles: shown in Figure 5, the air flow properties of cotton fabrics are significantly affected by humidity. Cotton fibers swell in high humidity and effectively close pore sizes to increase resistance to air flow. This effect is more acute for tightly woven fabrics.

Use of Additives in Electrospun Membranes

We have shown that electrospinning produces submicrometer size fibers that are laid down in a vapor transmissive, yet wind resistant membrane. Theoretically, electrospun membranes also possess exceptionally large surface area, as shown by the linear relationship between fiber diameter and surface area in Figure 6. 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.

Based upon the fiber sizes observed in Figures 2 and 3, we can estimate an average surface area of around 2m²/g for the electrospun cellulose acetate, while the spun-bonded nonwovens appear to have 0.2m²/g available cotton surface area.

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 enables 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 pesticides.

Two cotton-surfaced nonwovens, SBPP60 and SBPP50, and a sample of electrospun cellulose acetate were massed to 10 mg and exposed to a solution of suspended enzymes (protein concentration 71 µg/mL), OPAA and CBD-OPAA. OPAA is an organophosphorus acid anhydrase enzyme capable of catalytically degrading a wide range of organophosphorus compounds in solution (Cheng et.al. 1993). Cellulose-binding domains (CBD) have been added to the OPAA enzyme by use of a method of subcloning and preparation of the CBD-OPAA fusion protein from a Novagen (Madison, WI) CBD expression vector (Cheng, et.al. 2000). CBD-OPAA can be chemically bound to cotton, while OPAA cannot. After a one hour exposure of the cellulosic fibers to the enzyme solutions at room temperature, the nonwovens and electrospun CA were removed, rinsed twice with buffer, and immersed in a solution of acetonitrile with p-nitrophenyl ethylphenyl phosphate (PNEPP), a colorimetric substrate that reacts in the presence of active enzyme (DeFrank, et.al 1991). Enzyme activity against PNEPP was monitored by UV-VIS spectrometry at 412nm over a period of 10 minutes. Reaction of the PNEPP substrate with enzyme on the fibers produces a light absorbing product with a molar extinction coefficient of 13500. Product concentration can be related to enzyme activity (rate constant) in mmoles of enzyme hydrolyzed per gram of material per minute. We report this quantity as Units/g-min.

Absorbances of reacted and unreacted PNEPP are shown in Figure 7. Non-binding OPAA treated fibers have the same flat slope as the blank solution of PNEPP with no enzyme treated fiber. However, the CBD-OPAA treated fibers react with the PNEPP and an increasing absorbance of PNEPP product with time is recorded.

Table 2 shows the results of residual enzyme activity on the surface of the cotton samples after washing. There was no measurable enzymatic activity in any of the three samples treated with non-binding OPAA. There is

appreciable activity, measured in Units/min-gram(material) for the CBD-OPAA bound enzyme samples after exposure to PNEPP. Furthermore, there is an apparent increase in enzyme activity for the CBD-OPAA bound to the electrospun cellulose acetate (ESCA), compared to the cotton-surfaced nonwovens. Further analysis of these results are needed to account for the actual percentage of reactive sites for the CBD-OPAA binding reaction in all three samples.

Table 2. Activity of Enzyme-Treated Cellulosic Fabrics Against PNEPP.

Sample	Activity CBD-OPAA (Units/min-g material)
ESCA	39.8
SPPC60	17.7
SPPC50	13.8

Shown in Table 3, we have converted enzyme activity from Units/min-g material to Units/min-g fiber, accounting for the cellulosic fiber content in the material. The fraction of cellulosic fiber in SPPC50 is 0.30; the fraction for SPPC60 is 0.36; and the fraction for ESCA is 1.0.

Table 3. Adjusted Activity of Enzyme-Treated Cellulosic Fabrics Against PNEPP.

Sample	Activity OPAA-CBD (Units/min-g fiber)
ESCA	39.8
SPPC60	49.2
SPPC50	46.0

Now we can see that the activity of OPAA/CBD treated fabrics is higher for cotton-surfaced fabrics than for electrospun cellulose acetate. However, we might have expected the electrospun cellulose acetate to bind more CBD-OPAA and produce a higher activity than the cotton-surfaced nonwovens, based upon surface area and available sites for binding reaction. Estimated surface area is 10 times greater for the cellulose acetate, but the total number of reactive (hydroxyl) cellulose binding sites for the CBD-enzyme is 1/6 lower for cellulose acetate, compared to cellulose. Thus, the total relative number of reactive surface sites would be expected to be 10/6, or 1.7 times greater for electrospun cellulose acetate.

The decrease in measured enzyme activity for the electrospun cellulose acetate suggests that natural cotton fibers may bind the enzyme more effectively than the cellulose acetate. This would have to be verified by varying exposure concentrations of CBD-OPAA with cotton and cellulose acetate samples. It is also possible that a limiting concentration of CBD-OPAA was used, and saturation of the cellulose binding sites with enzyme was not achieved. A study to exhaust the binding sites with CBD-OPAA would be necessary to observe differences in fabric surface area for enzyme-catalyzed reactions. Follow-up studies are planned.

Summary

Electrospun fibrous membranes are highly porous structures that can be produced from a simple polymer/solvent mixture at room temperature in air. Air and moisture transport measurements on experimental electrospun fiber mats show better vapor transport and higher wind resistance than woven textiles and non-woven fabrics. The electrospun layers present minimal impedance to moisture vapor diffusion required for evaporative cooling. These properties make electrospun layers ideal for fabric coatings to impart added protection to a textile system. Cotton fabrics exhibit a marked humidity effect upon air resistance through the fabric at high humidities greater than 80%RH. Cotton-surfaced nonwovens do not show the same humidity dependence. Surface reactions can be successfully performed on cellulosic fibers, and the treatment is shown to be more effective with natural cotton fibers than with a higher surface area cellulose acetate nonwoven membrane. Cotton-surfaced nonwovens can be

conveniently treated with a solution of cellulose-binding domain enzyme to permanently functionalize the fabric for use as a decontaminating surface for protection against organophosphorus agent exposures.

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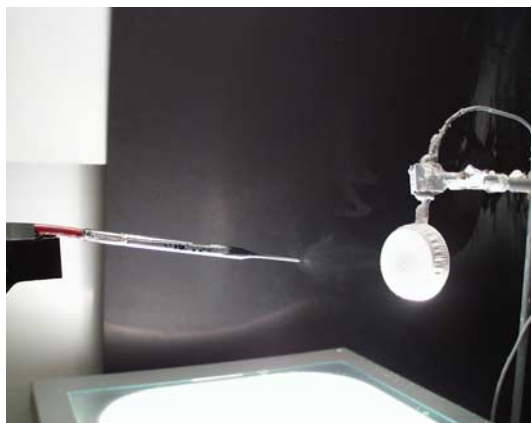


Figure 1. Laboratory scale apparatus for electrospinning charged polymer solutions from pipette.

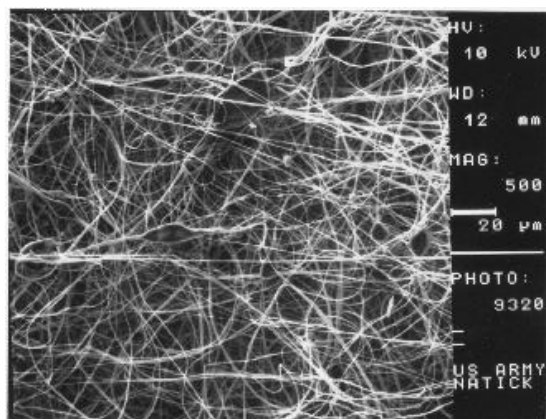


Figure 2. Electrospun cellulose acetate.

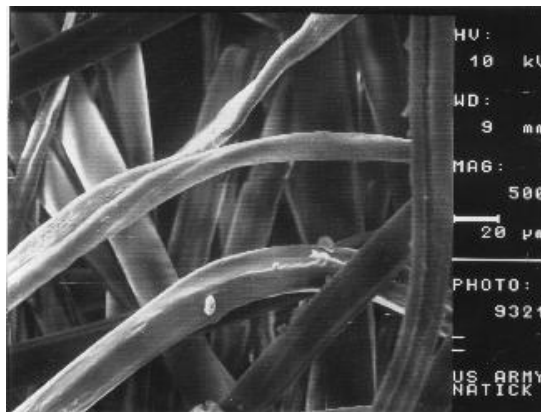


Figure 3. Cotton-surfaced nonwoven.

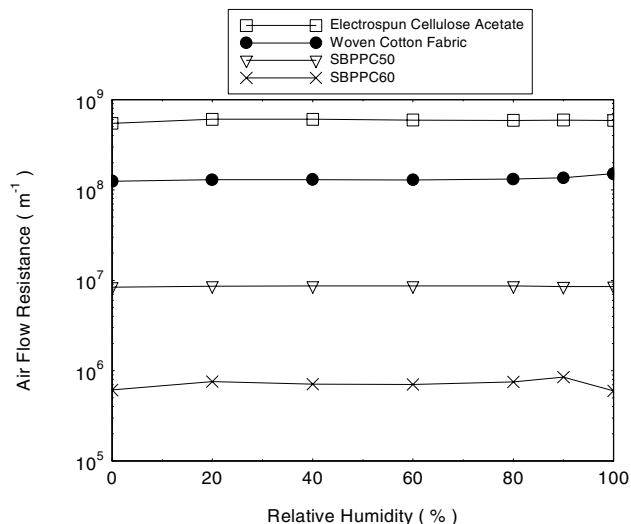


Figure 4. Convective air flow resistance of representative textile materials.

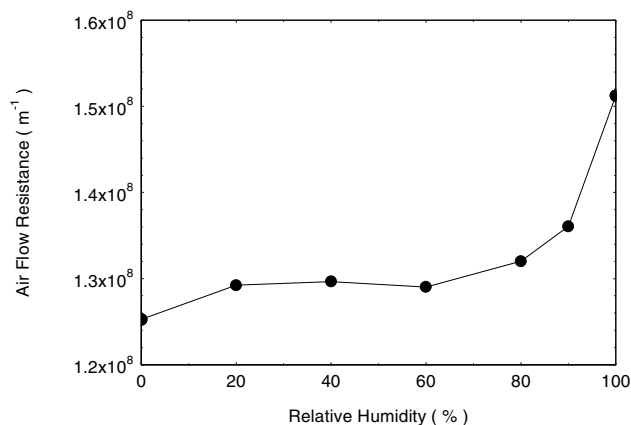


Figure 5. Effect of humidity on cotton fabric air flow resistance.

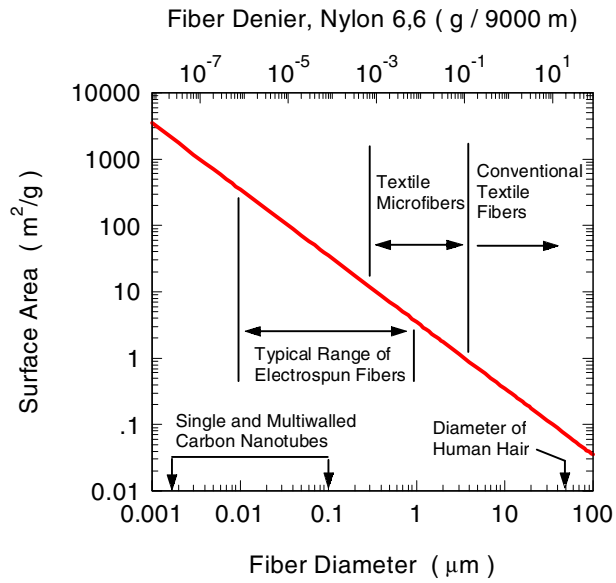


Figure 6. Calculated surface area based upon fiber diameter.

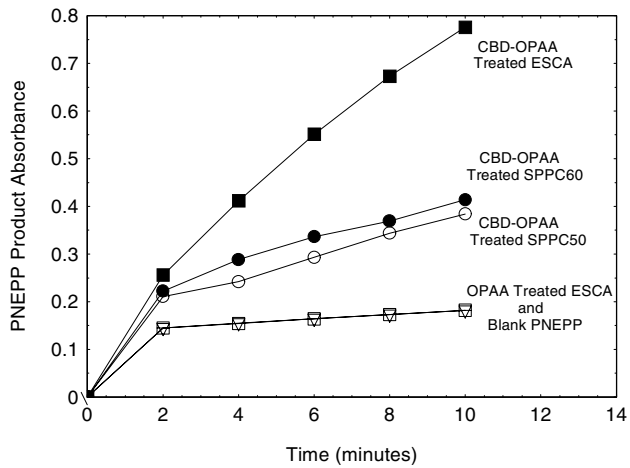


Figure 7. Effect of binding and non-binding enzyme on breakdown of PNEPP.