

FLEXIBLE COMPOSITE MEMBRANES FOR SELECTIVE PERMEABILITY

Dawn M. Crawford[†], Gene Napadensky[†], Jim Sloan[†], Donovan Harris[†],
Vivek Kapur[‡], Vaughn Samuelson[‡], Joe Perrotto^{*}

[†] Army Research Laboratory, Bldg. 4600 Deer Creek Loop, APG, MD 21005-5069

[‡] DuPont Central Research & Development, P.O. Box 80304, Wilmington, DE 19880-0304

^{*} DuPont Engineering, P.O. Box 80722, Wilmington, DE 19880-0722

ABSTRACT

This research effort focuses on the development of a novel composite membrane with multidimensional structural features and multifunctional capability. Two independently proven technologies are integrated creating a new membrane that can be engineered for selectively permeable performance to mutually facilitate water vapor transport and provide chemical agent resistance. Marrying the two technologies expands performance capabilities by allowing numerous variations in material selection for DuPont's microporous matrix, core and sheath polymers, and chemical functionalities that will provide a substrate for specialized features such as agent deactivation. ARL's nanostructured membrane is incorporated as the "filler" for the pores and has been investigated as both a post-process to the microporous membrane fabrication and as a fiber core polymer manufactured as a component of the microporous membrane. Our results have demonstrated that at least one formulation of ARL's nanostructured membrane exceeds the military threshold requirement against live chemical agents HD and GD according to Army test specification, and exhibits water vapor transport equivalent to the top commercial candidate alternative to the current JSLIST system.

A series of composite membranes were constructed and evaluated for their potential use as breathable (high water transport) barriers (low chemical agent transport) for military and civilian protective clothing apparel. The vapor transmission rates and effective permeabilities of water and dimethyl methyl phosphonate (DMMP, simulant for chemical agent Sarin) through standard commercially available membranes were compared to experimental polymeric membranes developed at ARL by using a modified ASTM method E-96-95.

1. INTRODUCTION

Chemical/biological protective clothing technology remains a high priority among people responsible for

the safety of US military personnel. Not just from the obvious point of exposure to chemical or biological agents abroad and at home, but also from another, less often considered, but still important safety factor: breathability. Until recently the main goal in the development of chemical/biological protective clothing was to maximize protection. In the past, one of the more commonly used materials for this application was butyl rubber working on principle of total blockage. Butyl rubber is an effective barrier to most harmful agents at certain thicknesses, but it has certain disadvantages. Wearing garments manufactured from this material in combat or in other situations which involves physical activity is not-practical, since the lack of breathability of this material causes heat fatigue and exhaustion [Lee et al, 1996]. A different approach for protection against chemical/biological threats is sorption materials. Protective suits such as MOPP (Military Oriented Protective Posture) suit and JSLIST (Joint Service Lightweight Integrated Suit Technology) work on principle of capturing toxic materials with fillers like activated carbon. JSLIST, is more breathable, but it does not provide as much protection as butyl rubber, it is still heavy and bulky and working in the suit is limited to about 45min/hr. [Siegrist, 2002]

A completely different approach to the problem of chemical/biological protection is the concept of semi-permeable membranes that allow passage of moisture (perspiration), but block harmful molecules and organisms. Such materials will offer protection in the hostile environment without causing significant heat fatigue and exhaustion. A number of semi-permeable membranes are being developed in industry and at ARL.

The scope of this work examines a series of semi-permeable membranes in order to evaluate their potential usefulness as a breathable, yet agent resistant material for military and civilian clothing. This paper addresses methods of composite membrane fabrication and the permeation of water vapor and dimethylmethylphosphonate (DMMP) vapor through a variety of materials to determine the best candidates that are both breathable and

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 01 NOV 2006		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Flexible Composite Membranes For Selective Permeability				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Army Research Laboratory, Bldg. 4600 Deer Creek Loop, APG, MD 21005-5069				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002075., The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

protective. DMMP is chemically similar to the nerve agent Sarin (GB) and is often used to imitate the behavior of chemical agents when the usage of actual agents is cost prohibitive due to safety concerns.

2. EXPERIMENTAL

2.1 Materials

Sulfonated poly(styrene-isobutylene-styrene) (S-SIBS) at 97 mole percent sulfonation, referred to as S-SIBS-97, was sulfonated at ARL, the details of this procedure can be found elsewhere [Elabd and Napadensky, 2004]. Mole percent sulfonation is defined as moles of sulfonic acid per moles of styrene repeat unit and was determined by elemental analysis. The unsulfonated polymer was provided by Kuraray Co., Ltd., Tsukuba research laboratories, with the reported properties: 30.84 wt% styrene, 0.95 specific gravity, $M_w = 71,920$ g/mol, $M_n = 48,850$ g/mol, and polydispersity index (PDI) = 1.47. Microporous membranes of different chemistries were provided by DuPont and were fabricated by a proprietary process.

2.2 Permeation Equipment

Equipment used for vapor permeation experiments consisted of a temperature controlled oven with a nitrogen gas sweep passing through a Drierite® packed column. Aluminum trays with Drierite® were also placed inside the oven to maintain a low relative humidity (approximately 10%). In addition, an analytical balance (precision = ± 0.0001 g) was used to measure weight loss and a digital micrometer was used to measure the thickness of each membrane (precision = ± 1.2 μm).

2.3 Composite Membrane Fabrication

This collaborative research project between the Army Research Laboratory (ARL) and DuPont is focused on an innovative membrane technology geared toward the development of high performance chemical protective suit technology for the soldier. The joint research, funded by the Institute for Soldier Nanotechnologies (ISN), addresses the technical challenges inherent in multifunctional advanced materials technologies for Future Combat Systems (FCS). DuPont has engineered unique microporous films that comprise uniform capillary pores oriented perpendicular to the plane of the matrix membrane. The resultant composite membrane is created by infiltrating ARL's permselective polymers, based on a sulfonated styrene-

isobutylene-styrene (S-SIBS-97) tri-block copolymer recently developed and patented at ARL, into the micro-capillaries of the high barrier (chemical protective) polymer matrix film. A schematic of the technical concept is shown in Figure 1. Once infiltrated, the S-SIBS-97 can be readily functionalized in place. Varying concentrations (10%, 5% and 1%) of S-SIBS-97 solutions in a mixture of toluene/hexanol were investigated for the infiltration process. Additionally, the counter ions Mg^{++} , Ca^{++} and Ba^{++} were used to neutralize the acidic protons and form a crosslinked system with reduced free volume.

Figure 1 shows a schematic of composite membrane (right) and micrographs of the actual microporous membranes (unfilled) (left).

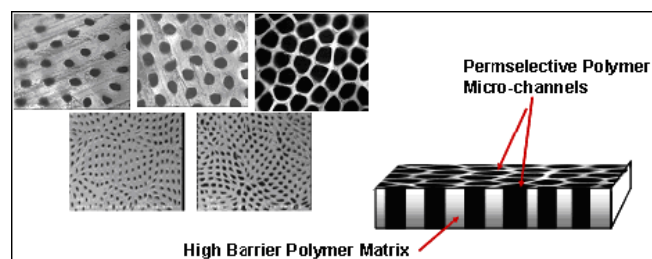


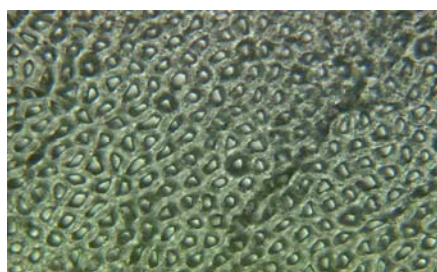
Figure 1 – Schematic of composite membrane (right) and various micrographs of actual microporous membranes (left).

Dupont provided ARL with samples of their microporous membranes. The strategy for fabricating the composite membranes was to use S-SIBS-97 to infiltrate the hollow fiber pores. Several processes were used to accomplish pore infiltration. The first process involved casting various concentrations (5-10%) of S-97-SIBS solutions onto a flat surface and allowing the films to partially dry. The semi-dry membranes were then placed on top of the microporous substrate with moderate levels of pressure to assist transfer of semi-dry but still viscous polymer into hollow fibers of the membrane. A second "solvent" method utilized lower concentrations (1-5%) of S-SIBS-97 solutions enabling the solution to flow into the hollow pores via capillary force. Residual solvent was subsequently evaporated.

Figure 2 shows SEM micrographs of the top view of filled and unfilled microporous membranes. In Figure 3, SEM images demonstrate the ability of the S-SIBS-97 to infiltrate the hollow fibers via the first method. In this case, a semi-solid S-SIBS-97 film is laminated on top of the microporous membrane and

pressure is applied to push the S-SIBS into the pores. The residual solvent was subsequently evaporated. The small nubs in Figure 3 are the S-SIBS lifting out of the hollow core corresponding to the shape and size of the hollow fibers of the substrate. As Figure 3 demonstrates, infiltration can be achieved however, only a small fraction of the pore was infiltrated.

Figure 4 shows the effect of allowing a 2.5% solution of SIBS to infiltrate the micropores by capillary force. The membrane was pretreated by 1 M sulfuric acid to improve compatibility between S-SIBS-97 and the inner core of the fiber. In Figure 4, the hollow fibers can be clearly seen and the small amounts of infiltrated S-SIBS are identified by the double meniscus shaped ends of the S-SIBS polymer that flowed into the hollow tube via capillary action.



Filled pores



Unfilled pores

Figure 2. Micrograph showing filled and unfilled pores (top view).

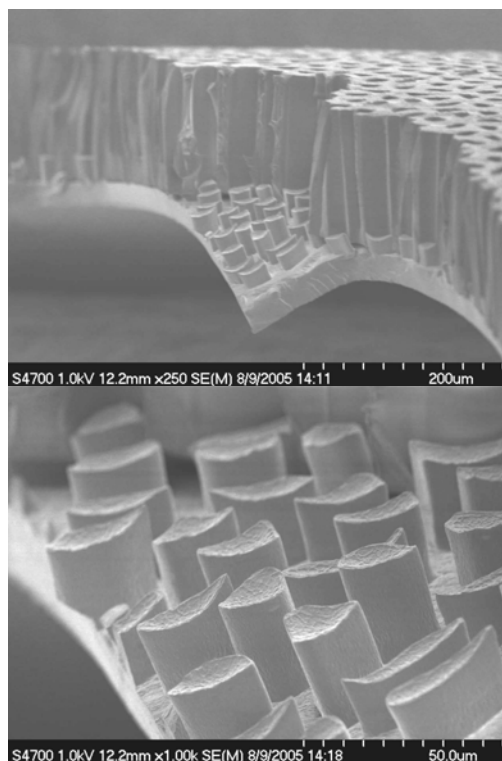


Figure 3: SEM images of S-SIBS-97 infiltrated microporous membrane, side view, cut and fractured. Here a SIBS film is laminated and pushed into the microporous substrate.

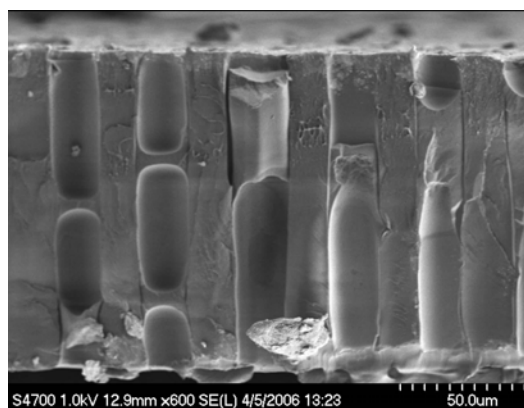


Figure 4: SEM images of S-SIBS-97 infiltrated microporous membrane, side view, cut and fractured. In this case, a 2.5 % solution of SIBS is deposited on the microporous surface and allowed to infiltrate.

Figure 4 clearly demonstrates that only a minimal amount of SIBS infiltrates the hollow pores. This method suffers from residual solvent in the matrix that is not easily evaporated. Thus, this method is not feasible for infiltration. Recent experiments at DuPont

utilizing a pressure method similar to method 1 (Figure 3) shows promise as an optimal infiltration method.

2.4 Vapor Permeation Procedure

2.4.1. Cap Loading

20 ml vials, with open-top caps (VWR) and Teflon® lined septa with a 14 mm hole cut in the center of the septa to match the hole in the cap, were used. Membranes were cut into circles with a 22 mm diameter, the size of the original septa. The thickness of each individual membrane was measured with a digital micrometer. Membranes were placed inside the cap with the cored septa placed behind to provide air tight seal.

2.4.2 Vapor Permeation

Vapor permeation experiments were conducted based on the ASTM E 96-95 (Standard Test Methods for Vapor Transmission of Materials) procedure. An oven, with nitrogen gas purge passed through a desiccant trap, was stabilized at 35°C and 10% relative humidity (RH). Vials were filled with 10-15 ml of liquid (water or DMMP) and placed in oven to equilibrate for about 24 hr. Vials were removed; regular caps were replaced with membrane lined caps. Total assembly weight was recorded and the vials were placed back into the oven to initiate the experiments.

Vial weight, temperature, and humidity inside the oven were recorded every 24 hr until a sufficient amount of data was collected to determine constant rate of weight loss for each vial (steady-state). Relative humidity (RH) remained constant at 10% throughout the duration of the experiment. When using water as a permeant, the conditions were 100% RH on one side of the membrane (inside the vial) and 10% RH on the other side (outside the vial). The concentration gradient provided the driving force for vapor transport. Experiments with DMMP vapor were at 100% DMMP saturation (6.77 mm Hg) on one side of the membrane (inside the vial) and 0% DMMP on the other side or outside the vial.

Three experiments were conducted for each membrane and the values calculated for each membrane are the average and standard deviation of those experiments.

3. Results and Discussion

3.1 Theory

Vapor transfer rate (VTR) is defined as steady state vapor transport rate per unit area and can be expressed as follows:

$$VTR = \frac{G}{(t * A)} \quad (1)$$

where G is weight of penetrant, t is time, and A is cross-sectional area. For this experiment, the cross-sectional area is 0.000154 m², since the diameter is constant at 14mm. G/t can be regressed from the steady state portion of the weight loss data versus time.

After calculating G/t from the data, VTR can be obtained using Equation 1.

VTR provides transport rate for a given penetrant through a membrane. However, VTR does not account for the thickness of the membrane effectively. More specifically, VTR will have different values for the same material at different thicknesses. To accurately compare materials independent of the processing thickness, an effective permeability must be calculated. Effective permeability (P_{eff}) can be expressed as:

$$P_{eff} = \frac{L * VTR}{S * (P_1 - P_2)} \quad (2)$$

where S is the saturation vapor pressure at the test temperature (mmHg), P_1 is the partial pressure or relative humidity on the challenge side, P_2 is partial pressure on the exit side, and L is the sample thickness (m).

3.2 Vapor Transmission Rates

Vapor transport rates (VTR) of the individual materials and composite membranes are shown in Figures 5 and 6 for two penetrants, water and DMMP. The composite membranes exhibited excellent water vapor transport rates (WVTR). As expected, the Dupont microporous membrane without S-SIBS-97 infiltration had the highest WVTR, essentially offering little resistance to water permeation. The infiltrated composite membranes exhibited nearly the same WVTR as the S-SIBS-97, the limiting component of the composite membrane. Ion exchanged S-SIBS-97 (Mg^{++} , Ca^{++} and Ba^{++}) exhibited reduced WVTR; however, they still offer

better WVTR performance than commercially developed chemical protective fabric. The DMMP VTR data revealed that the ARL SIBS and DuPont microporous membranes exhibited high vapor transport rate when the DMMP was used as the challenge permeant. However, when a neutralization reaction was carried out to bind the sulfonic acid groups of S-SIBS-97 (film form/non-infiltrated), a significant decrease in the transport rates of the chemical permeant was observed. The vapor transmission results shown in Figures 5 and 6 do not include composite membrane assemblies made with the ion-neutralized S-SIBS-97, however these results indicate that ion substituted SIBS will be necessary for chemical barrier properties. The next phase of this research will be focused on fabrication of ion neutralized S-SIBS-97 and comprehensive characterization of the composite membranes for both water and DMMP transmission and live chemical agent performance.

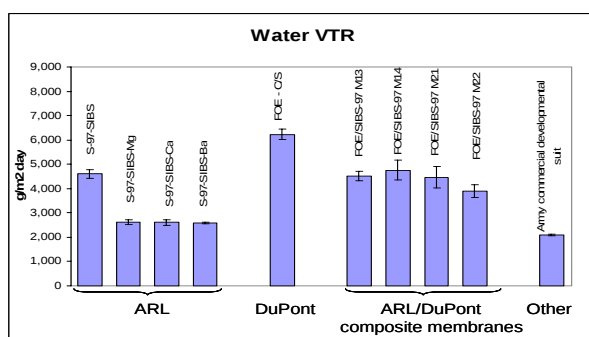


Figure 5. Water vapor transmission rate

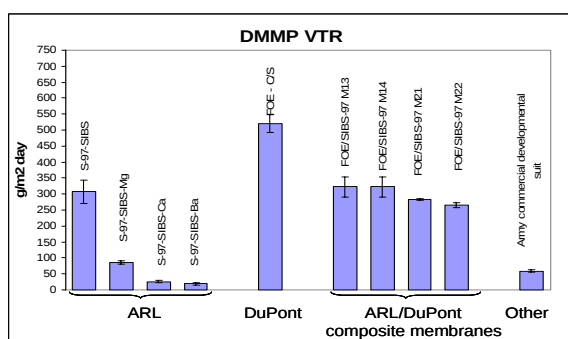


Figure 6. DMMP vapor transmission rate.

3. Conclusion

We have reported successful assembly of infiltrated porous membranes with a functionalized triblock copolymer ionomer to create novel semipermeable

membranes composites. The block copolymer membranes readily transport water, with transport rates increasing as sulfonation level increases. Future work will focus on optimization of the infiltration method and fabrication of larger size composites that will then be fully evaluated for water vapor transmission and live agent testing. Experimental results are promising, demonstrating the potential of the novel tri-block copolymer composite membranes for chemical protective clothing applications.

5. References

ASTM standard E 96-95. "Standard Test Methods for Vapor Transmission of Materials". American Society for Testing & Materials. Philadelphia, PA., 2002

David Siegrist, "Chemical – Biological Warfare: Protective Measures". Jane's Defense Weekly. April 17, 2002

Elabd, Y.A.; Napadensky, E. "Sulfonation and Characterization of Poly (styrene-isobutylene-styrene) Triblock Copolymers at High Ion-Exchange Capacities", Polymer, (submitted for publication, 2003).

Elabd, Y.A., Napadensky, E., Sloan, J.M., Crawford, D.M., Walker, C.W., in "Triblock copolymer ionomers membranes. Part I. Methanol and proton transport." Journal of Membrane Science, 217 (2003) 227-242.

"Handbook of Chemistry and Physics" 66th edition, CRC Press Inc. FL, 1985.

Lee, B. T., T. W. Yang, and E. Wilusz. "Moisture Effects on Isobutylene-Isoprene Copolymer-Based Composite Barrier. 1. Moisture Diffusion and Detection." Polymer Engineering & Science, vol 36, no. 9, p. 1217, 1996.

Weiss, R.A., Sen, A., Willis, C.L., Pottick, L.A. in "Block copolymer ionomers: 1 Synthesis and physical properties of sulphonated poly(styrene ethylene/butylenes styrene), Polymer, 1991, 32, 10.