Advanced Textile Laminates for Chemical Biological Protective Clothing

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ABSTRACT

Much of the chemical biological (CB) protective clothing used by the military is based on the use of activated charcoal as a major component of a composite textile system. This clothing does a good job in providing protection, however it is quite heavy, uncomfortable, and potentially subjects the wearer to heat stress. Lightweight textile systems are under development to address these issues. Laminates have been developed based on selectively permeable membranes as well as others incorporating filter fabrics. These novel materials have the potential to provide CB protection in lighter weight, more comfortable clothing systems.

1. INTRODUCTION

Today's chemical biological (CB) protective clothing does a very good job of providing protection against a wide variety of threats. In the civilian sector this clothing is used in numerous industrial workplaces and also by emergency responders. In these applications the clothing is usually made from an air-impermeable barrier material such as a thermoplastic polymer, elastomer, or coated fabric. The CB clothing used by the military is based on a textile system which has a degree of air permeability to maximize comfort while still retaining protection. An important component of the textile system is activated charcoal which serves as a universal vapor adsorbent. In general these CB clothing systems are still too heavy, uncomfortable, and subject the wearer to the threat of heat stress with prolonged usage and moderate work levels. Materials research is underway to develop lighter weight materials for this purpose which will still retain appropriate levels of protection.

One approach to lightweight materials for this purpose is the use of selectively permeable membranes (SPMs). Several SPMs have been developed which serve as effective barriers to hazardous chemicals and aerosols while allowing a degree of moisture vapor transport (MVT). It is expected that the MVT will provide a measure of relief from heat stress through evaporative cooling. Surface modification techniques have been employed for optimizing the properties of these SPMs including ion implantation and the addition of Langmuir-Blodgett monolayers of cyclic compounds. The SPM concept is shown in Figure 1.

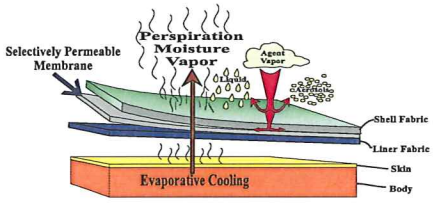


Figure 1. SPM Concept

A second approach is the use of a lightweight filter fabric in combination with a liquid repellant outer layer and a vapor adsorptive inner lining. Expanded poly(tetrafluoroethylene) (ePTFE) is a well known material for this application. A combination of longitudinal and transverse stretching of the PTFE membrane during manufacturing results in a lattice-like porous structure of micro-sized interconnected fibrils and nodes. The size of the micropores is controllable and is directly related to the moisture vapor transport of the film, which, in turn, is related to comfort. Furthermore, the ePTFE film and its adhered outer layers can be electrostatically charged for maximum aerosol filtration efficiency.

2. EXPERIMENTAL

2.1 Experimental for first phase of study

Laminates of ePTFE films with different weights were placed between lightly pre-bonded spunbond (SB) polypropylene (PP) webs with weights of 20 and 50 g/m^2 and bonded together by two advanced techniques. First a breathable adhesive was applied in a lined

pattern (4 lines/inch) to both sides of the ePTFE membranes. Then the SB PP webs were applied to each side, and the SB/ePTFE/SB laminates were lightly compacted between smooth rollers and cured at 210 °F. Similar ePTFE membranes were also laminated between 20 and 50 g/m^2 SB PP webs and were subjected to thermal calendering using a 2-roller B. F. Perkins thermal bonder with a 260 line/inch engraved calender roller. The combination of this new fine-lined engraved roller over a smooth steel roller was employed because this type of nip has been recently found by industry to be well suited to bonding fabrics with delicate textures and with nano-polymer finishes. It was hoped that these two techniques minimized pin-hole formation during the bonding of the laminates and reduced breathability less than more conventional adhesive and thermal bonding. Then both types of laminates were electrostatically charged (EC) using Tantret™ EC technology. It was believed that these minimally evasive techniques for bonding the laminates as well as the use of EC to improve the capture efficiency of aerosols would result in improved barrier, strength and comfort performance of the laminates. The laminates were characterized for mean pore diameter, filtration efficiency to sodium chloride aerosol particles, hydrostatic head, and for moisture vapor transmission rate. Gross morphology of the laminates, including the ePTFE membranes, adhesive, and thermally bonded areas, was analyzed using scanning electron microscopy.

It is known that expanded-polytetrafluoroethylene (ePTFE) film is a good barrier to chemical/biological (C/B) aerosols, especially when used in combination with an underlying adsorbent carbon layer in chemical protective liners for soldiers. A combination of longitudinal and transverse stretching of the PTFE membrane during manufacturing results in a lattice-like porous structure of micro-sized inter-connected fibrils and nodes (1-4). This structure can be seen in the SEM photomicrograph at 10,000X in Figure 2 of a Donaldson Company ePTFE film. However, the soldier or first responder in an emergency or terrorist threat would be even more comfortable and effective if the water vapor transmission rate (WVT) of the ePTFE membrane in C/B protective clothing could be markedly improved to enable the individual to safely function in high heat-stress situations for extended periods of time. Although the mean pore size and porosity of ePTFE increases with increasing longitudinal stretching ratio, transverse stretching ratio, and heat-treating temperature, additional stretching beyond that here-to-fore found to be satisfactory might result in a decreased level of performance.

The objective of this study is to prove that electrostatic charging (5-6) of the ePTFE membrane or adhered outer polypropylene (PP) nonwoven layers with high dielectric properties should substantially improve the ability of the ePTFE membrane and its component layers to attract and thereby minimize the penetration of aerosols in water or organic based aerosols or as solid particulate. The second hypothesis to prove is that electrostatic charging (EC) will enable the mean pore size and over-all porosity of the film to be increased by greater stretching of the ePTFE film to provide substantially higher moisture transport and consequently greater comfort.

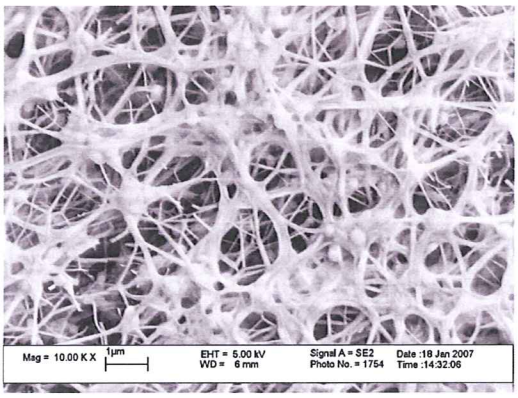


Figure 2. SEM at 10,000 X of Donaldson ePTFE

2.2 First phase results and discussion

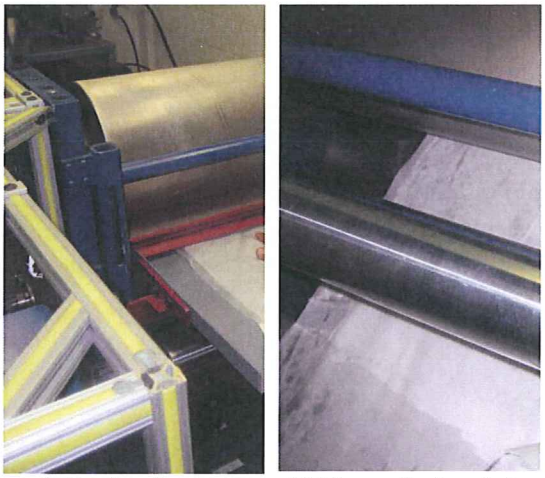
From the first phase of this study (7) our hypothesis that electrostatic charging (EC) the ePTFE film would increase the aerosol filtration efficiency (FE) had mixed results. It was found that EC of non-finished and FC hydrophobic finished ePTFE resulted in slightly decreased FE to NaCl and DOP aerosols. However, the EC of laminates of ePTFE with SB PP generally resulted in an increase in FE. With one laminate of spunbond (SB) PP/ePTFE/SB PP, EC resulted in a 7.3 fold decrease in penetration of 0.067µm NaCl particles. This demonstrates that the EC laminates of ePTFE and SB or melt blown (MB) PP fabrics promises to provide enhanced FE.

In an effort to improve FE of the ePTFE component, the film was treated with one-atmospheric electrical plasma. However, the plasma treatment reduced the FE and EC treatment further decreased FE. Stationary EC treatment of ePTFE films alone was tried, as well, for different lengths of time; however, FE decreased notably with increasing EC treatment time. In addition, it was found that the ePTFE film had to be biaxially heat-stretched instead of uniaxially to uniformly decrease film weight and thickness and to notably increase porosity. After many unsuccessful attempts with the stretching equipment at UT, we were able to have ePTFE films biaxially stretched uniformly at the Advanced Engineering Fibers and Films (CAEFF) Center, Clemson University. CAEFF has redesigned their T.M. Long stretcher and interfaced it with a computer for more precise control of films during heating and stretching. The ePTFE films were heat-stretched biaxially up to 2.2X. These ePTFE films were then EC and just as was found with the non-post-stretched ePTFE films, FE of the EC biaxially-stretched films decreased with EC. It did not appear to make a difference whether or not the ePTFE film was treated with a fluorochemical (FC) prior to heat-stretching and EC.

2.3 Experimental for second phase of study

During this second phase of the study, laminates of ePTFE films were placed between lightly pre-bonded spunbond (SB) polypropylene (PP) webs with weights of 20 and 50 g/m^2 and bonded together by two advanced techniques. Lightly pre-bonded SB PP webs were prepared for lamination with ePTFE so that subsequent thermal point bonding would not cause the laminate to be as stiff as if completely bonded SB PP was used because during thermal bonding of the laminate, the SB PP is being subjected to a second calendering process. In the first method, two laminates were prepared with both having a center layer of ePTFE but one had an outer layer of 20 g/m^2 SB PP on each side and the other had 50 g/m^2 SB PP on each side. They were bonded using Performax 8535 applied to the SB PP nonwoven substrate via print application in order to create a discontinuous deposit of the adhesive on one side of the nonwoven substrate. A print pattern of thin stripes was used in order to leave a large "uncoated" area to enable high WVT through the composite. After printing the adhesive on the two layers of nonwoven, the ePTFE film was placed between the two layers of SB PP, the laminates were then pressed together between two cold smooth steel rollers at 1,000 psi, and immediately dried/cured in an oven at 220-225 °F for 3 minutes (8).

In the second laminating technique, ePTFE membranes were laminated between a 20 g/m^2 SB PP on one side and a 50 g/m^2 SB PP web on the other side and these composites were subjected to thermal calendering using a 2-roller B. F. Perkins thermal bonder at The University of Tennessee Nonwovens Research Laboratory (UTNRL) with a Schreiner diagonally ribbed roll with 260 line/inch (Figure 3) at a surface speed of 1.5 m/min with a roller surface temperature of 275 °F and a bonding pressure of 150 PLI. The combination of this Schreiner roller over a smooth steel roller was employed because the fine ribs do not penetrate as much into the substrate as do typical diamond patterned engraved calendar rollers (9). It was hoped that both the special adhesive bonding and thermal bonding techniques employed minimized pin-hole formation during bonding the laminates and reduced breathability less that more conventional adhesive and thermal bonding. Then both types of laminates were electrostatically charged (EC) using Tantret™ EC technology. It was believed that these minimally evasive techniques for bonding the laminates as well as the use of EC to improve the capture efficiency of aerosols would result in improved barrier, strength and comfort performance of laminates which could be used in chemical protective liners for soldiers. The laminates were characterized for mean pore diameter and for water vapor transmission rate (WVT) according to ASTM E 96/E 96M-05, Desiccant Method, Procedure E at 37.8 °C and 90% RH. Gross morphology of the laminates, including the ePTFE membranes and adhesive and thermally bonded areas, was analyzed using scanning electron microscopy.



a) Feeding in un-bonded laminate b) Thermally bonded laminate

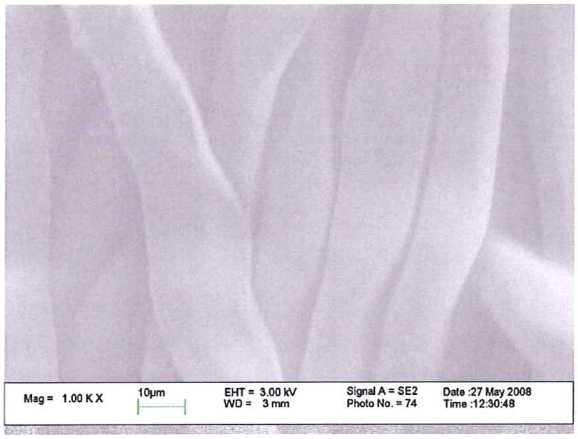
Figure 3. Thermal bonding with a) feeding of un-bonded laminate of 50g SB PP on top for direct contact with 260 line/in. Schreiner roll, ePTFE in center, and 20g SB PP on bottom for contact with smooth steel roller and b) thermally bonded laminate exiting calender nip

2.4 Second phase results and discussion

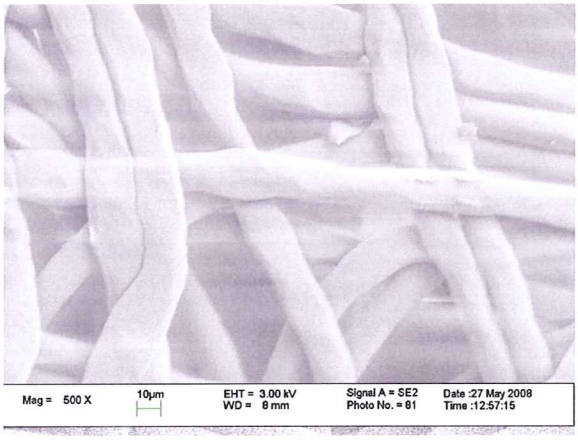
In Table 1, the WVTs of the non-electrostatically charged (NC) adhesively bonded laminates of ePTFE with SB PP ranged from 5,448 with the T2 ePTFE with outer layers of 50 g/m^2 SB PP to 5,711 g/m^2/day with the ePTFE with lighter the lighter 20 g/m^2 SB PP webs, although these WVT values are rather close. The WVTs of the corresponding EC laminates were 5,998 to 6,365 g/m^2/day, with the lighter outer SB layers apparently resulting in slightly greater WVTs. However, all of these samples had the same core of T2 ePTFE, which primarily contributes to barrier properties, while still allowing relatively high WVT. The mean pore diameter of the T2 ePTFE was 0.48 μm before lamination and increased to 1.10 and 2.09 μm after adhesive bonding with the outer SB PP layers. The latter mean pore sizes are still rather small, but some web distortion or pinhole formation may have occurred during hot pressing of the adhesively-bonded laminates prior to curing of the adhesive in the oven.

The WVTs of the NC thermally bonded laminates of ePTFE with SB PP ranged from 4,632 to 5,403 g/m^2/day with the corresponding EC laminates having values from 5,010 to 5,822 g/m^2/day. A clear trend could not be seen with respect to the effect of EC on WVT of either the adhesive or thermally bonded laminates of SB PP with ePTFE. The porosity of these samples is too low to determine filtration efficiency to 0.067 μm NaCl particles using the TSI Filter tester at the University of Tennessee. The mean pore size of ePTFE used in thermally bonded Sample 5 was 0.37 μm before thermal calendering and increased to 1.61 μm after bonding, indicating some fabric distortion or pinhole formation as a result of calendering. On the other hand, Sample 7, which had a different ePTFE film with a mean pore size of 0.27 μm before bonding, had an unchanged mean pore diameter of 0.30 μm after calendering using the Schreiner roller. In comparison, the thermally bonded laminate of SB PP and ePTFE obtained from a commercial source (Sample 9) had a mean pore size of 3.50 μm, and a WVT of 6,235 g/m^2/day before EC and 6,025 g/m^2/day after EC.

SEM analyses revealed that the fibrous structure of the outer SB layers of both the adhesive and thermally bonded was largely intact. It was surprising however, that the outer SB PP fibers of the adhesively bonded laminates were flattened (Figure 4) in both the non-adhesive area and in the adhesive stripe. It is possible that although the SB PP webs were only lightly calendered when they were prepared, that the flattened fibers resulted from the first calendering step on the SB line. Also the pressure of 1000 psi may have been too great in pressing the laminate together between smooth rollers prior to being placed in the oven at 220-225 °F for 3 minutes. The oven exposure was well below the temperature range of 250 -265 °F, at which PP can begin to undergo thermal shrinkage. Although the laminates bonded using the Schreiner roll/smooth roller nip had generally round outer SB PP fibers, there was an indication that some fibers had melted and fused fibers together (Figure 5). In comparison, a thermally bonded laminate of SB PP and ePTFE, Sample 9, obtained from a commercial source had many flattened SB PP fibers on the surface, apparently from the thermal bonding step (Figure 6).



a) Non-adhesive area of Sample 1 at 1000X



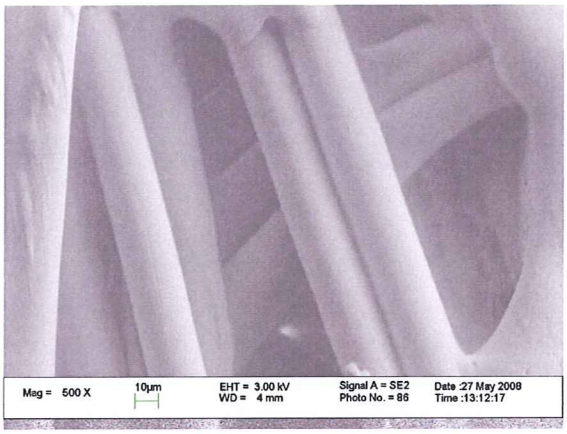
b) Adhesive bonded strip of Sample 1 at 500X

Figure 4. SEM photomicrographs of adhesive-bonded sample 1 in adhesive strip and in non-adhesive area

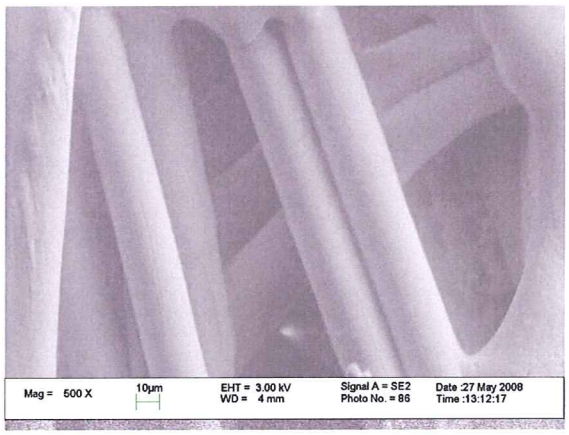
CONCLUSIONS

Textile laminates have been fabricated and shown to be feasible materials for consideration in the next generation of lightweight, CB protective clothing. Additional work is planned to optimize these materials.

The findings from the first phase of the study would be employed concerning post-stretching and laminating ePTFE with highly dielectric, yet strong materials on both sides such as spunbond (SB) PP, melt blown (MB) PP, and MB/SB composites, which can be electrostatically charged before or after



a) Thermally-bonded sample 5 at 500X



b) Thermally-bonded sample 5 at 100X

Figure 5. SEM photomicrographs of thermally-bonded sample 5

laminating and bonding by thermal or breathable adhesive methods.

On a larger scale (50 to 200 meters with a width of 0.5-2 meter) of commercial ePTFE films with different weights and mean pore sizes it would be possible to first post-heat stretch the ePTFE film and could utilize tenter frames such as those at North Carolina State University in Raleigh or at Precision Fabrics in Greensboro, NC to bi-axially post-heat-stretch ePTFE film to different weights, thicknesses, and mean pore diameters.

Much smaller diameter SB PP webs (8-12 µm) would be produced at Hills, Inc., Melbourne, FL or on the 1.5m wide SB line at Oerlikon Neumag Nonwovens in Neuműnster, Germany

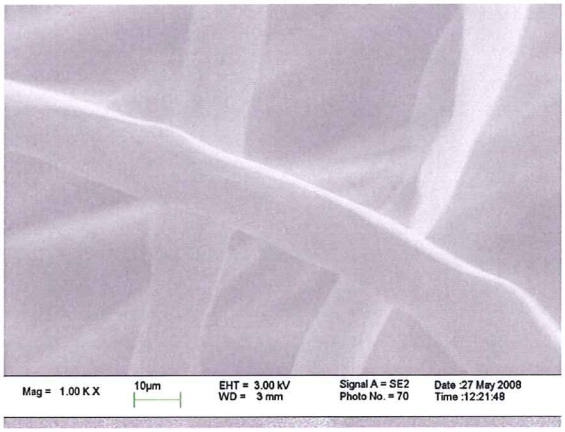


Figure 6. SEM photomicrograph of Donaldson Thermally-Bonded Sample 9

and micro-diameter MB webs will be produced on the 0.5 meter MB line at TANDEC (now called UTRNL). The different SB and MB PP webs will be laminated with single and multiple layers of non-post stretched and post-biaxially-heat-stretched commercial ePTFE films. Half of these laminates will the thermally point-bonded and the other half will be adhesively bonded. For thermal bonding, the new 0.5 meter B.F. Perkins calender at UTNRL with different bonding patterns will be utilized. For adhesive bonding, a company such as Lubrizol, Gastonia, NC, could be employed to produce batch and continuous samples. Care would be taken not to deform the SB PP fibers while compressing the laminates after application of adhesive between smooth rollers. It would also be determined if it is better to electrostatically charge (EC) the SB and or MB PP outer layers separately before lamination or after lamination and bonding. Even if EC of the ePTFE laminates with different weights and fiber diameters of SB and MB and combination SB and MB outer layers does not notably increase, it is believed that using multiple layers of thinner ePTFE films (obtained commercially or by post-stretching by these researchers), which are then adhesive and or thermally bonded with SB, MB or SB/MB PP nonwovens will result in greater WVT than ensembles with one thicker layer of ePTFE of the same weight.

ACKNOWLEDGEMENTS

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Table 1. Weight, Thickness, Mean Pore diameter and WVT of Adhesively and Thermally Bonded Laminates of ePTFE with SB PP Webs.

Sample No.	Description	Weight (g/m^2)	Thickness (mm)	Mean Pore Diameter (µm)		WVT (g/m^2/Day)
				Film Only	Lam	
	ADHESIVE BONDED (AB)					
1	NC[1] AB with core of Taiwan (T2) and outer 20gsm SB PP	73.4	0.280	0.48	1.10	5,711
2	Same as 1 but EC[2]	77.7	0.307			6,365
3	NC AB with core of T2 and outer 50gsm SB PP	120.6	0.478	0.48	2.09	5,448
4	Same as 2 but EC	121.9	0.567			5,998
	THERMALLY BONDED (TB)					
5	NC TB with 50gsm SB PP/Donaldson (D) ePTFE/20 gsm SB PP	88.3	0.145	0.37	1.61	5,403
6	Same as 5 but EC	87.1	0.136			5,010
7	NC TB with 50gsm SB/GEH ePTFE/20gsm SB			0.27	0.30	4,632
8	Same as 7 but EC	92.2	0.136			5,822
9	NC Donaldson AX 05-159 Lam of ePTFE and SB PP	53.5	0.197		3.50	6,236
10	Same as 9 but EC	57.2	0.214			6,025

[1]NC = Not Electrostatically Charged
[2]EC = Laminate Electrostatically Charged