Transport Properties of Layered Fabric Systems Based on Electrospun Nanofibers

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Abstract: Layered fabric systems with electrospun polyurethane fiber web layered on spunbonded nonwoven were developed to examine the feasibility of developing protective textile materials as barriers to liquid penetration using electrospinning. Barrier performance was evaluated for layered fabric systems, using pesticide mixtures that represent a range of surface tension and viscosity. Air permeability and water vapor transmission were assessed as indications of thermal comfort performance. Protection performance and air/moisture vapor transport properties were compared for layered fabric systems and existing materials for personal protective equipment (PPE). Layered fabric systems with electrospun nanofiber web showed barrier performance in the range between microporous materials and nonwovens used for protective clothing. Layered fabric structures with the web area density of 1.0 and 2.0 g/m^2 exhibited air permeability higher than most PPE materials currently in use; moisture vapor transport was in a range comparable to nonwovens and typical woven work clothing fabrics. Comparisons of layered fabric systems and currently available PPE materials indicate that barrier/transport properties that may not be attainable with existing PPE materials could be achieved from layered fabric systems with electrospun nanofibrous web.

Keywords: Electrospinning, Nanotechnology, Protective clothing, Transport, Barrier

Introduction

Various protective clothing materials are used to reduce the dermal exposure of workers to pesticides, ranging from single-use nonwoven PPE (personal protective equipment) to impermeable polymeric suits. Use of nonwovens for single-use protective clothing continues to grow due to relatively inexpensive, lightweight, and effective protection. According to a previous work, which examined barrier and comfort performance of 36 protective clothing materials currently in use [1], nonwovens used for protective clothing exhibit a wide range in barrier performance and thermal comfort depending on their structure and fiber type. A porous spunbond nonwoven with high air permeability exhibited low barrier performance, whereas a compact polyethylene spunbond nonwoven provided high level of protection but low level of thermal transport. Microporous membranes and laminated fabrics, which are used as barrier material for certain PPE applications, offer higher level of protection but lower air permeability. Monolithic polymeric films are used for impermeable polymeric suits for highly toxic chemicals and provide the highest level of protection at the cost of low level of comfort in a hot, humid environment.

Barrier effectiveness and thermal comfort are two most important factors to be considered in the selection of materials for PPE. As noted in earlier work [1,2], a negative relationship exists between thermal comfort and protection performance for currently available PPE materials. In order to provide improved protective clothing for agricultural workers and pesticide applicators, there is a need for development of a new material that offers a combination of high barrier performance and thermal comfort.

Electrospinning is an effective and promising technique for the production of fibers with small diameters. The technique provides an ultrathin membrane-like web of extremely fine fibers with very small pore size, which is attractive for various applications from textiles to biomaterials, sensors, and reinforced composites [3-6]. The basic mechanism of electrospinning involves applying an electric force between a suspended droplet solution or melt at a capillary tip and collector. When the intensity of the electric field overcomes the surface tension of the polymer solution or melt, a charged jet is ejected and travels to the grounded target, generating fibers typically in the form of a nonwoven mat. Nonwoven textiles composed of electrospun nanofibers have very small pore size compared to commercial textiles, which makes them excellent candidates for use in filtration, membrane, and possibly protective clothing applications [7,8].

One attractive feature of electrospun webs for protective clothing use could be the direct application of electrospun webs to garment systems [3]. Fibers may be sprayed directly onto three-dimensional forms, so that the thickness of the electrospun fiber web could be varied at various locations on a garment as needed, producing 'zoned' materials in protective garments. Direct application of electrospun webs to garment systems would eliminate costly manufacturing steps and solve seam-sealing problems that have been limiting factors in protective garments [3,9].

Potential of electrospun webs for future protective clothing systems has been investigated [9-11]. Electrospun polypropylene webs and laminates were developed using melt-electrospinning to explore an alternative way of manufacturing

protective clothing materials as barriers to liquid penetration [10]. An electrospun polypropylene layer in laminate system significantly enhanced barrier performance for challenge liquids with varying surface tension. Yet, the majority of fibers were in the micrometer. In our previous work [11], the possibility of developing a PPE system as liquid barriers based on electrospun polyurethane web was investigated. Much smaller fiber size was achieved from solvent-based electrospinning, and layered fabric systems were developed based on electrospun nanofiber web.

This research focuses on assessing protection and thermal transport of the new system and comparing them with those of existing PPE materials. Layered fabric structures were developed by electrospinning polyurethane nanofibers onto a nonwoven substrate at recommended web area density. We compared protection performance and thermal transport of layered fabric systems with those of currently available PPE materials, four microporous materials and nine nonwoven fabrics.

Experimental

Materials

Commercial-grade polyurethane pellets (Pellethane™, 2103-80AE) were obtained from Dow Chemical Company, Midland, MI. Pellethane™ 2103-80AE is a polyether-based thermoplastic polyurethane. N,N-dimethylformamide (DMF) (Mallinckrodt Baker, Inc., Phillipsburg, NJ) was used as a solvent. Electrospinning solutions were prepared by dissolving the polymer in DMF. Polymer solution concentration ranged from 10 to 15 %wt. polymer in DMF. To form a layered fabric system, a nonwoven fabric designed for protective clothing for dry particulates (Basics™, Kappler, Inc., Guntersville, AL) was used as a substrate. It was 100 % polypropylene, light-weight and highly porous spunbonded nonwoven. The thickness of nonwoven substrate was 0.18 mm; weight, 29 g/m^2; and air permeability, 236 cm^3/s/cm^2.

For comparisons of transport properties, four microporous membranes and laminated fabrics and nine nonwoven fabrics currently available for PPE were evaluated. Nonwoven fabrics with no surface treatments were selected to exclude any effect from finishing. Membrane and fabric descriptions are given in Table 1.

For pesticide penetration testing, atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine) were used for formulating pesticide mixtures. From a practical standpoint, commercially available pesticide formulations were used, atrazine as wettable dispersible granules and pendimethalin as an emulsifiable concentrate. They were selected based on differences in chemical solubility. Atrazine 90WDG from United Agri Products/Platte Chemical Company, Greeley, CO, contains 85.5 % active ingredient. Prowl® 3.3 EC, which consists of 37.4 % active ingredients of N-(1-

Table 1. Material descriptions

Code[a]	Fiber/membrane	Construction	Mass, g/m^2	Thickness, mm
M1	PTFE[b]	Membrane	29.1 (0.2)	0.0244 (0.0013)
M2	PTFE	Membrane	10.4 (0.2)	0.0036 (0.0013)
L1	PTFE membrane backed with nonwoven substrate	Composite	46 (3)	0.1168 (0.0197)
L2	PTFE membrane backed with nonwoven substrate	Composite	128 (1)	0.2294 (0.0024)
NW1	Polyethylene	Spunbonded	49 (6)	0.1295 (0.0018)
NW2	55 % woodpulp/ 45 % polyester	Spunlaced	73 (1)	0.2515 (0.0003)
NW3	Polypropylene	SMS[c]	60 (3)	0.3073 (0.0010)
NW4	Polypropylene	SMS	81 (5)	0.3658 (0.0011)
NW5	Polypropylene	Spunbonded	29 (2)	0.1753 (0.0006)
NW6	Polypropylene	Spunbonded	57 (1)	0.2896 (0.0012)
NW7	55 % woodpulp/ 45 % polyester	Spunlaced	66 (1)	0.2286 (0.0001)
NW8	Polyester	Spunlaced	53 (1)	0.2718 (0.0005)
NW9	Polyester	Spunlaced	76 (2)	0.2337 (0.0004)

Standard deviations in parentheses.
[a]M (microporous membrane), L (microporous membrane laminated material), NW (nonwoven), [b]PTFE (polytetrafluoroethylene), [c]SMS (spunbonded/meltblown/spunbonded).

ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine, comes from American Cyanamid Company, Parsippany, NJ. Based on previous studies [2,12], two pesticide mixtures representing a range of viscosity and surface tension were selected. Oil concentrate was added to the mixture to vary the surface tension and viscosity. Oil concentrate was All Seasons® Spray Oil concentrate, which consists of 98.8 % petroleum oil, manufactured by Bonide Products Inc., Yorkville, NY. Pesticide concentrations, surface tension and viscosity of selected mixtures are shown in Table 2.

Electrospinning Process

Electrospinning was performed in a horizontal electro-spinning setup. It consists of a syringe positioned horizontally with its needle, a precisely-controlled syringe pump (PHD2000, Harvard Apparatus, Holliston, MA), a high voltage power supply capable of 0-30 kV (ES30P-5W, Gamma High Voltage Research, Inc., Ormond Beach, FL), and a grounded collector.

Polyurethane solution was loaded into a syringe and an

Table 2. Pesticide amounts, surface tension and viscosity of pesticide mixtures

Pesticide	Sample code	Pesticide amounts used in mixtures			Surface tension (dynes/cm)	Viscosity (mPa·s)
		Water (g)	Atrazine 90 WDG or Prowl 3.3 EC (g)	Oil (g)		
Atrazine 90 WDG	P1	246.10	2.50	–	38.00	0.93
Prowl® 3.3 EC	P2	55.00	40.00	65.00	20.57	20.80

electrode was clipped onto the needle. The syringe pump was used to control a constant volumetric feed rate, which ranged from 0.003 to 0.02 ml/min. A high voltage of 10-20 kV was applied to the needle. The needle gauge was 30 (0.16 mm i.d.). As the applied voltage increases, a droplet at the needle tip deforms into a conical shape and, at sufficiently high voltage, an electrically charged jet is ejected from the tip. Fibers were laid down on the grounded copper collection plate, which was placed 10 to 15 cm from the tip, to form a nonwoven web.

Applying Electrospun Fiber Web onto Fabric Substrate

Polyurethane fibers were electrospun from DMF and deposited directly onto a nonwoven substrate to form a layered fabric system. The substrate was chosen to provide strength and durability to the system, whereas the nanofiber web imparts barrier performance. A highly porous nonwoven substrate was selected to allow an acceptable level of air/moisture vapor transport while providing appropriate mechanical properties.

Morphology

Morphologies of electrospun polyurethane fibers and layered fabric systems were examined using a scanning electron microscope (Leica 440 Scanning Electron Microscope, Cambridge, U.K.) after sputter-coating with Au/Pd. The morphologies of microporous materials and nonwoven fabrics were also examined.

Protection Performance

Pesticide repellency, retention, and penetration were assessed according to ASTM F 2130-01, Standard Test Method for Measuring Repellency, Retention, and Penetration of Liquid Pesticide Formulation through Protective Clothing Materials, using 0.1 ml of contamination load. For collector layers, absorbent paper backed with polyethylene film (Whatman® Benchkote™ Plus with polyethylene backing, Whatman 3 mm cr, Whatman plc, Whatman House, Kent, U.K.) was used. HPLC-grade acetone (AlliedSignal Inc., Burdick & Jackson, Muskegon, MI) was used for extraction. Tests were performed in triplicate for each combination of pesticide mixtures and materials.

A Hewlett Packard model 5890 gas chromatograph (Hewlett-Packard Company, Wilmington, DE) equipped with a nitrogen-phosphorus detector and automatic injector was used for pesticide analysis. Separation was achieved on a 30-m×0.25-mm i.d. capillary column (5 % phenyl substituted methyl-polysiloxane, HP-5, Hewlett-Packard Company, Wilmington, DE) with a nitrogen flow of 1.7 ml/min. Column temperature was maintained 50 °C for 1 min, then programmed at 25 °C/min to 260 °C and held 1 min. Injector port and detector temperatures were 250 °C.

Air and Moisture Vapor Transport Properties

Air Permeability

Air permeability of layered fabric systems, microporous materials, and nonwoven fabrics was measured according to ASTM D 737-96, Standard Test Method for Air Permeability of Textile Fabrics, using a Frazier Air Permeability Tester for four samples.

Water Vapor Transmission

Water vapor transmission rate was measured according to ASTM E 96-00, Standard Test Method for Water Vapor Transmission of Materials, using a dish assembly (Vapometer, Thwing-Albert Instrument Company, Philadelphia, PA) for three samples.

Results and Discussion

Morphology

Polyurethane fibers were electrospun under a variety of conditions including various polyurethane solution concentrations, electric voltages, feed rates, collecting distances, and capillary diameters, to find an optimum spinning condition. The preliminary experiments showed that 13 % wt. polyurethane solution with a 30-gauge needle (0.16 mm i.d.) at the feed rate of 0.003 ml/min, the voltage of 20 kV, and the collecting distance of 11 cm was the optimum condition to produce uniform nanoscale fibers for our electrospinning setup. Electrospun polyurethane nanofibers produced at the optimal condition are presented in Figure 1, showing that the fiber diameter is approximately 300 nm. Figure 1 also illustrates that smooth cylindrical polyurethane nanofibers were held together by bonding between intersecting fibers, constructing a cohesive network structure. For solvent-based electrospun fibers, the presence of residual solvent in the electrospun fibers facilitates bonding among fibers [3]. The bonding among intersecting fibers was typically observed in electrospun polyurethane mats, providing structural integrity of the mat [13,14].

At the optimal condition identified in the preliminary experiments, polyurethane nanofibers were electrospun directly onto a polypropylene nonwoven substrate to form a layered fabric system. A layered fabric system with electrospun
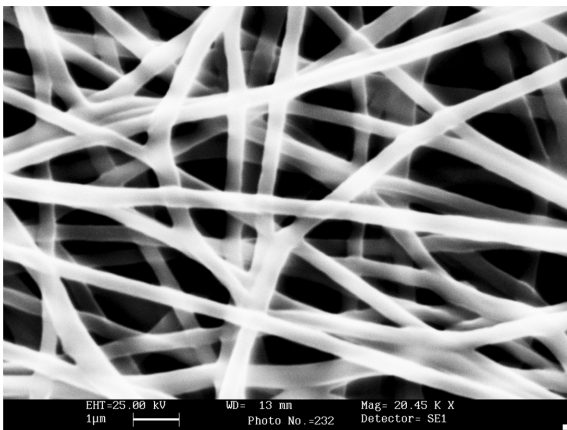
Figure 1. SEM micrograph of electrospun polyurethane nanofibers.

polyurethane nanofiber web is illustrated in Figure 2(b). Morphologies of microporous membrane and conventional spunbond nonwoven were also observed (Figure 2(a) and 2(c)). The layered structure with nanofiber web (Figure 2(b)) shows that macropores of nonwoven substrate are covered with numerous electrospun nanofibers, creating innumerable microscopic pores in the layered system. Considerable reduction in pore size is observed in the layered fabric system (Figure 2(b)) as compared with conventional spunbond nonwoven (Figure 2(c)). Microporous membranes revealed a structure consisting of nodes and fibrils constructing numerous microscopic channels (Figure 2(a)), which are much smaller than those in the layered fabric system. Note that the photomicrographs were taken at different magnification: microporous membrane at 33.34×10^3 magnification, layered fabric system at 2.08×10^3, and spunbond nonwoven at 500 magnification.

Protection Performance of Layered Fabric Systems, Microporous Materials, and Nonwovens

In our previous study [11], polyurethane nanofibers were electrospun onto a nonwoven substrate in a range of web area density, and two levels of web area density were suggested providing an acceptable level of thermal comfort and protection performance for layered fabric systems: 1.0 g/m^2 and 2.0 g/m^2. In this work, we investigate how layered fabric systems with these two levels of web area density perform compared with existing PPE materials.

Table 3 presents pesticide penetration of layered fabric systems, microporous materials, and nonwovens against challenge liquids representing a range of surface tension and viscosity (mixture P1 and P2). Differences were noted in penetration behavior between the two challenge liquids. For microporous materials and layered fabric systems, no penetration was observed for the challenge liquid of high surface tension and low viscosity (P1), whereas penetrate was found for the mixture of low surface tension and high viscosity (P2). While a range of pesticide penetration was observed for nonwovens depending on the fiber type and structural properties, higher penetrate was observed for the mixture P2 than P1 in general. This confirms that liquid properties have a considerable effect in determining liquid transport in protective material. Among the three different types of materials, microporous materials exhibited the lowest level of pesticide penetration, followed by layered fabric systems with nanofiber web, and conventional nonwovens. These penetration results are in agreement with pore size measurements on layered fabric systems, nonwoven, and microporous material [1,11]. Pore size distribution of layered fabric systems with electrospun nanofiber web showed pore sizes substantially smaller than those in conventional nonwoven [11]. Pore sizes of layered fabric systems decreased as the level of electrospun web area density increased, which agrees with research by Li *et al.* [15]. For microporous membranes, we were unable to complete pore size measurement because some of the pores were too small to be detected by the instrument, the lower limit of which is 0.013 μm. This indicates that microporous membranes have much smaller pore sizes than other materials; hence the

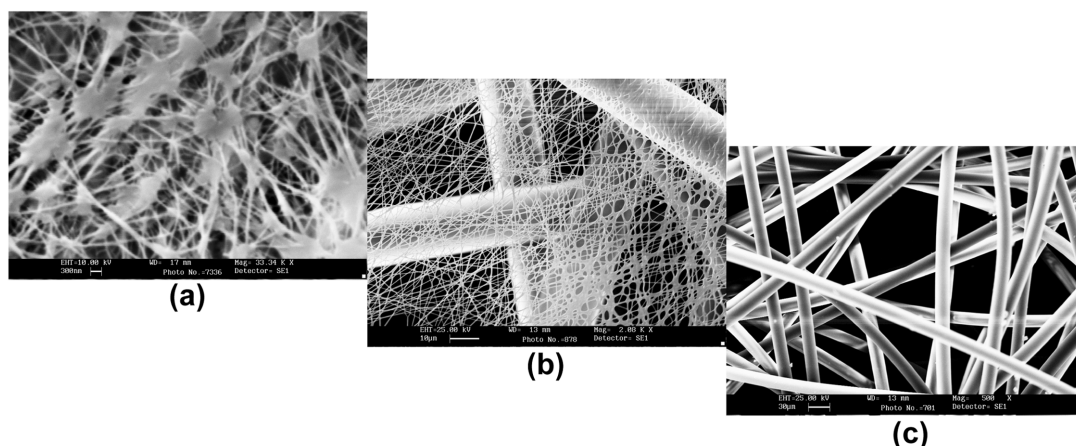**Figure 2.** Comparison of SEM micrographs; (a) microporous membrane at 33.34×10^3 magnification, (b) layered fabric system with electrospun polyurethane nanofiber web at 2.08×10^3 magnification, and (c) spunbond nonwoven at 500 magnification.

Table 3. Percentage penetration of pesticide, air permeability and water vapor transmission rate of layered fabric systems with electrospun polyurethane nanofiber web, microporous materials, and nonwovens

Code[a]	Penetration, %		Air permeability $(cm^3/s/cm^2)$	Water vapor transmission rate $(g/h/m^2)$
	P1[b]	P2		
M1	0	3	< 1	20.76
M2	0	6	< 1	22.08
L1	0	0	< 1	20.18
L2	0	3	< 1	20.72
LE_1.0 g/m^2	0	25	158.74	19.90
LE_2.0 g/m^2	0	20	116.56	19.35
NW1	0	13	< 1	15.02
NW2	56	51	26.59	20.44
NW3	0	51	9.81	20.02
NW4	0	33	5.10	20.19
NW5	4	97	236.34	20.23
NW6	0	73	37.28	20.23
NW7	68	61	49.55	21.48
NW8	60	74	89.03	20.60
NW9	100	82	166.12	19.81

[a]M (microporous membrane), L (microporous membrane laminated material), LE (layered fabric system with electrospun polyurethane nanofiber web), NW (nonwoven), [b]P (pesticide mixture).

lowest penetration.

Air and Moisture Vapor Transport Properties of Layered Fabric Systems, Microporous Materials, and Nonwovens

Air and moisture vapor transport properties were evaluated for layered fabric systems, microporous materials and nonwovens (Table 3). Microporous membranes and laminated fabrics exhibited very low air permeability as expected. The microscopic pores, which are much smaller than those in the layered fabric systems, would be too small to allow air flow at a prescribed pressure differential; thus result in very low air permeability. Microporous materials gave water vapor transmission comparable to that of most nonwovens.

Conventional nonwovens used for PPE exhibited a range of air permeability depending on its structure. NW1, a thin, compact spunbond nonwoven, showed very low air permeability, whereas NW5, a light-weight, porous spunbond nonwoven gave the highest air permeability, over 200 $cm^3/s/cm^2$.

Layered fabric systems with electrospun nanofiber web showed air permeability in the range between conventional nonwovens and microporous materials. Air permeability of layered fabric systems at the web area density of 1.0 and 2.0 g/cm^2 was above 100 $cm^3/s/cm^2$, which is higher than most PPE materials currently in use [1]. Water vapor transmission rates of layered fabric systems were in a range comparable

to nonwovens and typical woven work clothing fabrics [1].

An Overview: Transport Properties of Layered Fabric Systems Compared with Microporous Materials and Nonwovens

Competing parameters of chemical protection and thermal comfort are important in achieving an effective protective clothing system. To have a comprehensive assessment on layered fabric systems as protective textile material, protection performance was plotted against air and moisture vapor transport properties and compared with existing PPE materials. The protection property was calculated from the percentage of pesticide penetration as follows:

$$Protection\ (\%) = 100 - penetration\ (\%) \qquad (1)$$

Figure 3 illustrates chemical protection performance against the challenge liquid of low surface tension and high viscosity (P2), which exhibited higher penetrate through materials, relative to air permeability and water vapor transmission rate of materials.

Layered fabric systems with electrospun nanofibrous web exhibited different barrier and transport behavior from PPE materials currently in use. Layered structures with electrospun nanofiber web gave protection performance lower than microporous materials but higher than most nonwovens. Air permeability of layered fabric systems was higher than microporous materials and many conventional nonwovens used for PPE. For moisture vapor transport, layered fabric systems gave a similar range as conventional nonwovens.
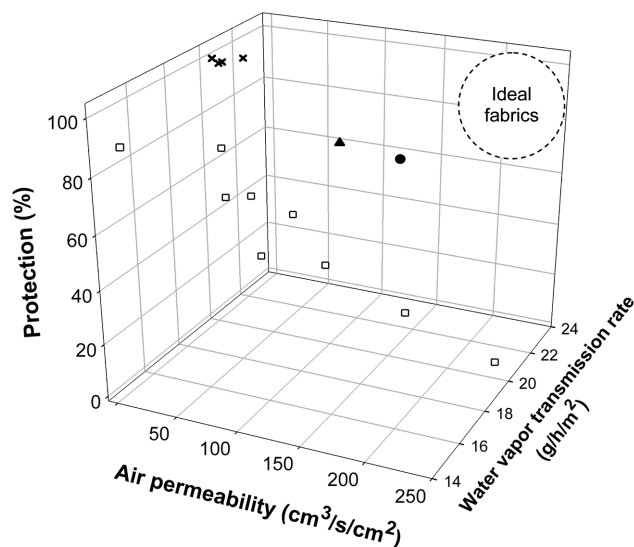

Figure 3. Air permeability, water vapor transmission rate and protection performance against pesticide mixture (P2) of layered fabric systems with electrospun nanofiber web compared with existing PPE materials; (●) layered fabric system with 1.0 g/m^2 web area density, (▲) layered fabric system with 2.0 g/m^2 web area density, (×) microporous membrane and laminated fabrics, (□) nonwoven fabrics.

Ideal protective clothing materials should have a combination of high barrier performance and thermal comfort as shown in Figure 3. Layered structures with electrospun nanofiber web exhibited protection and transport behavior closer to the ideal zone. This implies that engineering a PPE material that could balance between protection and thermal comfort, two competing properties, might be possible by electrospinnning technique. Figure 3 also indicates that in layered fabric systems the level of protection and thermal comfort could be controlled via the level of web area density of the electrospun web.

Conclusion

New materials are needed to provide enhanced performance in protective clothing. This research investigated the feasibility of developing a new PPE system as liquid barriers based on electrospun nanofiber web to provide improved protective clothing for agricultural workers. Following our previous study, layered fabric systems were developed by electrospinning polyurethane nanofibers onto a nonwoven substrate at suggested web area density. Air/moisture vapor transport and barrier effectiveness against two challenge liquids that represent a range of surface tension and viscosity were examined and compared with currently available PPE materials.

Observations of structural morphology showed that layered fabric systems with electrospun nanofiber web have numerous microscopic pores that are larger than those in conventional microporous membranes but much smaller than those in nonwovens used for protective clothing. Layered structures with electrospun nanofiber web exhibited barrier performance in the range between conventional nonwovens and micro-porous materials. Layered fabric systems with the web area density of 1.0 and 2.0 g/m^2 exhibited air permeability higher than most PPE materials currently in use. Moisture vapor transport of the layered systems was in a range comparable to nonwovens and typical woven work clothing fabrics.

A thorough examination of barrier performance and air/moisture vapor transport indicated that barrier/transport properties that may not be attainable with existing PPE materials could be achieved from layered fabric systems with electrospun nanofibrous web. This could open a possibility of engineering a PPE system that covers the gap in protection/comfort performance of existing PPE materials. By varying the area density of electrospun fiber web layers in layered fabric systems, barrier materials with different levels of thermal comfort and protection could be developed depending on their need and use. This research focuses on developing

protective materials for agricultural workers and pesticide applicators via electrospinning to provide improved PPE. The result also could be applicable to occupations where resistance to liquid penetration is needed, such as medical personnel and chemical workers.

Acknowledgements

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