Textile Research Journal Article

Use of Electrospun Nanofiber Web for Protective Textile Materials as Barriers to Liquid Penetration

Seungsin Lee and S. Kay Obendorf[1]

Department of Fiber Science and Apparel Design, Martha Van Rensselaer Hall, Cornell University, Ithaca, New York 14853, USA

Abstract To examine the potential of electrospun nanofibrous webs as barriers to liquid penetration in protective clothing systems for agricultural workers, layered fabric systems with electrospun polyurethane fiber web layered on spunbonded nonwoven were developed. Barrier performance was evaluated for the layered fabric systems with different levels of electrospun web area density, using three pesticide mixtures that represent a range of surface tension and viscosity. Effects of electrospun web density on air permeability and water vapor transmission were assessed as indications of thermal comfort performance. Pore size distribution was measured to examine the effect of electrospun fiber web layers on pore size. Penetration testing showed that a very thin layer of electrospun polyurethane web significantly improved barrier performance for challenge liquids with a range of physicochemical properties. Air permeability decreased with increasing electrospun web area density, but was still higher than most of protective clothing materials currently available. No significant change was observed in moisture vapor transport of the system from electrospun nanofibrous web layers. Pore size distribution measurements indicated the feasibility of engineering pore size via the level of electrospun web area density, hence, controlling the level of protection and thermal comfort of layered fabric systems depending on their need.

Key words electrospinning, nanotechnology, protective clothing, barrier performance, 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 a variety of applications from textiles to biomaterials, sensors and reinforced composites [1–4]. Electrospinning is of great

[1] Corresponding author: Department of Fiber Science and Apparel Design, Martha Van Rensselaer Hall, Cornell University, Ithaca, New York 14853, USA. Tel: 1 (607) 255-4719; fax: 1 (607) 255-1093; e-mail: sko3@cornell.edu

interest because not only can it produce polymer fibers with nanometer-scale diameters, but it also has the advantage of being simple and convenient compared with traditional fiber forming methods [5].

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. Non-woven 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 [6, 7].

One attractive feature of electrospun webs for protective clothing use could be the direct application of electrospun webs to garment systems [1]. 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 [1, 8].

The potential of electrospun webs for future protective clothing systems has been investigated. The U.S. Army Natick Soldier Center studied enhancement of barrier materials via a fine layer of electrospun fibers, focusing on preventing penetration of chemical warfare agents in aerosol form [8]. They found that the electrospun webs of nylon 6,6, polybenzimidazole, polyacrylonitrile and polyurethane provided good aerosol particle protection, without a significant change in moisture vapor transport of the system.

In our previous work, electrospun polypropylene webs and laminates were developed using melt-electrospinning to explore an alternative way of manufacturing protective clothing materials for agricultural workers [9]. An electrospun polypropylene layer significantly enhanced barrier performance for challenge liquids with varying surface tension. Yet, the majority of fibers were in the micrometer. Much smaller fiber size can be achieved from solvent-based electrospinning, since solvent evaporation leads to additional decrease in fiber diameter. Submicron, solvent electrospun fibers create a much lighter and thinner membrane-like web with very small pore size. There is a need to investigate the barrier performance of electrospun nanofiber webs against liquid penetration for use in protective clothing systems.

While ultrathin nanofiber webs offer exciting properties, it has been reported that they have limited mechanical properties [10, 11]. In order to provide strength and durability, nanofiber webs must be used in a composite structure, with some other substrate material as a support [10]. For use in protective clothing, electrospun nanofiber webs need to be used as a component in a layered fabric system; thus, the protection and comfort performance should be assessed in layered structures.

Polyurethanes have been used successfully in clothing and textile coatings for garments, such as rain coats and industrial safety clothing, and they are distinguished as being comfortable to wear and easy to care for [12]. Thermoplastic polyether-based polyurethanes are elastomeric, resistant to microorganisms and have excellent hydrolytic stability [11]. As indicated in previous research on barrier and comfort performance of 36 protective clothing materials currently in use [13], there is a need for development of new materials capable of providing a combination of high barrier performance and thermal comfort not attainable with available protective clothing materials. Via the electrospinning technique, which produces very thin membrane-like webs with very small pore size, protective materials that provide resistance to liquid penetration while allowing moisture vapor and thermal transport could be achieved. In addition, controlling pore size by varying the area density of electrospun fiber web layers would be useful for developing materials with different levels of protection and thermal comfort depending on the need and use.

This study examined the potential of electrospun nanofibrous webs as barriers to liquid penetration in protective clothing systems for agricultural workers. Barrier performance of layered fabric systems with an electrospun polyurethane fiber web layer was evaluated against challenge liquids of different physicochemical properties. Effects of electrospun web area density on the air/moisture vapor transport properties were examined.

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 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

Table 1 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	M1	246.10	2.50	–	38.00	0.93
Prowl® 3.3 EC	M2	125.00	133.80	–	22.62	8.49
Prowl® 3.3 EC	M3	55.00	40.00	65.00	20.57	20.80

a practical standpoint, commercially available pesticide formulations were used following previous studies [14, 15], 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-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine, came from American Cyanamid Company, Parsippany, NJ. Based on the previous studies, three 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 1.

Electrospinning Process

Electrospinning was performed in a horizontal electrospinning setup. It consisted 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 electrode was clipped onto the needle. The syringe pump was used to control a constant volumetric feed rate, which ranged from 0.003 to 0.020 mL/min. A high voltage of 10–20 kV was applied to the needle. The needle gauges used were 24 and 30 (0.31 mm and 0.16 mm i.d., respectively). As the applied voltage increased, a droplet at the needle tip deformed into a conical shape and, at sufficiently high voltage, an electrically charged jet was 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 imparted barrier performance. A highly porous nonwoven substrate was selected to allow an acceptable level of air/moisture vapor transport, while providing appropriate mechanical properties.

Fiber Morphology

Morphology of electrospun polyurethane fibers was examined using a scanning electron microscope (SEM) (Leica 440 Scanning Electron Microscope, Cambridge, U.K.) after sputter-coating with Au/Pd to minimize charging.

Pore Size Distribution

Pore size distribution was measured by a Capillary Flow Porometer (Model CFP-1200-AEX, Porous Materials, Inc., Ithaca, NY). Gas flow rates through wet and dry samples versus differential pressure were measured and pore diameters of through-pores at the most constricted part of the pore were determined.

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 and Jackson, Muskegon, MI) was used for extraction. Tests were performed in triplicate for each combination of pesticide mixtures and layered fabric systems.

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 methylpolysiloxane, HP-5, Hewlett-Packard Company) with a nitrogen flow of 1.7 mL/min. Column temperature was maintained at 50°C for 1 min, then programmed at 25°C/min to 260°C and held for 1 min. Injector port and detector temperatures were 250°C.

Air and Moisture Vapor Transport Properties

Air Permeability

Air permeability of each layered fabric system 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

Fiber 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 indicated 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. With a 24-gauge needle (0.31 mm i.d.), thicker fibers with diameters less uniform were observed.

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. An electrospun polyurethane nanofiber web layer on a conventional polypropylene nonwoven is illustrated in Figure 1, which conveniently shows the relative fiber sizes of electrospun nanofibers compared to conventional spunbond fibers. The nanofiber diameter was approximately 300 nm (see enlarged Figure 1(b)), as compared to spunbond fibers with diameters around 20 µm (Figure 1(a)). Figure 1(b) also shows 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 [1]. The bonding among intersecting fibers was typically observed in electrospun polyurethane mats, providing structural integrity of the mat [5, 11]. In Figure 1, also note that macropores of conventional nonwoven substrate were filled with numerous electrospun nanofibers, which created innumerable microscopic pores in the layered system.

(a)
(b)

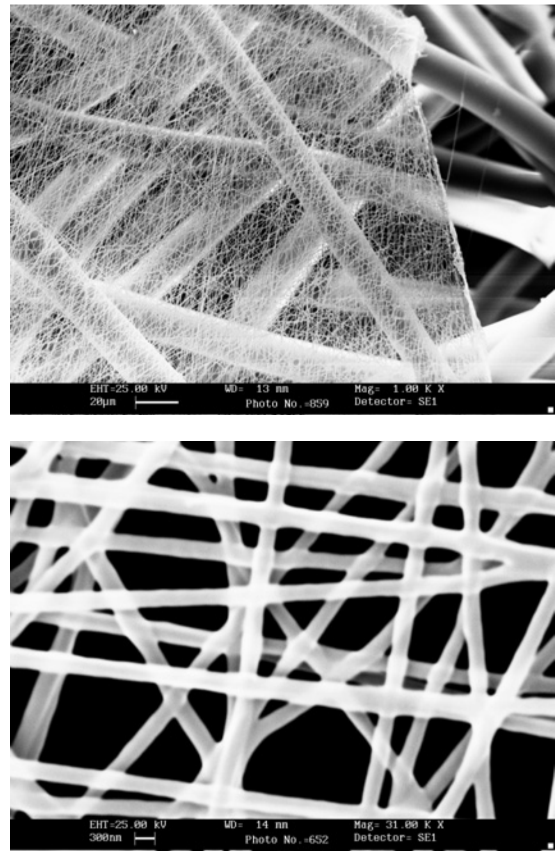

Figure 1 SEM micrographs of electrospun polyurethane nanofiber web (a) layered on a conventional nonwoven (b) electrospun polyurethane fibers enlarged.

Selection of Web Area Density

In electrospinning, the level of electrospun fiber web layers i.e. web area density, can be controlled by direct spray time. Previous research [1, 9] demonstrated that air transport properties of electrospun fiber mats correlate well with the electrospun layer coating level. In order to deter-

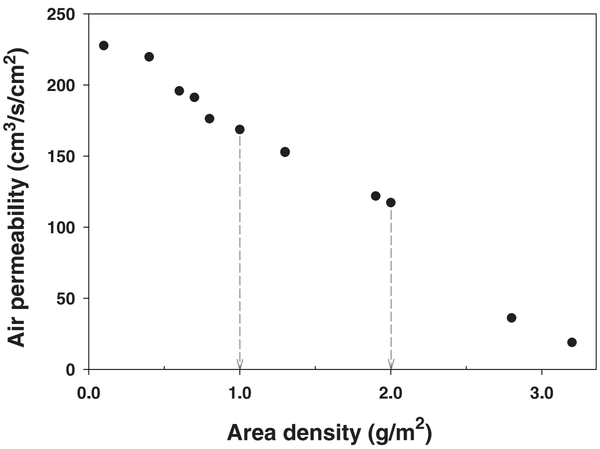

Figure 2 Air permeability of layered fabric systems as a function of area density of electrospun polyurethane web.

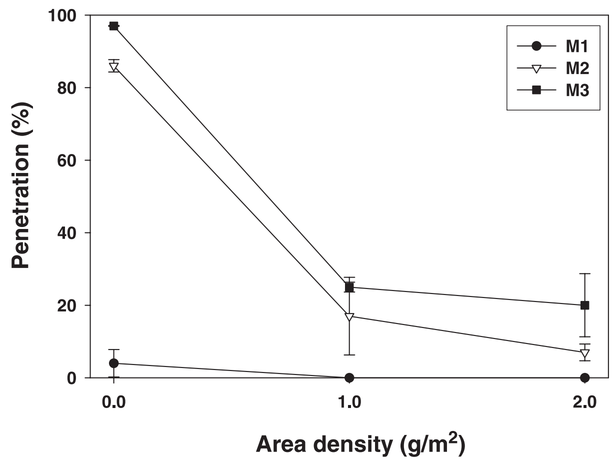

Figure 3 Effects of area density of electrospun polyurethane web on percentage of pesticide penetration of layered fabric systems against pesticide mixtures M1, M2 and M3.

mine a range of electrospun web density that could provide acceptable thermal comfort properties for layered fabric systems, polyurethane nanofibers were electrospun onto a nonwoven substrate in a range of density and the relationship between the web area density and air permeability was examined (Figure 2). The scatter plot of web area density against air permeability of layered fabric systems shows that air permeability decreased with increasing web density.

Based on our previous study, which examined protection and air/moisture vapor transport properties of 36 available protective clothing materials [13], web density to be produced and examined hereafter for layered fabric systems was selected. Most protective materials currently in use exhibit air permeability in the range between 0 to 100 $cm^3/s/cm^2$. With an aim of developing a material that could provide a combination of high barrier performance and an acceptable level of thermal comfort, two levels of web area density were chosen: 1.0 g/m^2, which corresponds to about 170 $cm^3/s/cm^2$ in air permeability and 2.0 g/m^2, which corresponds to around 120 $cm^3/s/cm^2$ in air permeability (Figure 2).

Protection Performance of Layered Fabric Systems

Effects of electrospun fiber web layers on protection performance were evaluated against challenge liquids representing a range of surface tension and viscosity. Figure 3 illustrates pesticide penetration of layered fabric systems and nonwoven substrate against a series of pesticide mixtures M1, M2 and M3, relative to electrospun web density. Nonwoven substrates were assessed as a control. Percentages of penetration were reduced via a very thin layer of polyurethane nanofiber web, especially for the challenge liquids M2 and M3. For mixtures M2 and M3, percentage of penetration through a nonwoven substrate alone was over 85 %, but with a nanofibrous layer, the percentage of penetration reduced to below 25 %. The mass per unit area of electrospun polyurethane layers examined, 1.0 to 2.0 g/m^2, was an order of magnitude smaller than that of conventional microporous polytetrafluoroethylene (PTFE) membranes, which is typically in the range of 10 to 29 g/m^2 [13].

Liquid parameters, such as surface tension and viscosity, are critical factors affecting penetration behavior. Challenge liquids of low surface tension and high viscosity, such as the mixtures M2 and M3, exhibit higher penetrate through materials [14, 15], thus, requiring different material properties to provide protection for such challenge liquids. Penetration results indicated that a fine layer of polyurethane nanofibrous web was effective in limiting liquid penetration for those challenging liquids. As presented in Figure 3, nonwoven substrates without an electrospun web layer exhibited a wide range of penetration behavior from 4 to 98 % depending on the property of challenge liquids, whereas the layered fabric system with a nanofibrous web showed much lower penetration with less deviation for challenge liquids with a range of physicochemical properties.

Air and Moisture Vapor Transport Properties of Layered Fabric Systems

To examine how electrospun fiber web layers affect thermal comfort properties of material, air permeability and water vapor transmission rate were assessed for layered fabric systems and nonwoven substrate as indications of thermal comfort performance. Figure 4 presents the effects of electrospun web density on air/moisture vapor transport prop-

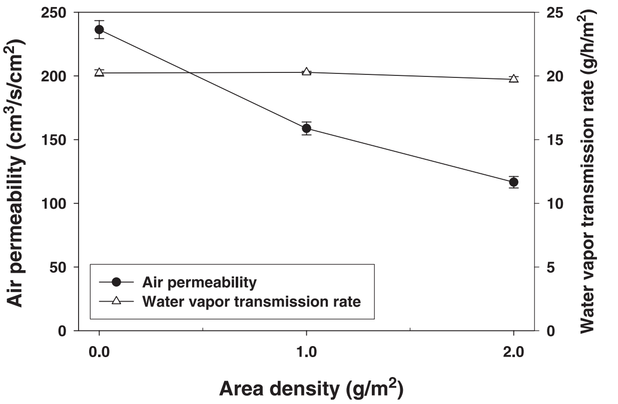

Figure 4 Effects of area density of electrospun polyurethane web on air/moisture vapor transport properties of layered fabric systems.

erties of layered fabric systems. A statistical difference was observed in air permeability due to the electrospun fiber web layers, but no significant change in moisture vapor transport. Air permeability decreased by 33 to 51 % with increasing electrospun polyurethane web area density for the range tested. However, no statistical difference was observed in moisture vapor transmission. This may be attributed to the large number of microscopic pores throughout the electrospun nanofibrous layer. The tiny pores constructed by nanofibers, which are substantially smaller than those in a nonwoven substrate, would still be large enough for moisture vapor transport.

The air permeability of layered fabric systems was above 100 $cm^3/s/cm^2$, which is higher than most protective clothing materials currently in use [13]. The water vapor transmission rates of layered fabric systems were in a range comparable to typical woven work clothing fabrics [13]. Thus, we could say that layered fabric systems are in an acceptable range in terms of air and moisture vapor transport.

Pore Size Distribution of Layered Fabric Systems

Pore size distribution was assessed for layered fabric systems and nonwoven substrate to examine the effect of electrospun polyurethane nanofibrous web layers on pore size. Figure 5 shows considerable reduction in pore sizes of layered fabric systems (b and c) as compared to a nonwoven substrate (a). As presented earlier in the SEM image of an electrospun nanofiber web layered on a nonwoven substrate (Figure 1), numerous electrospun nanofibers covered open pores of the nonwoven substrate, constructing a large number of microscopic pores in the layered structure. The pore size distribution of layered fabric systems sug-

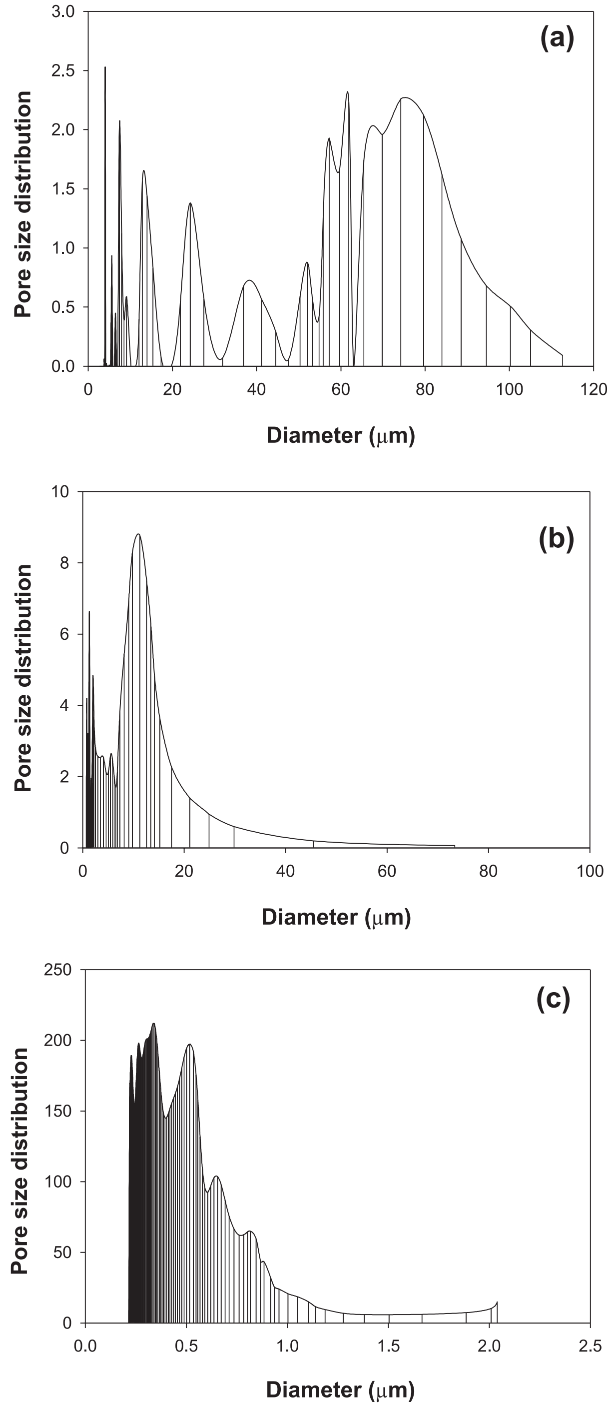

Figure 5 Through-pore size distribution of nonwoven substrate and layered fabric systems with an electrospun polyurethane web layer (a) nonwoven substrate (b) layered fabric system with 1.0 g/m^2 web area density (c) layered fabric system with 2.0 g/m^2 web area density.

gested that polyurethane nanofiber layers governed pore size of the layered system. The reduced pore sizes were expected to restrict the penetration of challenge liquids, thus, enhance the protection performance. As discussed earlier, there was a statistically significant reduction in air permeability, but no significant change in moisture vapor transmission.

Figure 5 also shows substantial decrease in pore sizes as the web area density increased. This indicated that engineering pore size would be feasible by controlling the level of web area density, implying the potential of developing materials with different levels of protection and thermal comfort depending on their need and use.

Conclusions

This research investigated developing protective textile materials via electrospinning to provide improved protective clothing for agricultural workers. Electrospun polyurethane nanofibers were applied to a highly porous nonwoven substrate to examine the potential of layered fabric systems with a nanofibrous web providing a combination of high barrier performance against liquid penetration and thermal comfort.

Electrospun polyurethane nanofibers formed a cohesive membrane-like structure, which covered macropores of a nonwoven substrate, creating numerous microscopic pores in the layered system. A very thin layer of electrospun polyurethane web significantly improved barrier performance of the nonwoven substrate for challenge liquids with varying physicochemical properties. Air permeability of the layered systems was reduced with increasing electrospun web area density, but even at the higher level of web density, the air permeability was still higher than most protective clothing materials currently in use. No significant change was observed in moisture vapor transport of the layered fabric systems from electrospun nanofiber web layers.

Pore sizes substantially smaller than those in conventional nonwovens and wovens were attained by layering electrospun nanofibrous web and pore size distribution indicated that pore size could be controlled by the level of web area density. This may be very useful in developing protective materials that would meet different needs for comfort and different levels of protection from various challenge liquids.

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