

Incorporation of Electrospun Nanofibers into Functional Structures

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INTRODUCTION

Electrospun nanofibers may have broad application in composite nonwoven structures in traditional markets. Electrospun nanofibers are being considered for a variety of applications where their unique properties contribute to product functionality. Those properties include high surface area, small fiber diameter, potential to incorporate active chemistry, filtration properties, layer thinness, high permeability, and low basis weight.

As the fibers themselves have a small diameter, the thickness of the nanofiber web can likewise be quite small, under one micron. The thin web has limited mechanical properties that preclude the use of conventional web handling techniques and instead require the formation of a layered composite structure by incorporating the nanofibers with a substrate material. Substrate materials are selected to provide appropriate mechanical properties and complementary functionality to the nanofiber web. Composite structure design is an important step in the development of a structure incorporating electrospun nanofibers.

A composite nanofiber filter media consisting of nanofibers from electrospinning in combination with a wet-laid substrate material has been successfully used in Ultra-Web[®] filter cartridges in a wide range of industrial, consumer and defense filtration applications since 1981. Researchers are currently exploring additional nanofiber composite designs for several new uses including providing a highly permeable aerosol barrier in protective gear such as facemasks, medical gowns and drapes, and protective clothing applications. Nanofibers are a natural fit for these applications, as high air permeability is desired to improve user comfort, and high aerosol efficiency is needed to provide adequate protection from aerosolized threats. The potential to include active chemistry in the nanofiber layer provides additional opportunities for functionality.

This paper will discuss the incorporation of electrospun nanofibers into a layered composite material for protective apparel applications. Application requirements, composite material design, and critical performance attributes will be explored.

APPLICATION REQUIREMENTS

Aerosol barrier properties are either currently specified or being considered for specification in a variety of protective apparel applications. Each of these applications also has complementary system requirements that may include permeability specifications, resistance to penetration by specific liquids, flammability, laundering, mechanical durability, mechanical strength properties, and

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wearer comfort. In many applications the different requirements are effectively addressed by using a layered material structure. For example, medical facemasks have five specific performance characteristics^a:

- Bacterial filtration efficiency
- Submicron particulate filtration
- Differential pressure (an indicator of breathing comfort)
- Fluid penetration resistance (to protect the wearer from blood spurts)
- Flammability

To meet these varied requirements, a layered composite structure is used, which is typically comprised of an inner cover, one or multiple meltblown fiber layers, a porous film layer, and an outer cover. The meltblown fiber layers provide the aerosol filtration performance, while the porous film layer provides the fluid resistance. The remaining layers are incorporated to improve wearer comfort by minimizing abrasion and to allow for high-speed processing of the composite material.

Polymeric nanofiber webs are a relatively new addition to the range of materials that may be used in a composite structure design for protective apparel applications.

Another example of a layered structure is the chemical protective fabric used in military applications, such as the Battle Dress Overgarment (BDO), consisting of a carbon-loaded foam liner with a protective shell covering for the adsorption of chemical warfare agents. The BDO is the old chemical protective suit worn by the military. The new chemical protective suit is the JSLIST – Joint Service Lightweight Integrated Suit Technology system that consists of a liner of adhesively-bound activated carbon beads with a protective cover shell fabric. Critical performance requirements for chemical protection suits include:

- Chemical protection from a variety of liquid- and vapor-phase chemical contaminants.
- Resistance to liquid (rain) intrusion
- Air permeability to maintain wearer comfort
- Tear strength and fabric weight requirements
- Durability - launderings and hours of wear

Current material systems incorporate a variety of layers to meet the requirements: the inner layer of activated carbon-based chemical vapor filtration media is supported by a fabric and protected by a top layer of adhesively bound nonwoven scrim. This inner liner is covered by a durable outer shell fabric treated with a water repellent to provide resistance to liquid intrusion.

There is an opportunity to improve the performance of this system through the incorporation of polymeric nanofiber webs. First, a polymeric nanofiber web can provide enhanced protection against aerosols (e.g. chemical agent micro-droplets, biological aerosols, radioactive dusts, etc) without adding weight or thickness, and while maintaining adequate permeability for wearer comfort. Second, the polymeric nanofiber web can be used as a carrier for active chemistry that may allow for improvements in chemical protective properties (and/or permeability, and/or weight).

GOAL OF THE STUDY AND SCOPE

The goal of this work was to evaluate the inclusion of a polymeric nanofiber layer within the existing layered structure of the JSLIST fabric.

To demonstrate proof-of-concept, the following performance requirements were set:

- Aerosol barrier performance in excess of 98% efficiency for particles sized 2 microns and larger
- Minimal change in the composite fabric permeability.
- Maintain aerosol and permeability performance through a military laundering cycle and 1500 Gelbo flex cycles (Gelbo flex was used as a surrogate for field wear).

A second goal of the work was to explore opportunities to add active chemistry to the nanofibers in order to produce a “self-decontaminating” fabric system. A catalyst for the oxidative degradation of the chemical agent, HD (sulfur mustard) was evaluated in two electrospun elastic polymers.

AEROSOL BARRIER MODELING

Aerosol barrier filtration properties for nanofiber structures can be modeled using proprietary modeling tools. Fiber size and thickness of the nanofiber web was varied to achieve 98% efficiency on a 2 micron particle, and resulting Frazier permeabilities were noted. Figure 1 summarizes the model results.

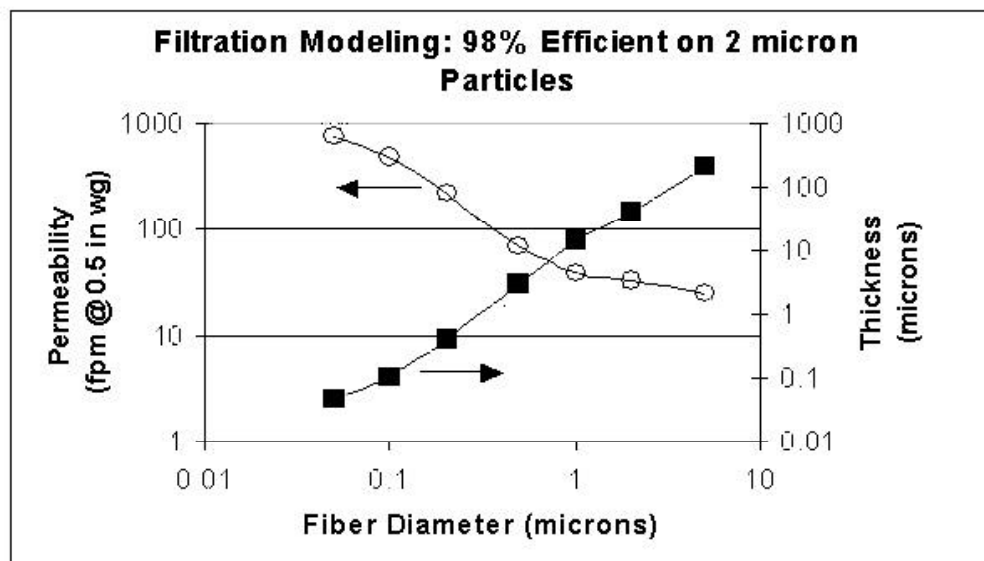


FIGURE 1: AEROSOL BARRIER MODELING

The aerosol barrier filtration efficiency modeling shows that smaller fibers lead to improved permeability and reduced thickness. For the purposes of this study, a fiber diameter of 0.25 microns was chosen. In order to maintain high permeability for the fabric system, a Frazier permeability for the nanofiber layer exceeding 45 feet/min was determined to be acceptable.

COMPOSITE FABRIC DESIGN

The first design option considered was to electrospin the nanofiber web directly on the inner surface of the outer shell fabric. Figure 2 is a SEM of such a construction. It can be seen that loose fibers in the woven shell material can produce holes in the nanofiber layer. Ultimately, when the composite material is stretched, bent, or subjected to surface abrasion, the nanofiber layer is easily destroyed by the movement of the larger fibers in the woven material. Relative movement of the large, loose fibers of the shell material is much larger than the elasticity of the nanofibers can tolerate. An effective nanofiber carrier material will have attributes that contribute to the durability of the nanofiber layer: a flat material with fibers bonded together. Spunbond materials tend to work well as nanofiber carriers, so subsequent work focused on optimization of a fabric architecture that included nanofibers applied to a spunbond material.

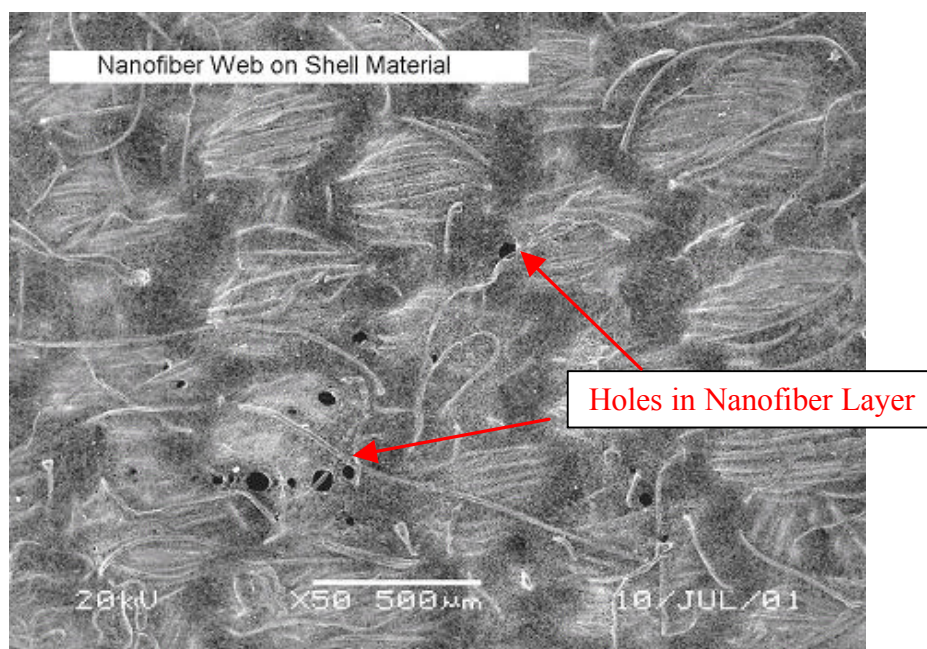


FIGURE 2: NANOFIBER WEB APPLIED DIRECTLY TO WOVEN SHELL

The following design approaches were evaluated for the composite layered material design:

- **Nanofiber constructions:** nanofibers were applied to a 0.6 osy nylon spunbond material and to a 1.0 osy nylon spunbond material. The nylon spunbond materials were chosen because it was thought that the adhesion and durability of the polyamide nanofibers would be improved by choosing a carrier of like material.
- **Nanofiber composites:** nanofibers were applied to the surface of the spunbond material and incorporated into the final fabric architecture. Additionally, some samples were made

where lighter layers of nanofibers were applied to the spunbond materials, then two layers of spunbond/nanofiber composite were laminated together in a face-to-face configuration, i.e. a structure of spunbond-nanofiber-lamination-nanofiber-spunbond. It was thought that this configuration would protect the nanofiber layers from surface scuffing.

- **Final fabric architecture:** The way in which the nanofiber layers are placed into the final composite may affect the durability of the materials. Samples were made with two different architectures:
 1. the nanofiber/spunbond layer laminated to the outer shell fabric, which free-floats against the chemical filtration layer.
 2. The nanofiber/spunbond layer free-floats between the outer shell fabric and the chemical filtration layer.

Each of these options is illustrated in Figures 3, 4, and 5.












Nanofiber Constructions							
Nanofibers applied to 0.6 osy nylon spunbond							
Nanofibers applied to 1.0 osy nylon spunbond							
KEY	<table style="width: 100%; border: none;"> <tr> <td style="width: 60%;">Nanofibers</td> <td style="text-align: center;"></td> </tr> <tr> <td>0.6 osy spunbond</td> <td style="text-align: center;"></td> </tr> <tr> <td>1.0 osy spunbond</td> <td style="text-align: center;"></td> </tr> </table>	Nanofibers		0.6 osy spunbond		1.0 osy spunbond	
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FIGURE 3: NANOFIBER CONSTRUCTION OPTIONS


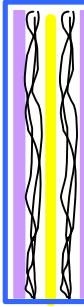






Nanofiber Composites	
C: 0.6 osy spunbond plus nanofibers, laminated to 0.6 osy spunbond	
D: 0.6 osy spunbond plus nanofibers, laminated to 0.6 osy spunbond plus nanofibers	
A: 1.0 osy spunbond plus nanofibers, laminated to 1.0 osy spunbond	
B: 1.0 osy spunbond plus nanofibers, laminated to 1.0 osy spunbond plus nanofibers	
Key	<p>Lamination </p> <p>Nanofibers </p> <p>0.6 osy spunbond </p> <p>1.0 osy spunbond </p>

FIGURE 4: NANOFIBER COMPOSITE OPTIONS

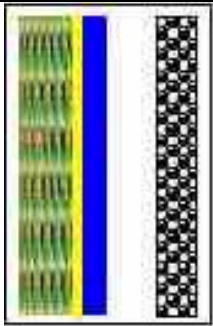
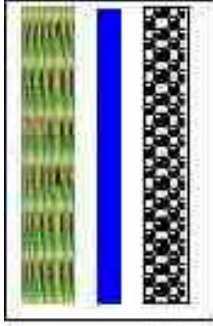




Final Fabric Architectures	
Nanofiber composite laminated to outer shell	
Nanofiber composite free floating between outer shell and carbon layer	
Key	<p>Outer Shell Material </p> <p>Nanofiber Composite </p> <p>Lamination </p> <p>Carbon Layer </p>

FIGURE 5: FINAL FABRIC ARCHITECTURE OPTIONS

For samples that were laminated, a gravure lamination method was used, with a moisture-cured hot melt polyurethane adhesive for the laminating resin. For testing of the composite structure, component layers were sewn on an industrial sewing machine using a single row of stitching around the edges of the sample rectangle.

Aerosol Barrier Efficiency and Permeability

Samples of the nanofiber composition were made and tested for initial aerosol barrier efficiency and permeability. The results of these tests are shown in Table 1 below. For each weight of spunbond substrate, we deposited nanofibers with two different levels of particle barrier efficiency. The higher efficiency samples (~80 % at 0.8 micron) would be utilized as the basic substrate-nanofiber composite for the single nanofiber layer designs, and the lower efficiency ones (targeted to result in a final efficiency of ~ 80%) for the double nanofiber layer composites. Although the goal for aerosol barrier efficiency is for a 2 micron particle, a 0.8 micron particle size was used in testing the samples. Previous testing and computer modeling have confirmed that 85% efficiency on a 0.8 micron

particle is equivalent to 98% efficiency on a 2 micron particle. Thus the test method specified in ASTM 1215, using 0.8 micron PSL particles at 20 feet per minute was used.

The shell material of the fabric composite has an initial aerosol efficiency of approximately 45%. Thus the aerosol efficiency of the nanofiber layer must be at least 70% in order to achieve a composite efficiency of 85%. Initial efficiency and permeability measurements were adequate to meet the goals of the project.

TABLE 1: NANOFIBER COMPOSITION INITIAL TEST RESULTS

Nanofiber Composition	Initial Efficiency (0.8 μm) – Nanofiber Layer(s)	Initial Frazier Permeability – Nanofiber Layer(s)
1.0 osy spunbond + nanofibers	70%	86
1.0 osy spunbond + nanofibers (doubled)	85%	49
0.6 osy spunbond + nanofibers	81%	82
0.6 osy spunbond + nanofibers (doubled)	83%	69

Durability

As the durability of the nanofiber layer can be affected by many different characteristics of the ultimate material composite, we will consider the results at each step toward the fabrication of the final composite material. This allows us to gain some insight into the degree of relevance of the aspects being considered for the different designs. Many aspects of these inventions are covered by a pending US patent application^b.

Mechanical durability testing was conducted in order to assess the durability of the nanofibers under mechanical strain. A commercial Gelbo Flex Tester instrument, Model 5000 ES, was used for this purpose. Gelbo flex tests were conducted at different points during the fabrication process. Tests were carried out with nanofiber constructions, laminated nanofiber compositions, as well as for the final fabric architecture. A constant cycling frequency of 45 cycles/min was used for all tests. For nanofiber constructions and compositions a 6 inch stroke was set, and barrier efficiency measurements were taken after 1500 cycles. The stroke was adjusted to 4.5 inches for the final fabric architectures to accommodate the increased material thickness. For all the Gelbo Flex tests the ambient conditions were kept at constant temperature and relative humidity, $70 \pm 2^\circ \text{F}$ and $35 \pm 2\% \text{RH}$ respectively.

Nanofiber Constructions

The four nanofiber constructions discussed previously (see Figure 3) were tested for durability. Table 2 compares the initial aerosol efficiency to the aerosol efficiency following Gelbo flex testing for each sample. The goal was 85% efficiency with 0.8 micron particles. Figure 6 shows an SEM of one of the constructions.

TABLE 2: GELBO FLEX RESULTS FOR NANOFIBER CONSTRUCTIONS

Nanofiber Construction	Initial Efficiency	Post-Gelbo Efficiency	Efficiency Percent Retained
1.0 osy spunbond + nanofibers	67%	48%	72%
1.0 osy spunbond + nanofibers (doubled)	85%	75%	88%
0.6 osy spunbond + nanofibers	81%	52%	64%
0.6 osy spunbond + nanofibers (doubled)	83%	55%	66%

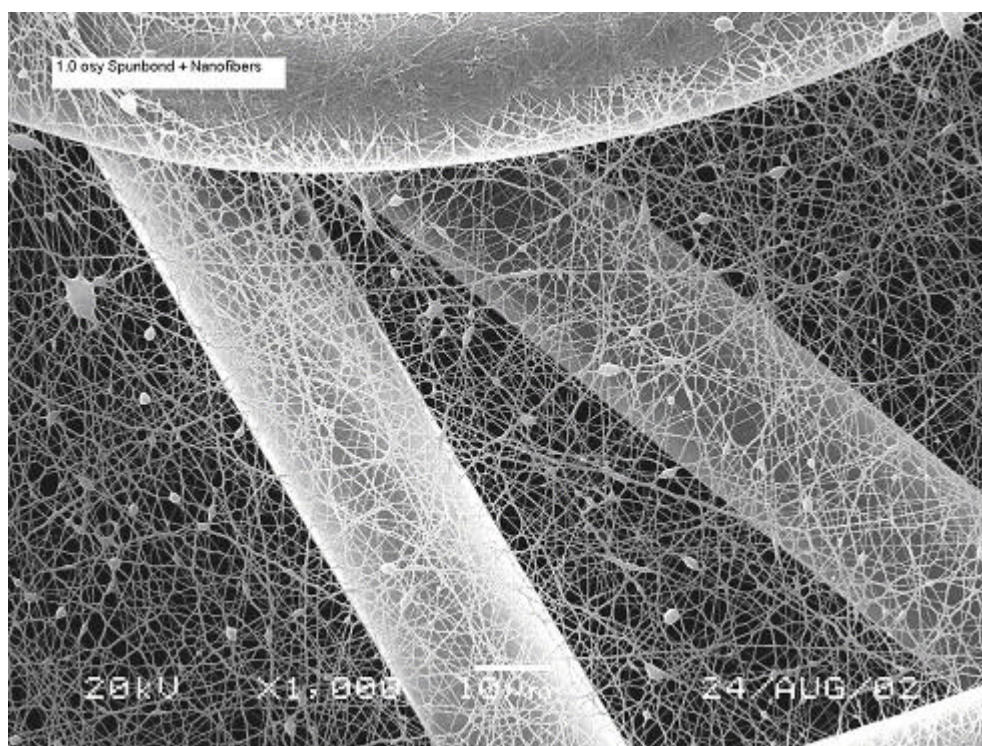


FIGURE 6: SEM OF NANOFIBER CONSTRUCTION

The data reveals the difference in durability among the individual samples when challenged with flexing-crumpling action of the Gelbo Flex test. All the samples demonstrated a decrease in efficiency under the flexing-crumpling action of the Gelbo Flex test. In general, samples with nanofibers applied to the heavier weight substrate, and those with a smaller quantity of nanofibers (subsequently doubled) appeared to have improved durability.

It appears that a heavier weight material leads to modest improvements in nanofiber web durability, and using two layers of spunbond material with applied nanofibers in a face-to-face configuration

also provides a modest improvement in durability. Improvements resulting from a higher weight substrate are expected as more robust substrates offer a stronger structure for the nanofiber web.

Damage to the nanofiber layer is typically caused by gross movements of the substrate fibers. As the spunbond fibers are all bonded together, gross movements tend to be localized at areas of high stress, where the spunbond itself begins to fail. When the substrate fibers don't move around, damage to the nanofiber web is minimized. In a woven fabric construction, the fibers are not bonded together and can readily move relative to one another. This relative movement gives the fabric some stretch characteristics. It also provides a poor surface for nanofiber web application.

Nanofiber Composites

As the next step in the fabrication of samples of the final fabric architecture, we proceeded to laminate the substrate/fine fiber layer into the planned nanofiber composites (please see Figure 4 for a description). Table 3 compares the pre- and post-Gelbo efficiency data for the samples. The goal was 85% efficiency with 0.8 micron particles.

TABLE 3: GELBO FLEX RESULTS FOR NANOFIBER COMPOSITIONS

Nanofiber Composite	Initial Efficiency (0.8 μm)	Post-Gelbo Efficiency (0.8 μm)	Efficiency % Retained
A: 1.0 osy spunbond + nanofibers laminated to 1.0 osy spunbond	72%	38%	53%
B: 1.0 osy spunbond + nanofibers laminated face-to-face to 1.0 osy spunbond+ nanofibers	80%	69%	86%
C: 0.6 osy spunbond + nanofibers laminated to 0.6 osy spunbond	73%	51%	70%
D: 0.6 osy spunbond + nanofibers laminated face-to-face to 0.6 osy spunbond + nanofibers	82%	72%	88%

These results indicate that the nanofiber web durability is improved by applying a lighter layer of nanofibers to the spunbond material, and creating a face-to-face laminated composite structure. Figure 7 is an SEM of this type of construction. The face-to-face lamination method provides some protection to the nanofiber layers from surface abrasion thus enhancing their durability in Gelbo flex testing.

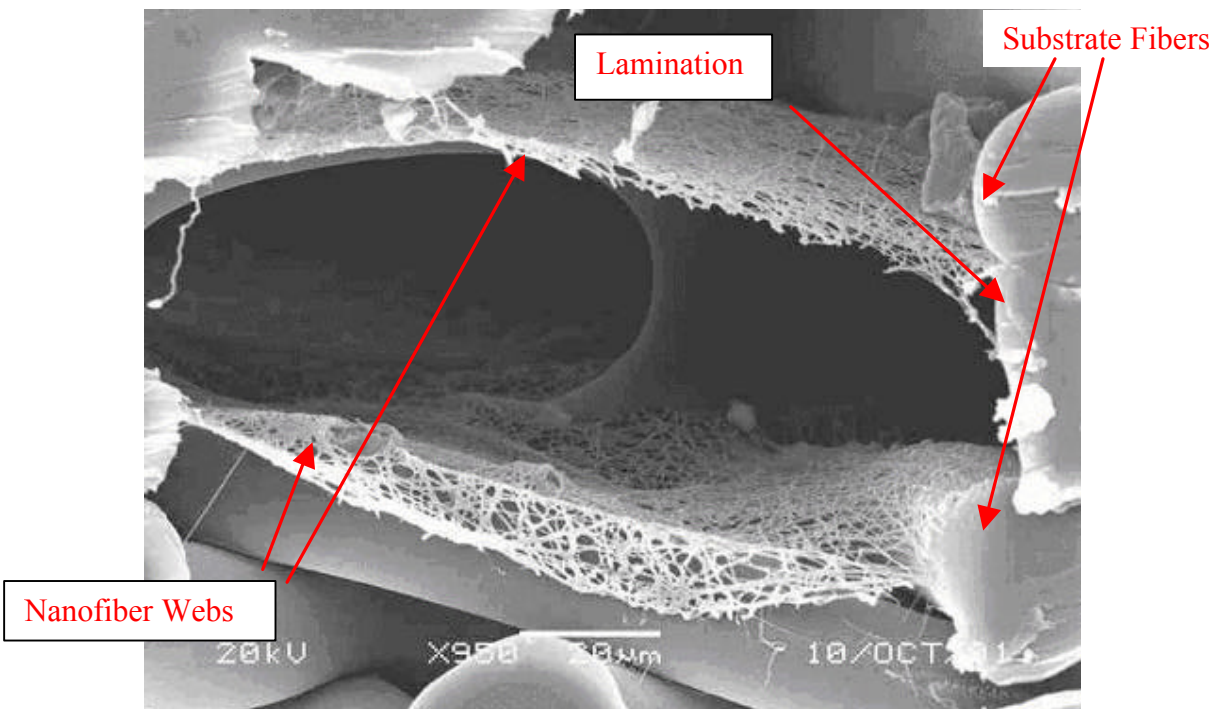


FIGURE 7: SEM OF FACE-TO-FACE LAMINATION COMPOSITE

Fabric Architectures

The durability performance of the nanofiber layer will also be dependent on the finished fabric architecture. The fabric architectures considered are shown in Figure 5. The results for Gelbo Flex tests for each design are summarized in Table 4. The goal was 85% efficiency with 0.8 micron particles.

TABLE 4: GELBO FLEX RESULTS FOR FABRIC ARCHITECTURES

Fabric Architecture	Initial Efficiency (0.8 µm) - Nanofiber Layer	Post-Gelbo Efficiency (0.8 µm) - Nanofiber Layer	Efficiency % Retained
Composite A Laminated to Shell	70%	56%	80%
Composite A Free Floating	75%	41%	55%
Composite B Laminated to Shell	75%	30%	40%
Composite B Free Floating	83%	74%	89%
Composite C Laminated to Shell	71%	27%	38%
Composite C Free Floating	74%	51%	69%
Composite D Laminated to Shell	77%	56%	73%
Composite D Free Floating	80%	61%	76%

The fabric architecture flex testing results are inconclusive. It is not clear from these test results if the fabric architecture has an impact on the durability of the nanofiber layer. It is clear from these results that the durability goals for the project have been met with the free floating fabric architecture incorporating nanofiber composite B (two layers of 1.0 osy spunbond/nanofiber laminated together in a face-to-face configuration).

We observe that for the free-floating design the performance is comparable to that of the nanofiber composite materials, suggesting that the addition of the two other layers of the garment (shell and carbon layer) do not add new stresses to the fine fiber composite.

LAUNDRY

As a preliminary simulation of laundry conditions, a sample of the A nanofiber construction (nanofibers applied to 1 osy spunbond) was soaked in a water/detergent mixture for 5 minutes at 140 F. The results are shown in Table 5.

TABLE 5: RESULTS OF HOT DETERGENT SOAK TEST

Nanofiber Construction	A: Nanofibers applied to 1.0 osy spunbond	B: Nanofiber + 1.0 osy spunbond laminated to Nanofiber + 1.0 osy spunbond
Initial Efficiency (0.8 μm)	83%	92%
Post-soak Efficiency (0.8 μm)	85%	90%
% Efficiency Retained	100%	98%

A SEM of a sample A following hot detergent soak is shown in Figure 8. A cross-section of sample B after hot detergent soak, stirred with added ISO Fine Dust to simulate dirty laundry, is shown in Figure 9.

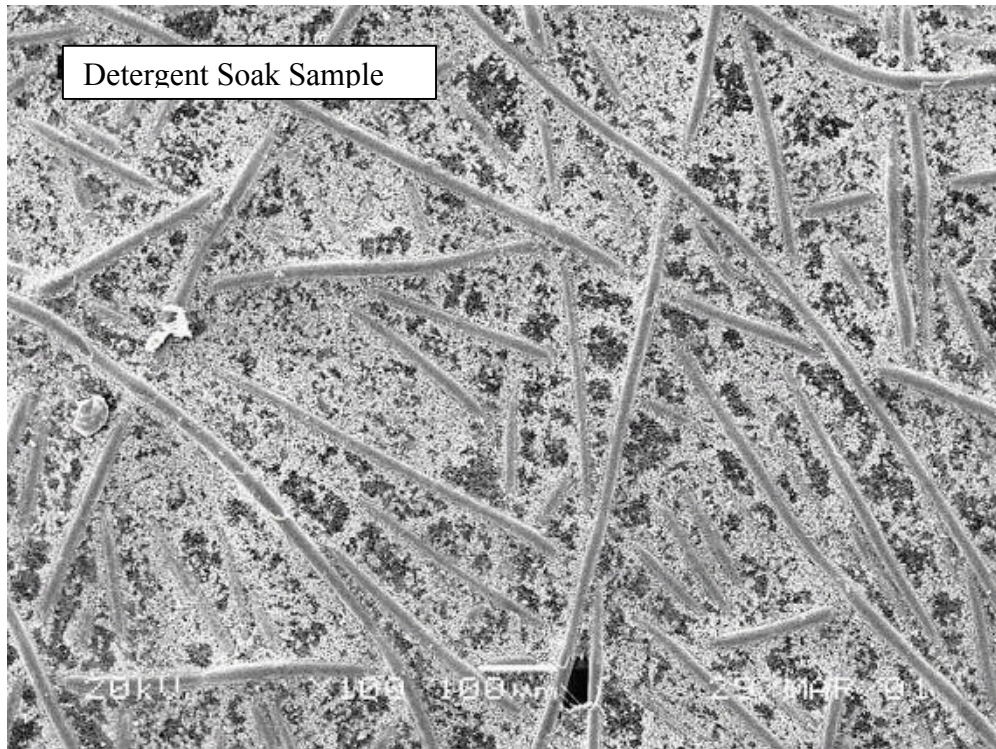


FIGURE 8: SEM OF SAMPLE A AFTER HOT DETERGENT SOAK

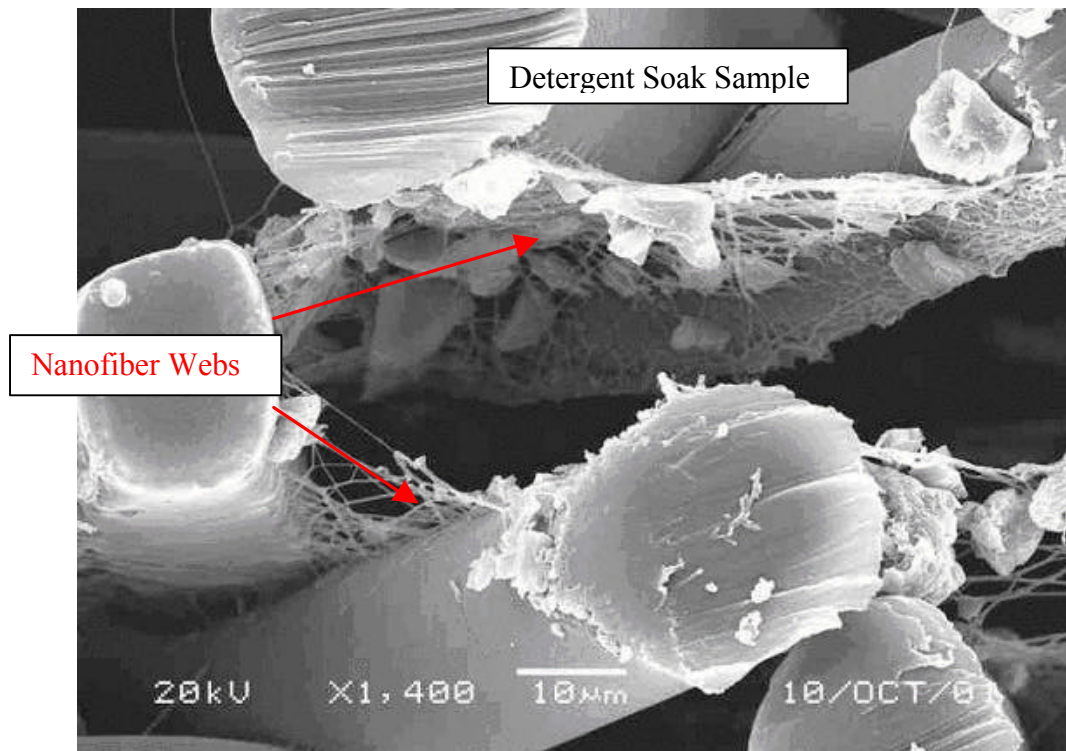


FIGURE 9: CROSS SECTION OF SAMPLE B AFTER HOT DETERGENT SOAK

From a review of the SEM images, we can see that the nanofiber web layers act as very efficient filters, capturing and retaining significant quantities of dust and detergent. It is thought that retention of dust and detergent particles could lead to increased abrasion damage as the particles are rubbed against the nanofiber layer.

Samples were also subjected to a single military laundry cycle. Results are shown in Table 6.

TABLE 6: RESULTS OF LAUNDERING

Nanofiber Construction	A: Nanofibers applied to 1.0 osy spunbond	B: Nanofiber + 1.0 osy spunbond laminated to Nanofiber + 1.0 osy spunbond
Initial Efficiency	83%	92%
Post-Laundry Efficiency	55%	79%
% Efficiency Retained	66%	86%

These results indicate that the retention of detergent particles, coupled with the agitation of a laundry cycle, damages the nanofiber layer. As in the previous durability testing, the lamination of two lighter-efficiency nanofiber/spunbond structures together in a face-to-face configuration provides a significant durability enhancement.

REACTIVE NANOFIBERS

Reactive nanofibers were produced from mixtures of a polyoxometallate (an HD catalyst) and two types of elastic polymers. The polyoxometallate (POM) is a new compound synthesized by Craig Hill and Nelya Okun at Emory University, and is not yet fully characterized. It's chemical formula is presumed to be $((C_4H_9)_4N) 5H_2(Fe_3PW_9O_{37}NO)_3$. We refer to this new POM as ND-1121B.

The polymers used with the new POM were Estane® 58238, a Noveon, Inc. thermoplastic polyurethane (TPU), and a Donaldson elastomer, FP-10. Both were dissolved to a level of 10 wt% in organic solvents. The new POM, ND1121B was dissolved into each polymer solution at a 1 wt% content. These solutions were electrospun at a voltage of 10kV, over a distance of 10cm to a grounded aluminum collection target. Final dry weight of the electrospun fibers contained 10% by weight catalyst ND1121B. These electrospun fiber mats were removed from the target and placed in a solution of acetonitrile, containing the simulant, half-mustard, or 2-chloroethylethylsulfide (CEES). The initial concentration of half-mustard was 0.287mg in solution. Depletion of CEES by the catalyst-loaded nanofiber mat was followed by gas chromatography of the exposure solution over time. Figure 10 shows the depletion of CEES by TPU/ND1121B and FP10/ND1121B. We can see that the reactive FP10 electrospun fibers (efibers) deplete the most CEES in a 24-hour period, and exhibit a faster depletion rate than the TPU efibers or the catalyst alone in an equivalent concentration in the CEES solution. There is an apparent enhancement of the ND1121B reaction rate when this compound is dissolved into nanofibers – the nanofibers of FP10 function as an immobilized catalyst decontamination layer.

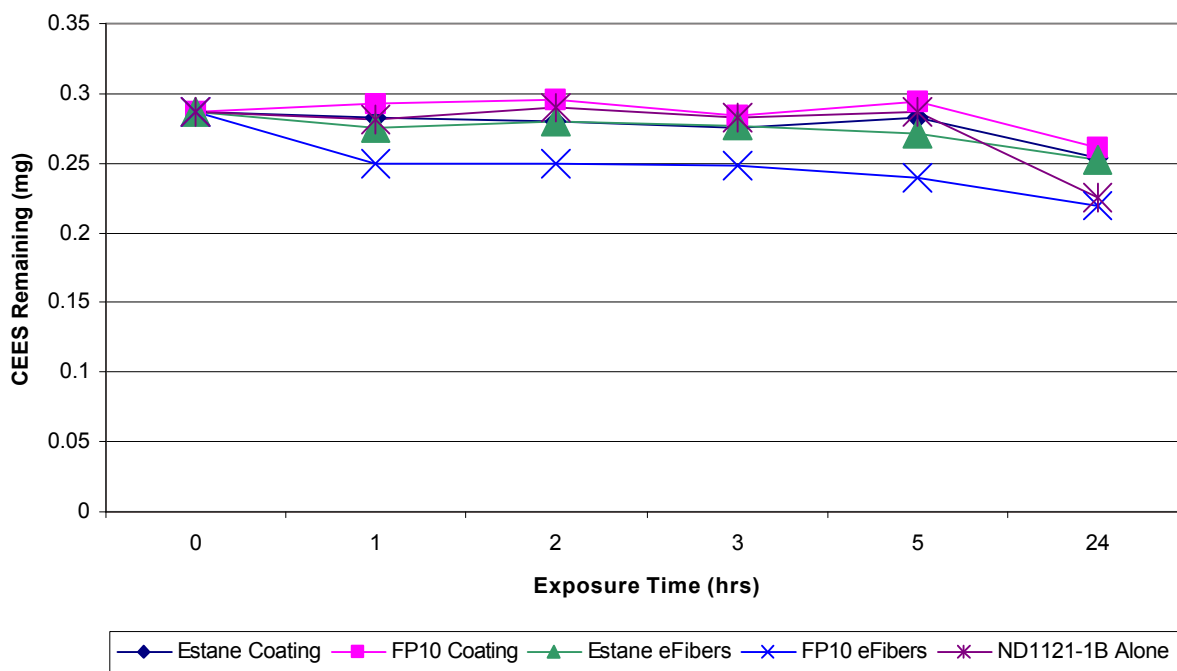


FIGURE 10: DEPLETION OF CEES BY TPU/ND1121B AND FP10/ND1121B

The catalyst used in this test was at 24% strength in this study, due to an instability in the structure of this experimental compound. When used fresh, this compound is capable of breaking down 65% of the CEES in a 24 hour period. The effect of the electrospun fiber substrate on the activity of this catalyst is significant and further optimization of the catalyst-loaded nanofibers is currently underway at the U.S. Natick Soldier Center.^c

CONCLUSIONS

Several significant technical advances were made during this project.

- Aerosol barrier and permeability modeling and testing confirmed the performance advantages of nanofibers for aerosol barrier materials.
- Advancements in design of a durable composite structure were made. The best durability performance was achieved using two layers of nanofibers captured between two layers of a very strong, smooth, and flexible spunbond material. This combination protected the nanofibers from direct abrasion and provided a dimensionally stable supporting structure.
- Some of the same attributes that make nanofiber layers attractive as aerosol barriers also lead to challenges for durable structures. Since the nanofiber layer efficiently removes particles yet allows flow through high permeability, dirt and detergent particles are caught and retained, leading to reduced durability as these particles grate against the nanofiber layer and ultimately create holes in the structure.
- This project primarily focused on using nanofibers as an add-on layer within an existing garment system. Re-engineering the entire system with the capabilities and limitations of the

nanofibers in mind is more likely to result in success. New fabric layers, redistribution of the nanofibers, repositioning the components, etc. could resolve many of the durability issues.

- Incorporation of catalysts directly into the electrospun nanofibers enhances the reactivity of the catalysts, rather than diluting their effectiveness within the fiber bulk.

In looking forward to future work, aerosolized chemical and biological agents are a clear threat, and a threat that is likely to grow in the future. Nanofibers offer clear performance advantages as aerosol barriers with superior air permeability. We believe there are several productive areas of focus in developing this technology and using it to mitigate aerosol threats. Military outerwear must endure the most brutal environment of any clothing, undergoing the harshest conditions during use and laundry. Current nanofiber technology may be useful in similar but less harsh applications such as catalytically reactive fibrous substrates, single use garments, tents, tarps, casualty bags, facemasks, and surgical gowns.

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