



**Transport Properties of N-Methylolated Nylon-6:
Chitosan Blend Membranes**

by Eugene Napadensky and Yossef A. Elabd

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14. ABSTRACT A series of N-Methylolated Nylon-6–chitosan blend membranes was evaluated for their potential use as breathable (high water transport) barriers (low chemical agent transport) for military and civilian protective clothing apparel. Nylon-6 was methylolated and subsequently blended with chitosan at different compositions and processing conditions (room temperature, 100 °C, and 200 °C). Vapor transport rates of water (breathability) and dimethyl methylphosphonate (protection) (a simulant of the nerve agent Sarin) were measured as a function of these blend parameters with the use of a modified ASTM (American Society for Testing Materials) method E-96-95 and were compared to Nafion ¹ 117. Water transport rate was found to be between 1,000 and 2,000 g/m ² day, depending on specific composition of the membranes and thermal treatment. The effective dimethylmethylphosphonate permeability (a thickness independent value) of the blend membranes was two orders of magnitude lower than Nafion 117. The selectivity of N-Methylolated Nylon-6–chitosan blend was 15.3, seven times higher than Nafion 117. It was shown that these membranes, manufactured when hydrophilic and hydrophobic polymers were conjoined, have resulted in a material that is both breathable and protective. These semi-permeable membranes will be economically attractive for military and civilian applications in the area of personal protection since the polymer components are inexpensive and the membrane fabrication is simple. ¹ Nafion is a registered trademark of DuPont.					
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1. Introduction

Chemical-biological protective clothing technology remains a high priority among people responsible for the safety of U.S. 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, which worked on the 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 that involve physical activity is not practical since the lack of breathability of this material causes heat fatigue and exhaustion (1). A different approach for protection against chemical-biological threats is sorption materials. Protective suits such as MOPP (mission-oriented protective posture) and JSLIST (Joint Service Lightweight Integrated Suit Technology) work on the principle of capturing toxic materials with fillers such as activated carbon. JSLIST is more breathable, but it does not provide as much protection as butyl rubber and is still heavy and bulky, and working in this suit is limited to about 45 min/hr (2). In addition, the absorbent materials last no longer than 3 to 6 months after initial unpacking of the garment. The time starts the moment when the garment is removed from its hermetically sealed packing for the first time, regardless whether it was actually worn. After that time period, activated carbon loses a significant amount of its sorption ability and no longer provides the required levels of protection.

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

The scope of this work was to examine membranes manufactured when hydrophilic and hydrophobic polymers are conjoined, which results in a material that is both breathable and protective. In this study, the transport properties of polymer blend membranes of chitosan and N-methylol Nylon-6 were examined and evaluated for their use as chemical and biological protective clothing. Shieh and Huang (3) recently investigated N-methylol Nylon-6: chitosan blend membranes as they apply to the separation of ethanol-water mixtures via a pervaporation process. In this work, Nylon-6 was methylolated and subsequently blended with chitosan at different compositions and processing conditions. Vapor transport rates of water (breathability) and dimethyl-methylphosphate (DMMP¹) (protection) were measured as a function of these blend parameters.

¹a simulant of the nerve agent Sarin

2. Experimental

2.1 Materials

Experimental membranes were manufactured from Nylon-6 (Collomer Associates, Inc., molecular weight approximately 150,000) and chitosan (Aldrich, 75% to 85% deacetylation, molecular weight 190,000 to 310,000). Other materials in this study included BDU (battle dress uniform) fabric, (50/50 Nylon/cotton, obtained from the U.S. Army Natick Soldier Center), and Nafion²-117 purchased from Aldrich. In addition, other chemicals used in these experiments were dry nitrogen gas, water (J.T. Baker, HPLC [high performance liquid chromatography] grade), DMMP (Lancaster Synthesis, 97%), Drierite³ (anhydrous calcium sulfate, 97%), 37% formaldehyde solution (J.T. Baker, reagent grade), formic acid (EM⁴ Science, 98% assay), acetone (Warner-Graham Co., reagent grade), and glacial acetic acid (J.T. Baker).

2.2 Methylation Procedure

Nylon-6 was modified through a reaction with formaldehyde in formic acid (see figure 1), described in detail by Cairns et al. (4). Specifically, we dissolved Nylon-6 in 88% formic acid by stirring for 12 hours at room temperature in a covered beaker, which yielded a 6.5% (weight per volume) solution. To this solution, five molar equivalents of 37% formaldehyde were added and allowed to react for 4 hours at 60 °C. According to Shieh and Huang (5), this molar ratio of formaldehyde to Nylon-6 should result in 33% methylation of amide functional groups in the “backbone” of the polymer. The modified polymer was precipitated from solution by the addition of water and was washed repeatedly with alternating water and acetone to remove residual formic acid. The purified polymer was dried in a convection oven at 40 °C.

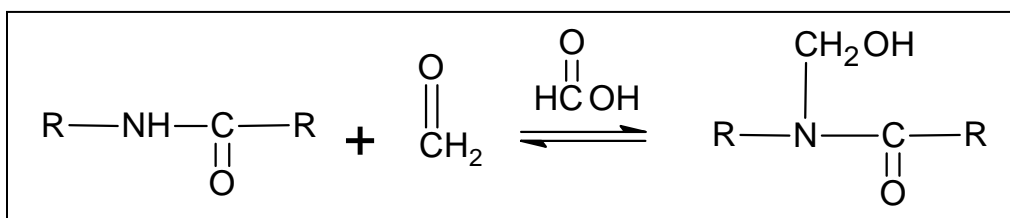


Figure 1. Methylation of Nylon-6 with formaldehyde.

This reaction incorporates methylol groups in Nylon-6, which may improve miscibility with chitosan. More importantly, these added methylol groups provide an avenue for thermal crosslinking. When the material is exposed to heat, methylol groups react with secondary

²Nafion is a registered trademark of DuPont.

³Drierite is a registered trademark of W. A. Hammond Drierite Co.

⁴EM is not an acronym.

amines, expelling water and creating a $-\text{CH}_2-$ crosslink (see figure 2). This reaction could also lead to improved strength in the polymer blend.

By varying the initial methylation content, we can selectively control the crosslink density and subsequently, the physical properties. In addition to reactions with amines in the Nylon-6 backbone, methylol groups should react with chitosan when the polymer blends are exposed to thermal treatment. Since deacetylation of chitosan is listed as 75% to 85%, 15% to 25% of secondary amines remain completely available for participation in this reaction. This new covalent bond between chitosan and Nylon-6 should prevent chitosan dissolution during acidic conditions, allowing for the use of the membranes in a wider range of applications.

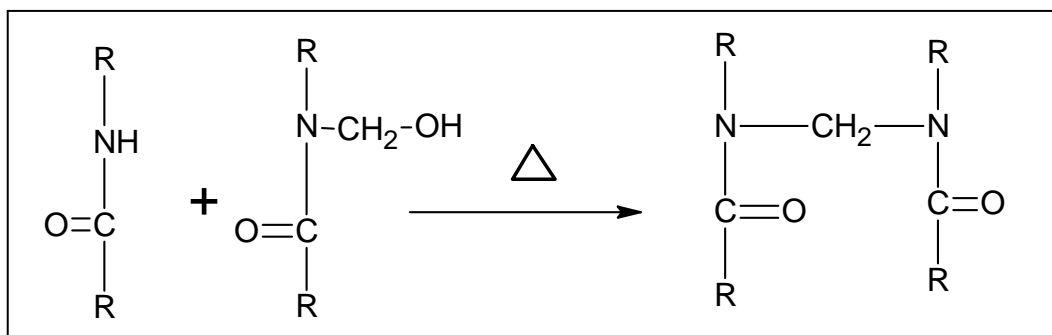


Figure 2. Thermal crosslinking reaction illustrating cross linking of Nylon-6 with methylol group to form a $-\text{CH}_2-$ bridge.

2.3 Membrane Preparation

Before blending, solid debris present in the chitosan solution (1% weight per volume [w/v] chitosan in a 5% acetic acid) was removed by vacuum filtration. After filtration, the solvent was evaporated and the chitosan film was dried in convection oven at 40 °C for 2 days. We prepared membranes of N-methylol Nylon-6: chitosan by dissolving the two polymers together in 88% formic acid and then solution casting onto a Teflon⁵ surface. Methylolated Nylon-6 dissolves quickly; however, chitosan dissolution above 2% w/v was difficult because of gelation. Because of this, different blend compositions were cast at different polymer concentrations (see table 1) to facilitate chitosan dissolution. After the cast films were dried (~24 to 48 hours), portions of each film were retained for evaluation and are referred to as “as cast” (labeled “Nox” in table 1), while other portions were thermally crosslinked by heat pressing at 20,000 lb/in² for approximately 30 to 60 minutes at 100 °C. In addition, selected samples were annealed (thermally crosslinked) at 200 °C and 20,000 lb/in² for 30 minutes to further investigate the effects of thermal treatment.

Table 1 lists the information on each blend investigated. MNC-ab (c) is used for sample names, in which ab refers to the weight ratio of N-methylol Nylon to chitosan and c refers to the thermal

⁵Teflon is a registered trademark of E. I. DuPont de Nemours and Co., Inc.

treatment (Nox represents no thermal treatment, T100 represents heat pressed at 100 °C, and T200 represents heat pressed at 200 °C).

Table 1. N-methylol Nylon-6: chitosan blend membranes: blend compositions and processing conditions.

Blend Membrane	Polymer Concentration (percent; w/v)	Blend Composition N-methylol Nylon-6: chitosan	Temperature and Heat Pressing (20 Klb/in ²) Time
MNC-12 (Nox)	3.3	1:2	NA
MNC-12 (T100)	3.3	1:2	100 °C (1 hr)
MNC-11 (Nox)	3.3	1:1	NA
MNC-11 (T100)	3.3	1:1	100 °C (1 hr)
MNC-21 (Nox)	2.8	2:1	NA
MNC-21 (T100)	2.8	2:1	100 °C (30 min)
MNC-21 (T200)	2.8	2:1	200 °C (30 min)
MNC-41 (Nox)	4.2	4:1	NA
MNC-41 (T100)	4.2	4:1	100 °C (30 min)
MNC-41 (T200)	4.2	4:1	200 °C (30 min)

NA = not applicable

2.4 Sorption Experiments

Sorption of the cast films was evaluated by exposure to water and DMMP (separately). Samples were dried, weighed (dry weight), and submerged in the corresponding liquid. After a specified period of time, samples were removed, excess moisture was dabbed from the surface, the weight of swollen samples was recorded (wet weight), and samples were returned to the solvent. This operation was performed at intervals of 24 hours until no weight change was observed. Even though this procedure is unsophisticated and simple to perform, it generally yields good, reproducible results. Difficulties start to arise when material becomes tacky or slimy and starts to break apart during the dabbing process. Of course, with any analytical method, a certain scatter is associated with the measurements and if the weight change is small overall, it becomes undistinguishable from zero. Sorption is defined here as

$$\text{wt}\% = \frac{(\text{wet polymer wt} - \text{dry polymer wt})}{\text{dry polymer wt}} * 100 \quad (1)$$

A balance with 0.01 mg accuracy was used. Three experiments were conducted on each sample. The weights and errors reported are the averages and standard deviations of these experiments, respectively.

2.5 Vapor Permeation Procedure

Vapor permeation experimental procedure was based on a modified ASTM (American Society for Testing and Materials) E 96-95 (Standard Test Methods for Vapor Transmission of Materials) method and is described in more detail elsewhere (6). Equipment for this experiment consisted of a temperature-controlled (35 °C) oven with a nitrogen gas sweep, which maintained a low relative humidity (10%). Equipment consisted of 20-ml vials with open-top caps and

Teflon-lined septa with a 14-mm hole cut in the center of the septa to match the hole in the cap. Sample membranes were cut into circles with a 22-mm diameter (the size of the original septa) and placed inside the cap with the cored septa placed behind to provide an air-tight seal (see figure 3).

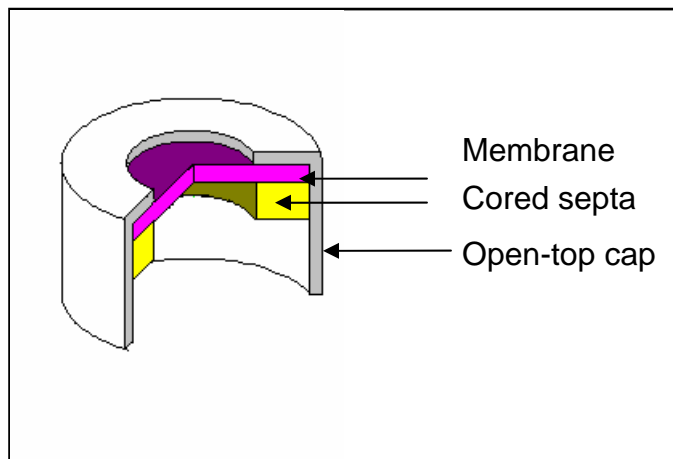


Figure 3. Schematic representing a cutaway of the cap-membrane assembly showing an open-top cap, membrane, and cored septa.

Vials were filled with 10 to 15 ml of liquid (water or DMMP), capped with the previously described caps, and placed in the oven. Liquid inside the vials creates a 100% saturated environment on the internal side of the membrane; this provides a concentration gradient across the membrane. Vial weights were recorded every 24 hours as more vapor penetrated through the membrane, until a sufficient amount of data was collected to determine constant (steady state) rate of weight loss for each vial. From these data, vapor transfer rates for water and DMMP, effective permeability, and selectivity were calculated.

The vapor transport rates (VTRs) of water and DMMP through the membranes were calculated on the basis of weight loss from permeant-containing vials described in the previous section. VTR is defined as steady state transport rate per unit area and can be expressed as follows:

$$\text{VTR} = \frac{G}{(t * A)} \quad (2)$$

in which A is exposed area of the membrane that covered the vial (for this experiment, the diameter of the opening in the cap is constant at 14 mm, and that corresponds to area of 0.000154 m²), and G/t can be regressed from weight loss data, as explained before. However, VTR does not account for the thickness of the membrane effectively; its value is different for the same material of different thicknesses. To accurately compare properties of evaluated materials independently of the thickness, an effective permeability must be calculated. Effective permeability (P_{eff}) can be expressed as

$$P_{\text{eff}} = \frac{L * VTR}{S * (P_1 - P_2)} \quad (3)$$

in which S is the saturation vapor pressure at the test temperature (millimeters mercury [Hg]), 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). Saturation vapor pressure for water at 35 °C is 41.175 mm Hg (7) and for DMMP at 35 °C is 6.77 mm Hg. We determined the DMMP vapor pressure by interpolating from known values at 25 °C and 65 °C (8).

Another important parameter for perm-selective membranes is selectivity (α), which is defined as a ratio of effective permeabilities (equation 3):

$$\alpha = \frac{P_{\text{eff}} (\text{water})}{P_{\text{eff}} (\text{DMMP})} \quad (4)$$

It provides numerical assessment of preferential transport of the desired permeant compared to the undesired permeant. In this case, water vapor transport (desired permeant) is compared to DMMP vapor transport (undesired permeant).

A high value for selectivity indicates high affinity to transport water vapor (thus providing breathability to reduce heat fatigue), while having low affinity to transport of DMMP vapor (providing protection from chemical agents). Thus, a material with high selectivity is desirable for breathable chemical and biological protective garments. High water permeability will help to remove perspiration and thus reduce possibility of heat fatigue, while low DMMP permeability indicates that harmful chemical agents (e.g., nerve agent gas) will have difficulty penetrating the garment and affecting the Soldier.

3. Results and Discussion

3.1 Elemental Analysis

Elemental analysis was performed by Atlantic Microlabs, Inc., on Nylon-6 and methylolated Nylon-6 samples to quantify the level of methylation. The theoretical molar ratio of nitrogen:oxygen:carbon for Nylon-6 is 1:1.6 and the analytical result for Nylon-6 was 1:1.07:6. For 33% methylolated Nylon-6, it was expected to be 1:1.3:6.3, but actual results were 1:1.22:6.08. Based on these data and taking into account that oxygen is present in amounts slightly elevated over the theoretical level, it is estimated that the actual level of methylation is approximately 15%.

3.2 Visual Evaluation of Membranes

Visual observations of blend membranes show some differences that are attributed to individual composition ratios and thermal treatments of the examined membranes. All films possess a yellowish tint, which is not really surprising if we consider the presence of chitosan. Also, it was noted that the yellow color darkens with thermal treatment.

Samples appear to be semi-transparent and show differences in optical clarity. Optical clarity, unlike color, does not seem to be significantly affected by thermal treatment. For example, MNC-41 films do not become more opaque with thermal treatment; only a color change from white to yellow is observed. The transparency of the material ranges from almost completely transparent (MNC-21) to borderline opaque (MNC-41). Figure 4 shows photographs of several of the membranes in this study.



Figure 4. Comparison of optical clarity of selected MNC membranes. (Membranes are weighed down with glass slides.)

These different levels of transparency may be an indication of relative levels of phase separation. Increase in opacity may be a sign of gross (large scale) phase separation. For the case of MNC-41 membranes (80 wt% N-methylol Nylon-6), a close visual examination clearly reveals significant phase separation. A multitude of roughly circular regions ~1 to 3 mm diameter, evenly spaced throughout the film, is easily discerned even without any special optical equipment, as shown in figure 5.

3.3 Sorption Experiments

As shown in table 2, weight uptake in DMMP is, for all intents and purposes, zero. This suggests that blend membranes at all compositions will be good barriers (resistant) to harmful chemical nerve agents. Water sorption increases with increasing chitosan content in the blend. This is not surprising since chitosan is hydrophilic. The only exception is MNC-11 (Nox), and it is not really clear what is the cause of such low values associated with that particular sample. Another observation can be made about the effects of thermal processing. Again, as would be expected, water sorption levels decrease for membranes that were exposed to higher temperatures. This indicates that higher temperatures result in a higher crosslinking density.

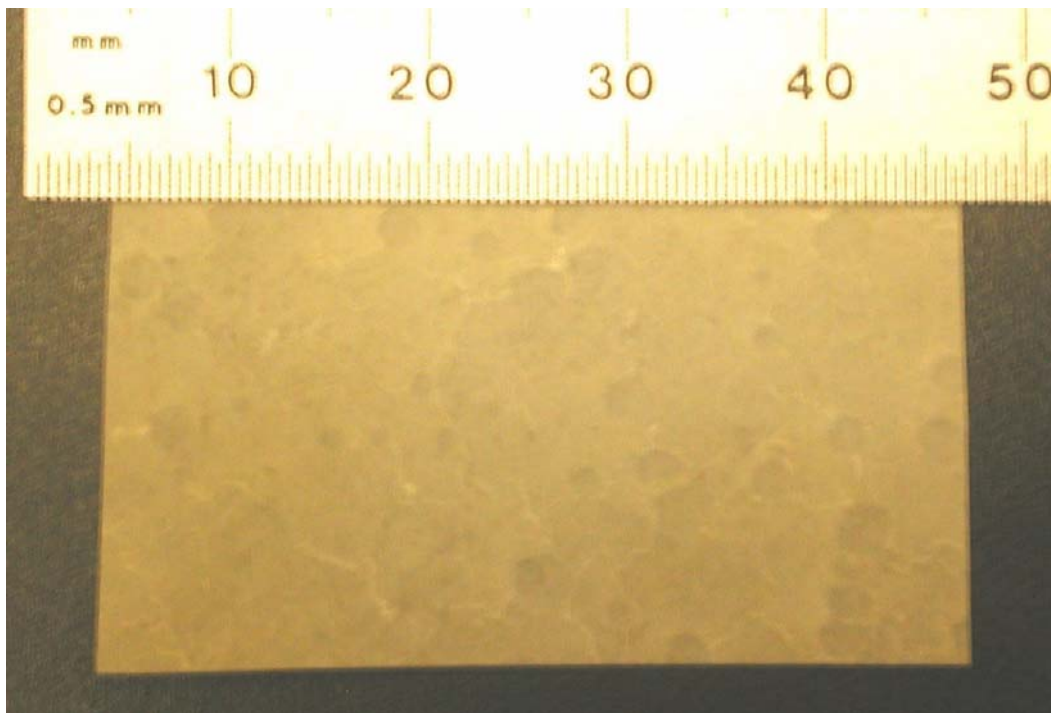


Figure 5. MNC-41-(T200) showing phase segregation regions.

Table 2. Water and DMMP sorption of blended membranes.

Blend Membrane	Blend Composition N-methylol Nylon-6: Chitosan	Sorption (wt%)	
		Water	DMMP
MNC-12 (Nox)	1:2	134 ±4	-8 ±1
MNC-12 (T100)	1:2	90 ±9	3 ±3
MNC-11 (Nox)	1:1	68 ±2	-4 ±1
MNC-11 (T100)	1:1	99 ±13	3 ±17
MNC-21 (Nox)	2:1	112 ±10	10 ±10
MNC-21 (T100)	2:1	89 ±13	0 ±2
MNC-21 (T200)	2:1	36 ±9	-2 ±1
MNC-41 (Nox)	4:1	77 ±8	12 ±6
MNC-41 (T100)	4:1	66 ±5	1 ±1
MNC-41 (T200)	4:1	28 ±10	2 ±1

In addition to measuring water and DMMP uptake, we checked selected samples of N-methylolated Nylon-6 for solubility in 88% formic acid. The rationale for this experiment was to verify cross-linking. Although this material dissolves in formic acid initially, after going through thermal processing, it becomes insoluble. This confirms the ability to modify Nylon-6 to create a cross-linked network.

3.4 Vapor Permeation and Selectivity

Figures 6 and 7 and show VTR results for water and DMMP, respectively, of the chitosan-methylolated Nylon-6 blend membranes. Table 3 shows numerical values for the data in

figures 6 and 7. Data for Nafion 117 were collected and included as a standard frame of reference.

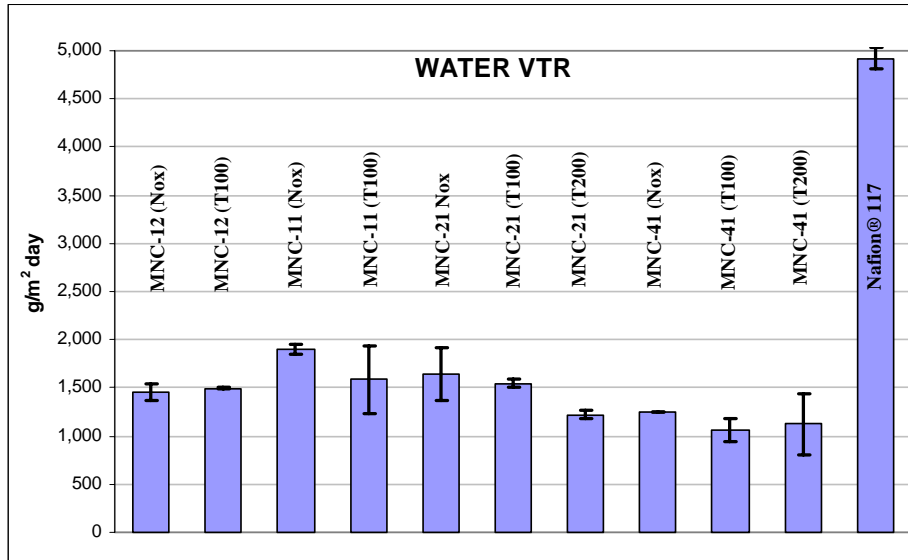


Figure 6. Water vapor transmission rate.

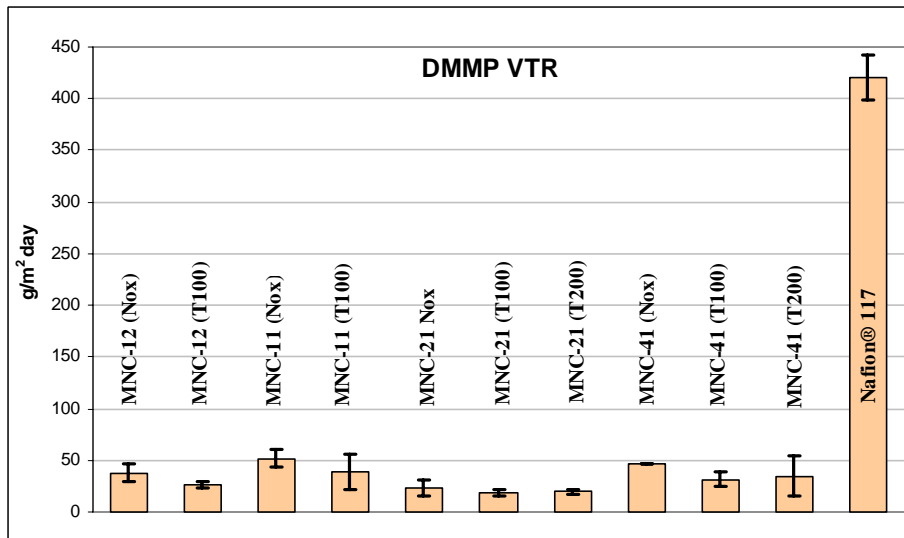


Figure 7. DMMP vapor transmission rate.

As mentioned before, VTR corresponds to amount of permeant diffusing through a given membrane during given conditions. A value above 1000 g/m²•day is generally considered “breathable” and should provide comfort. Water VTR for a standard BDU fabric was measured at approximately 5,600 g/m²•day (9). Since this is an open, air-permeable structure and most likely will be integrated into final garment produced for actual use, it is an upper limit of what can be achieved. MNC membranes show water VTR values between 1000 and 2000 g/m²•day and can be classified as a breathable material. The more impressive results were found when we

examined VTR data for DMMP (a simulant for Sarin nerve agent). The values are truly spectacular: 20 to 50 g/m²•day at steady state, an order of magnitude lower than Nafion 117. The effective DMMP permeability (a thickness-independent value) is two orders of magnitude lower than Nafion 117. When a delay for the initial break-through time is incorporated, these values are certainly within reach of U.S. Army target requirements for nerve agent permeation levels of less than 13 g/m²•day.

Table 3. Vapor permeability and selectivity results.

Blend Membrane	Water VTR (g/m ² •day)	P effective (water) (g/mm Hg•m•day) Average	DMMP VTR (g/m ² •day)	P effective (DMMP) (g/mm Hg•m•day) Average	Selectivity
MNC-12 (Nox)	1,457	2.26E-03	38	3.21E-04	7
MNC-12 (T100)	1,494	1.86E-03	27	1.82E-04	10.2
MNC-11 (Nox)	1,903	1.71E-03	52	2.61E-04	6.6
MNC-11 (T100)	1,589	1.58E-03	39	2.10E-04	7.5
MNC-21 (Nox)	1,642	1.52E-03	23	1.14E-04	13.3
MNC-21 (T100)	1,543	1.92E-03	19	1.26E-04	15.3
MNC-21 (T200)	1,221	1.67E-03	20	1.48E-04	11.3
MNC-41 (Nox)	1,247	2.90E-03	46	6.03E-04	4.8
MNC-41 (T100)	1,068	2.13E-03	31	3.45E-04	6.2
MNC-41 (T200)	1,122	2.03E-03	35	3.03E-04	6.7
Nafion 117	4,921	2.45E-02	421	1.13E-02	2.2

The selectivity for MNC materials, shown in figure 8, is an order of magnitude higher than Nafion 117. It indicates a substantial preferential transport of water vapor to DMMP and serves as a great indicator for potentially a new membrane for chemical and biological protective clothing.

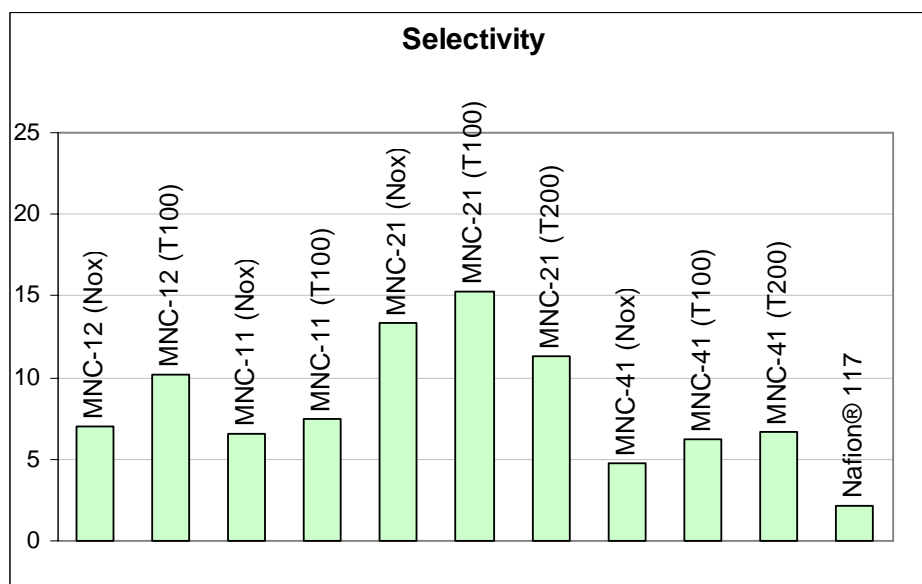


Figure 8. Selectivity of materials.

3.5 Effect of Composition and Thermal Treatment

Figure 9 demonstrates the effect of membrane composition on transport rates of water and DMMP vapor. As can be observed from this plot, the most promising composition is MNC-21. It provides balanced values for both Army requirements: high water permeation and low DMMP permeation. This observation is also confirmed by high values from selectivity measurements. MNC-21 films have a selectivity of ~11 to 15, depending on the thermal treatment. That is five to seven times higher (more selective) than Nafion 117.

The effect of thermal treatment of N-Methylolated Nylon-6–chitosan blends on the permeation of water and DMMP vapor can be observed in figure 10. It is clear that for most of the samples, water VTR across the membrane decreases by ~10% to 20% after thermal processing at 100 °C. The additional effect from processing membranes at 200 °C is less clear. The water VTR for MNC-21 membrane decreases significantly, while the transport rate for MNC-41 membrane remains relatively constant.

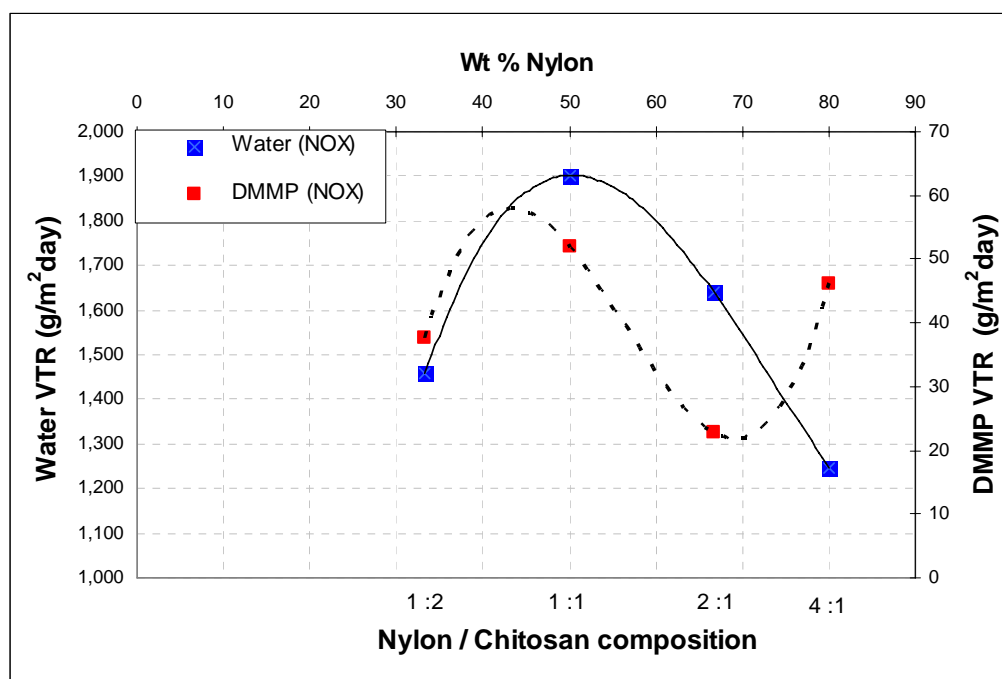


Figure 9. Water and DMMP transport rates as a function of blend composition.

A similar trend is observed for DMMP vapor transport. Although thermal treatment at 100 °C shows improvements in resistance against DMMP vapor transport, annealing at 200 °C does not produce any significant additional improvement. In general, the temperature treatment of the membranes at 100 °C seems to provide a better ensemble of properties for chemical protection. It is also interesting to note that for some compositions, the thermal treatment effect is significantly larger than for the others.

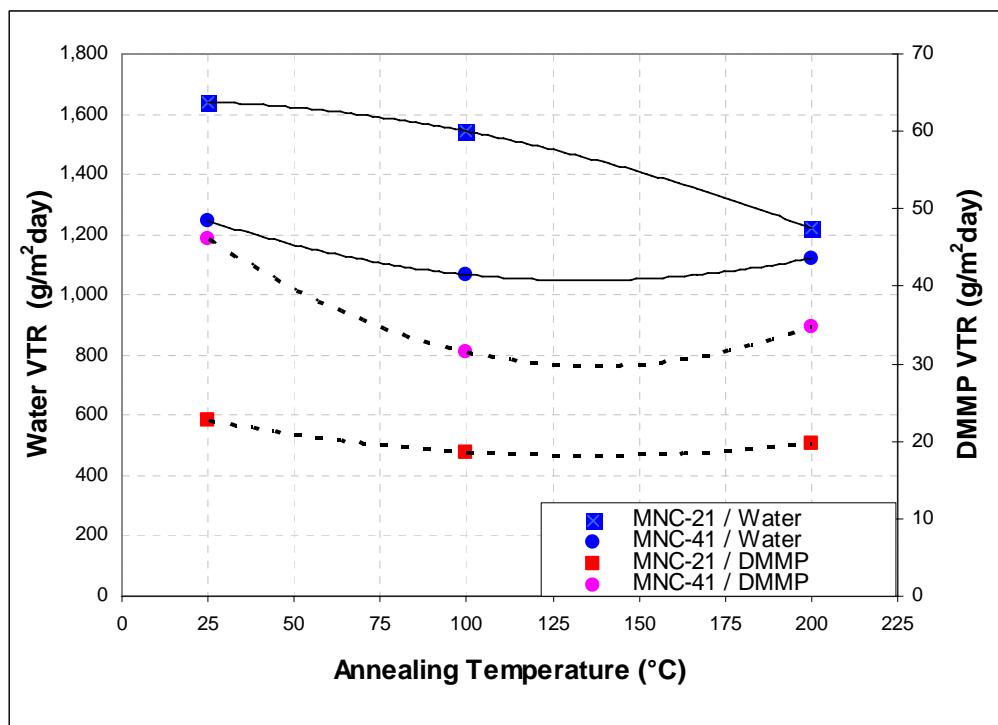


Figure 10. Effects of thermal treatment on transport of water and DMMP vapor.

4. Conclusion

In this study, the water vapor transmission rate, effective permeability, and selectivity of water vapor and DMMP vapor were measured for blends of N-methylol Nylon-6 and chitosan. It was found that these membranes have unusually high selectivity, especially in the case of the membrane with the blend composition of a 2:1 weight ratio of N-methylol Nylon-6: chitosan annealed at 100 °C. For that particular membrane, selectivity was measured to be 15.3, seven times higher than Nafion 117. It was also determined that methylolated Nylon-6: chitosan blends can be thermally crosslinked, but it does result in a slight decrease in both water and DMMP transport rates. Water transport rates were found to be between 1,000 and 2,000 g/m²·day, depending on specific composition of the membrane and thermal treatment. This value is promising, especially when such a high level of selectivity is taken into account. Low permeation of DMMP is critical for Army application. Overall, these blends are good candidates for breathable chemical and biological protective garments for Army and civilian applications. In addition, these membranes are economically attractive for personal protection since the polymer components are inexpensive and the membrane fabrication is simple.

5. References

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