

Transport Properties of Electrospun Nonwoven Membranes

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Abstract

Recently measured transport properties of electrospun materials have shown that the microporosity present in electrospun membranes enables exceptional breathability with accompanying wind resistance. Recently prepared elastomeric polyurethane nonwovens have been prepared with and without crosslinking after fiber formation. The effect of crosslinking on microstructure, wettability and liquid retention, as well as transport properties, has been studied.

Introduction

Electrospinning is a technique that produces extremely fine submicron fiber by a process of charging polymer solutions with 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 [1]. Since that time, many patents and publications have been reported on 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 [2]. 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 ultrahigh efficiency filtration webs [3-5]. 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 μm in diameter. Commercial production size equipment produces fibers in the 0.5 to 10 μm diameter range. Fiber size depends upon solution viscosity, field strength, and field uniformity [6].

There have been a number of patents on the electrospinning process for the production of fibers, of filter media, and of medical materials [7-11]. There is one major producer of electrospun products in Europe and the United States. Freudenberg Nonwovens of Weinheim, Germany, has been electrospinning for over 20 years, producing electrospun filter media from a continuous web feed for ultra high efficiency filtration markets [8]. Smaller companies are now beginning to electrospin, including eSpin Technologies in Chattanooga, Tennessee and Foster Miller, Inc. in Waltham, Massachusetts.

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 1*. 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, absorbent media and encapsulated active ingredients, such as activated carbon and various biocides.

Despite the long history of electrospinning technology, it has never been applied to fabrics as a protective membrane layer. This new application has been a recent focus of 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 [12].

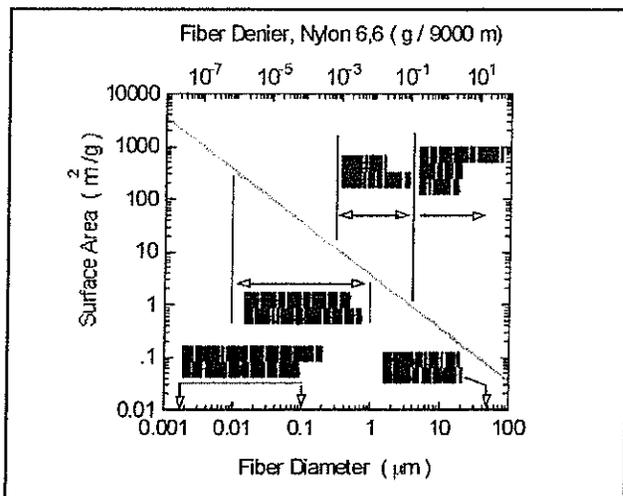


Figure 1
EXPECTED SURFACE AREAS OF MAN-MADE
AND NATURAL FIBERS

In this study, thermoplastic polyurethane elastomers were electrospun into thin nonwoven webs resembling microporous membranes and evaluated for use as protective membranes for textiles.

Thermoplastic polyurethane (TPU) elastomers are unique materials that possess the elasticity of thermoset crosslinked rubber and the processability of thermoplastics. TPUs are soluble in a variety of solvents and can be solution processed into films and electrospun webs. TPUs can be melt blown into webs of overall larger microstructure than electrospun webs, and the relative merits of each nonwoven structure can be assessed with respect to transport properties. TPU chemistry varies depending upon the requirements of the application: aliphatic polyethers are used for flexibility and moisture vapor breathability; aliphatic polyesters are also breathable, but slightly more rigid and less tacky than polyethers; aromatic polyethers and polyesters are available for injection molding of flexible elastomeric parts. Aliphatic and aromatic polycarbonate-based TPUs are also manufactured. For this study, a crosslinkable TPU from Noveon (formerly B.F. Goodrich) was used. Sanres, 13100C, an experimental carboxylated Estane, product of Noveon, was provided for this purpose and compared to Sanres, 13100, uncarboxylated, as well as meltblown Estane, 58277 and electrospun Estane.

Experimental Methods

Process Conditions for Electrospun Fabrics

Estane 58277 pellets were received from Noveon and dissolved into tetrahydrofuran (THF, Aldrich). Dimethyl formamide (DMF) was added to improve spinnability; the final solution composition was 10/80/10 in Estane/THF/DMF. Estane solutions supplied by Noveon are named Sanres 13100 and Sanres 13100C, a carboxylated polymer that can be crosslinked. Crosslinking agents from Noveon were evaluated: an aziridine compound called XAMA-7 capable of room temperature cure after 3 days, and a melamine formaldehyde

called AeroTex that cures in 4 hours at 96°C after electrospinning. Sanres solutions were diluted 50:50 with THF and used for electrospinning. Crosslinkers were added, 2 wt% relative to polymer content. All solutions were loaded into Pasteur pipettes for electrospinning. A positive lead from a high voltage power supply (30kV, 100µA, Gamma High Voltage Research, Inc, Ormond Beach, FL) was inserted into the end of a pipette, and a grounded target was positioned 15 cm from the pipette tip. Application of 10kV produced a spray of fine fibers which collected rapidly upon the grounded target. Target substrates included flat aluminum surfaces, metal screens, and fabric-covered aluminum backing plates. Solvent vapors were removed in a standard fume hood. The final web of Estane fiber was peeled from the target surface and evaluated.

Electron Microscopy

Microstructures of electrospun and meltblown webs were examined by scanning electron microscopy using a Zeiss CSM 950 and environmental scanning electron microscopy (ESEM) using a Phillips XL-30. Working distances of 10-16 mm and acceleration voltages of 10-20 kV were used on melt blown samples coated for 4 min with evaporated platinum.

Capillary Liquid Expulsion Porometry

Pore size measurements were made with an automated capillary flow porometer manufactured by Porous Materials, Inc. Pore sizes were measured by saturating the porous material with a wetting liquid of known surface tension. Gas pressure on one side of the sample was increased until liquid from the largest pores was expelled. As the pressure increased, smaller pores opened up and the flow rate of gas through the sample increased until all the accessible pores are emptied. A plot of the pressure versus flow rate through the wetted sample, when compared with the equivalent pressure/flow rate curve for a dry sample, gave an estimate of pore size distribution in the material [13].

Moisture Vapor Diffusion and Air Flow Resistance

Moisture vapor diffusion measurements and air flow-through capacity of textile materials is tested using an apparatus developed at the Natick Soldier Center [14-16]. 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.

Liquid Transport in Fabric Structure

Liquid movement in the porous nonwoven medium is driven by capillary action, which is governed by the liquid's properties, liquid-medium surface interaction, and geometric configurations of the pore structure in the medium. External wetting contact angle and internal liquid transport were determined by microbalance measurements of the electrospun and melt blown nonwoven fabrics, according to the method

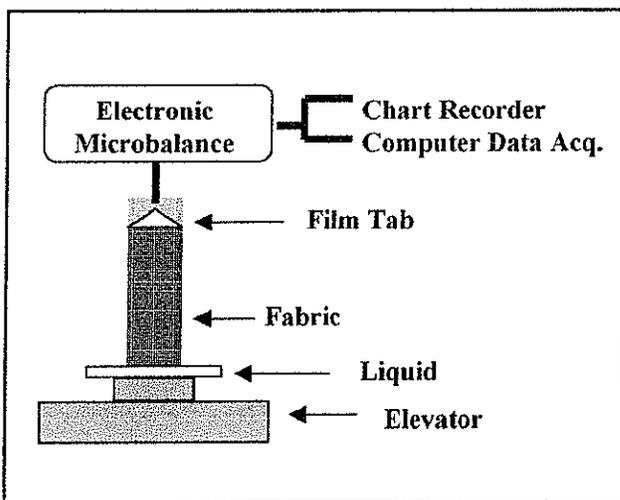


Figure 2

LIQUID WETTING TENSIOMETER APPARATUS

described by Hsieh [17]. The experimental setup is shown in Figure 2. Liquid retention was measured for both hexadecane and water to discriminate between organic and aqueous contact properties.

Melt Blown Fabric Processing

Liquid wetting was performed on electrospun fabrics as well as on meltblown fabrics of Noveon Estane TPU. Melt blowing was performed on the 6-inch line at The University of Tennessee Textiles and Nonwovens Development Center, as reported by Wadsworth, et. al. Electrospun top layers were sprayed onto a meltblown fabric of nominal basis weight 82.8 gsm, adding approximately 15% to the basis weight of the meltblown. Electrospun nonwovens are denser nonwovens with basis weights ranging from 200-600 gsm. Aerosol testing was performed on a meltblown fabric of average basis weight 183.6 gsm.

Aerosol Testing

The aerosol particle filtration test system was assembled at the Natick Soldier Center and consists of a nebulizer, a drying chamber, and sample chamber, an aerosol analyzer and a vacuum pump [18]. A dilute solution of aqueous potassium iodide is atomized with an ultrasonic nebulizer; the resulting mist of liquid salt solution is diluted with dry nitrogen, and flows to a heated drying chamber. The liquid evaporates in the drying chamber to create a solid salt aerosol, which is passed through the sample. Aerosol particle size and concentration are monitored by an aerosol analyzer (API

Aerosizer, Amherst Instruments, Inc.) which measures the time of flight of individual particles as they pass through two laser beams. The aerosol analyzer is capable of particle size measurement over the range of 0.5 to 200µm. Sample clamping in the chamber exposes a circular area of $1.34 \times 10^{-3} \text{ m}^2$ to the aerosol stream. The approximate test temperature at the sample holder is 40°C. The nominal flow velocity through the sample is 0.0157 m/s. Typical mean particle size is 2.5 µm.

Results

The microstructure of electrospun Estane TPUs was found to depend upon the type of substrate used to collect the fibers. Shown in Figure 3, there were differences between the top air surface of the electrospun fiber mat and the bottom collection surface. As electrospinning is a wet spinning method, this indicated a possible difference in solvent evaporation rates between the top and the bottom surfaces of the fiber mat during processing. Shown in Figure 3a, the air surface of the carboxylated Estane (Sanres 13100C) exhibits a network of discrete fibers, while in contrast, the bottom surface of the same electrospun sample (collected on a meltblown fabric covered aluminum plate) shows significant fiber welding.

Pore size differences were evident for three types of electrospun samples. Listed in Table 1 are the average pore diameters of electrospun fiber mats, measured with the PMI porosimeter. The sample electrospun onto a wire mesh screen exhibited pore sizes smaller than the limit of the PMI equipment at the available gas pressures for testing and is estimated to have an average pore size smaller than the limit of 0.2 µm.

Pore sizes of electrospun samples are found to be 4-100 times smaller than average pore sizes for the meltblown webs used in this study, Table 2.

These porosity differences have an effect on transport properties of the electrospun fabrics as compared to the meltblown nonwovens. Air, vapor, liquid and solid transport measurements were conducted to examine the differences between electrospun and meltblown nonwoven structures.

Using the DMPC, the air flow resistance and moisture vapor diffusion resistance were measured for a sample of

Figure 3
ELECTROSPUN SANRES 13100C, A CARBOXYLATED ESTANE, ELECTROSPUN FROM THF/DMF (8/2) ONTO A MELTBLOWN COVERED AL SUBSTRATE: A) AIR SURFACE; B) BOTTOM SURFACE IN CONTACT WITH COLLECTION SUBSTRATE

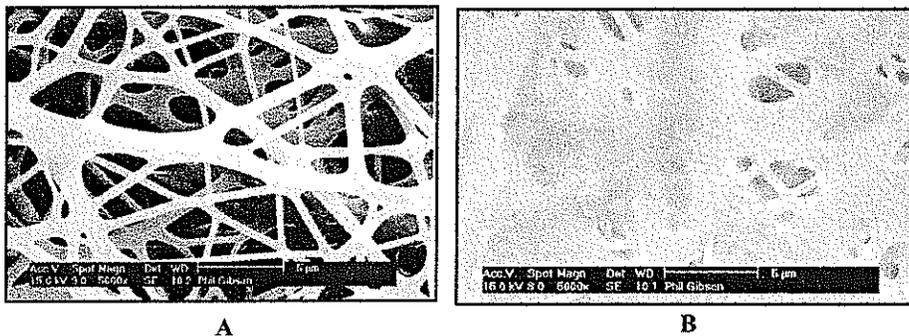


Table 1
POROSITIES OF ELECTROSPUN WEBS –
EFFECT OF COLLECTION SURFACE

Collection Surface	Ave Pore Size (μm)
Meltblown Web	4.4
Al Surface	2.1
Mesh	<0.2

Table 2
POROSITIES OF ESTANE MELTBLOWN WEBS

Basis Weight (gsm)	Ave Fiber Size (μm)	Ave Pore Size (μm)
82.8	12.4	19
183.5	17.4	18

Table 3
EFFECT OF WEB STRUCTURE UPON AIR AND
MOISTURE TRANSPORT

Sample	Air Flow Resistance (1/m)	Moisture Vapor Diffusion Resistance (s/m)	Average Pore Size (μm)
Electrospun			
Estane	5.6x109	152.7	0.44
Meltblown			
Estane	3.6x107	165.9	19

electrospun Estane (uncrosslinked and collected on an aluminum plate) and a sample of meltblown Estane of basis weight 82.8 gsm. Data shown in Table 3 were collected at a relative humidity across the sample of 50%.

We see that the electrospun nonwoven mat is 156 times more air resistant than the more porous meltblown. Moisture vapor diffusion resistance is only slightly affected by web structure, as both samples are highly porous and present very little resistance.

In addition to air and vapor transport measurements, the liquid wetting and transport properties were determined for crosslinked and uncrosslinked samples, as well as layered meltblown/electrospun composite structures.

Crosslinking of the electrospun Estane membranes was accomplished by adding crosslinker to a solution of carboxylated Estane (Sanres 13100C) in THF/DMF, at a concentration of 2% crosslinker

to polymer. Electrospun Estane, uncrosslinked carboxylated Estane, and Estane crosslinked with Aerotex melamine formaldehyde and with XAMA-7 aziridine were examined with respect to wettability.

Data in Table 4 show that liquid retention of both hexadecane and water are very low for crosslinkable Estane and diminishes upon crosslinking. Unmodified Estane (Estane 58277 with no carboxylic functionality for crosslinking) has higher liquid retention than the crosslinkable Estane, although the water contact angle has not significantly changed for the carboxylated Estane. When the carboxylated Estane is electrospun and crosslinked, we find a significant drop in liquid retention for both the organic and the aqueous liquids. With crosslinking, the water contact angle increases, indicating that the crosslinked web is more hydrophobic, but also more resistant to uptake of both water and organic liquids.

There is a significant improvement in the retention of organic liquids for Estane when it is meltblown, compared to electrospun webs. However, combining the two webs into a composite structure by simply spraying the electrospun web onto the top surface of the meltblown web significantly increases water retention to levels far exceeding the meltblown web alone or the electrospun web alone.

The final transport measurement conducted with electrospun and meltblown Estane webs was a study of the aerosol filtration properties of the two structures.

Filtration efficiency of a meltblown Estane nonwoven fabric of 183.5 gsm basis weight is shown in Figure 4 to be 90% initially, and increases with time as the web clogs with aerosol particles. In comparison, electrospun Estane achieved better than 99% filtration efficiency. Particle

Table 4
EFFECT OF CROSSLINKING CHEMISTRY UPON LIQUID CONTACT
FOR ELECTROSPUN WEBS COLLECTED ON ALUMINUM PLATE
BACKING

Electrospun Sample Type	Hexadecane Ret. (ml/mg)	Water Ret. (ml/mg)	Water Contact Angle (deg)
Estane	1.03 +/- 0.03	1.66 +/- 0.06	45.4 +/- 2.5
Crosslinkable Estane	0.31 +/- 0.05	0.98 +/- 0.02	42.6 +/- 2.4
Aziridine-Estane	0.07 +/- 0.01	0.21 +/- 0.2	52.5 +/- 3.3
Melamine Formaldehyde- Estane	0.01 +/- 0.00	0.06 +/- 0.00	62.2 +/- 5.3

Table 5
COMPARISON OF ESTANE 58277 - MELTBLOWN VS ELECTROSPUN
FOR ELECTROSPUN WEBS COLLECTED ON POROUS BACKINGS

Sample	Hexadecane Ret. (ml/mg)	Water Ret. (ml/mg)	Water Contact Angle (deg)
Meltblown Estane	3.34 +/- 0.20	0.18 +/- 1.4	81.6 +/- 1.4
Meltblown Estane + Electrospun	3.58 +/- 0.14	3.13 +/- 0.58	37.2 +/- 0.58
Electrospun Estane on Mesh	0.34 +/- 0.08	0.97 +/- 0.14	43.3 +/- 6.9

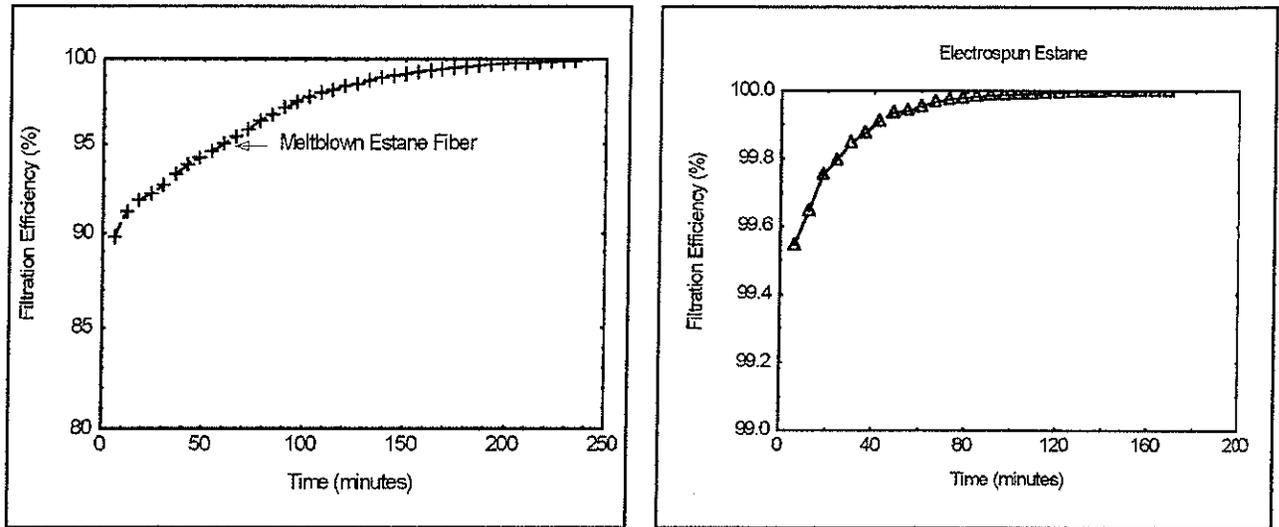


Figure 4
FILTRATION EFFICIENCY OF MELTBLOWN AND ELECTROSPUN ESTANE WEBS

entrapment is shown in Figure 5 for these two nonwovens. Average pore size in the meltblown was found to be 5x greater than the pore size of the electrospun web, but filtration efficiency increases significantly as particles are not only entrapped by small pores, but also caught on fiber surfaces by van der Waals forces. The surface area of an electrospun web of average fiber diameter 1 μm is approximately 10x greater than a meltblown web of average fiber diameter 10 μm , as seen in Figure 1. This increased surface area enables the fine electrospun web to screen out better than 99.5% of aerosol

Conclusions

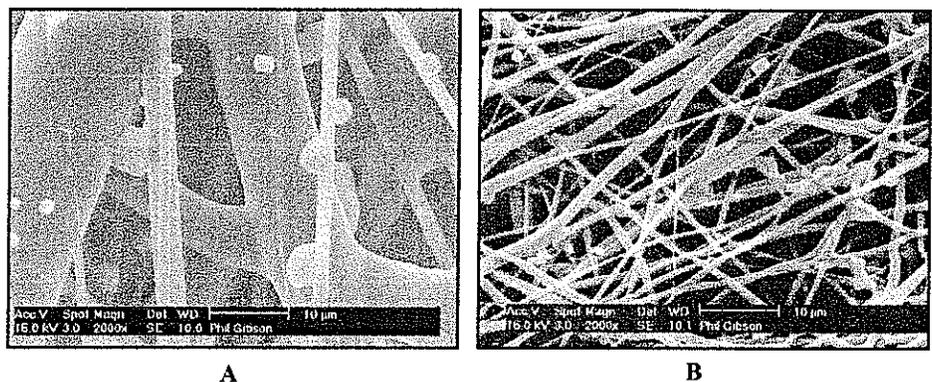
Transport of gas, vapor, liquid and solid through fine electrospun webs and meltblown webs has been studied. Average pore size of electrospun nonwovens ranges from 4-100x smaller than meltblown nonwovens. This increases air flow resistance by as much as 156 times, but has no significant effect on the "breathability," or moisture vapor diffusion resistance of the nonwovens. There is a contribution of fiber surface properties and fabric pore structure to liquid transport and retention within the nonwoven materials. Water contact angle significantly increases upon crosslinking, with an accompanying drop in water retention. Organic liquid retention also decreases with crosslinking. Liquid retention of a composite layered structure of meltblown coated with electrospun material is higher than liquid retention

capacity of either layer alone. Filtration of solid aerosol particles increases from 90% filtration efficiency for a meltblown to over 99% for an electrospun web.

Electrospinning produces a fine nonwoven consisting of a structure similar to a microporous membrane, with many of the transport features of a microporous membrane. This study has identified methods to modify the transport properties of the membranes for use with fabrics such as meltblowns. Crosslinking the fibers of the electrospun membrane significantly decreases liquid transport through the membrane. Combining electrospun and meltblown nonwovens of identical materials increases water transport through the structure. Addition of electrospun layers would also increase air flow resistance and aerosol protection of fabrics such as meltblown nonwovens without affecting breathability.

Acknowledgements

Figure 5
AEROSOL PARTICLE CAPTURE ON A) MELTBLOWN ESTANE AND B) ELECTROSPUN ESTANE



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