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Permeation Tests on Polypropylene Fiber Materials

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14. ABSTRACT

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) evaluated polypropylene nanofiber materials for their potential in air filtration to remove toxic vapors. This work was completed in parallel with the development of novel organosilicate sorbent materials directed at these applications. The fiber materials were evaluated independently as well as in combination with novel NRL developed sorbent materials.

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The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) evaluated polypropylene nanofiber materials provided by Apollo NanoTech Inc for their potential in air filtration to remove toxic vapors. This work was completed in parallel with the development of novel organosilicate sorbent materials directed at these applications (NRL 69-1H46; U.S. Patents 9,689,111 and 7,754,145). The fiber materials were evaluated independently as well as in combination with NRL developed materials. The polymer materials were considered as a low cost, scalable material suitable to modification for application in air filtration applications.

PERMEATION TESTS ON POLYPROPYLENE FIBER MATERIALS

INTRODUCTION

The Toxic Industrial Chemical/Toxic Industrial Material (TIC/TIM) Task Force MFR#1 published in February 2009 focuses on inhalation hazards in an operational environment and provides a list of compounds prioritized based on toxic hazard and the likelihood of an encounter. [1] With these types of vapor threats, cartridge-based air purifying respirators are used to protect the warfighter against chemical exposure. Traditional air purification materials often rely on porous carbons such as activated carbon or activated charcoal. [2] Through modification of these types of carbon materials, functional moieties can be combined with high surface area and adsorptive properties to provide air purification materials with improved characteristics or novel function. [3, 4] Ongoing efforts seek to improve the performance of carbon materials in air purification applications as well as to provide alternatives to these materials. [5, 6, 7, 8, 9] Improvements such as active residual life indication and regenerable or catalytic cartridge materials are of ongoing interest.

We have previously reported on our efforts directed at combining the materials characteristics provided by organosilicate scaffolds with the optical and catalytic properties of porphyrins. [10-14] For larger targets in aqueous solutions, the scaffold provided high binding capacity and selectivity for the targets. [11, 12, 14] For light gases, we used the scaffold as purely that and incorporated binding sites through grafting onto the scaffold surface. [13, 15, 16] In air filtration applications, the porphyrins provide binding capacity and affinity, and the spectrophotometric characteristics offer the potential for residual life indication. In addition, the catalytic activity of the porphyrins may provide avenues for extending the functional lifetime of a sorbent bed.

For the study described here, polypropylene nanofiber materials provided by Apollo NanoTech Inc are evaluated for their potential utility in removal of vapor phase targets (Figure 1). These materials have previously been considered for application to capture of glycerol from biodiesel preparations. [17] Here, performance of the sheet type materials is evaluated with and without modification using the NRL-developed microwave deposition of technique for application of porphyrin incorporating sorbents. Variants of the nanofiber fiber materials were also generated through Apollo NanoTech's incorporation methods to evaluate the potential of those modified materials as well as the incorporation approach in air filtration applications.

Fig. 1 — Images of as received nanofiber materials: hydrophilic (A), hydrophobic (B), and sheet type (C) variations.

METHODS

A Thermolyne incubator (Compact Series 5000) was modified to conduct water vapor transport studies based on guidance provided by the ASTM E 96 protocol. [18] Water vapor transport through a material is determined by measuring the rate of water loss through the material over a period of time. For our implementation, a scintillation vial (20 mL) was filled with 16.9 mL deionized water ($\pm$ 0.1 mL) over which the sample material was sealed with parafilm (water 1.27 cm from sample surface). The sample was weighed and placed in the incubator. Drierite was used to lower the humidity in the incubator and a dry nitrogen stream was flowed across the surface of the sample (250 sccm). Weight measurements were collected at 30 to 45 min intervals using an analytical balance. The temperature of the incubator was 25 °C ($\pm$1°C). This instrument was used to evaluate permeation of water through the various functionalized fabrics. Permeation of water through coated and functionalized fabric samples was found to be similar to that of permeation through the unmodified fabrics.

The apparatus for evaluation of target vapor permeation through fabric samples was based on the stations employed by the Chemical Technology Team (CTT) at Natick Soldier Research Development and Engineering Center (NSRDEC). The temperature in the custom environmental chamber is controlled using a probe inside the chamber which adjusts an Air-Therm ATX heater (World Precision Instruments). Mass flow controllers, regulated by an inline Vaisala humidity probe, govern the ratio of humid to dry air entering the chamber. An Aerosol Vapor Liquid Assessment Group (AVLAG) test cell is used for these evaluations. These cells are stainless steel and hold the sample horizontally with O-ring seals (refer to TOP 8-2-501). The AVLAG cell is set up for single flow diffusive penetration testing using a single air or nitrogen stream. The "headspace" above the swatch is stagnant, and the differential pressure above and below the swatch is zero. A sample (2.54 $\times$ 2.54 cm) is sandwiched between two supports with 0.64 cm^2 circular openings. The sample assembly is placed in the AVLAG cell and equilibrated to the desired humidity for 2 h. Target is introduced by placing liquid drops on top of glass wool using a repeating dispenser. Glass wool is used to help increase the volatility of the simulant. Challenge is applied to the surface of the sample in the static region of the AVLAG cell; therefore, evaporation is not a significant consideration. A direct line from the permeation cell to a dedicated FID (SRI model 110) allows for continuous monitoring of target concentrations. The FID uses Peak Simple, six-channel data acquisition software (SRI) for signal capture and peak integration. Excess flow from the direct line (above 50 mL/min) is filtered through a carbon scrubber.

Microwave modification of fabrics has been described previously [10]; this procedure was used for modification of the polypropylene sheets with minor modifications to the temperatures used during curing. The initiation solution is prepared by mixing 5 mL ammonium hydroxide (28 – 30%) with 92 mL of isopropanol. To this solution, 3 mL tetraethyl orthosilicate (TEOS) is added to the ammonium hydroxide solution. [19] The fabric substrate is fully submerged in the TEOS mixture and removed to a glass, microwave safe dish. The sample is microwaved using 1,200 W for 30 s. This process was repeated for a total of three cycles. Treated fabric was dried at 100 °C for 30 min. To prepare the sol, 1.9 g Pluronic P123, 0.5 g mesitylene, and 2.12 g 1,2-bis(trimethyoxysilyl)ethane (BTE) were mixed with 16 g ethanol at room temperature with a magnetic stir bar in a sealed container. [13, 15, 20, 21, 22, 23] At this point, 6.07 g 0.1 M HNO$_3$ was added dropwise, and stirring continued for 6 h. The TEOS treated fabric was dipped into the prepared sol at a rate of 270 mm/min. The sample was hanged to dry in a 60°C oven for 24 h followed by drying in a vacuum oven at 60°C for an additional 24 h. The fabric sample was then immersed in ethanol at 60°C for 48 h to extract surfactant. The sample was rinsed with additional ethanol and dried overnight at 60 – 65°C. To functionalize the sorbent material with primary amine groups, the fabric was submerged in a solution of 3-aminopropyltriethoxy silane (APS) in toluene at 0.5% volume/volume [15, 20] for 1 h. Samples were then rinsed thoroughly with toluene and dried at 100°C. The porphyrin was added to this sample by submerging in a solution of 0.6 mg/mL porphyrin in 0.1 M 2-(N-morpholino)ethansulfonic acid (MES) buffer pH 5.5 with 5 mg 1-ethyl-3-(3-

dimethylaminopropyl)carbodiimide (EDC). Samples were incubated overnight before rinsing thoroughly with water and drying at 100°C overnight.

Samples were evaluated using the permeation system with 2-chloroethyl ethyl sulfide (half mustard; CEES), dimethyl methylphosphonate (DMMP), and methyl salicylate (MES) as the targets. Evaluations used 1 μL of the targets. The total exposed area in the AVLAG system is 0.64 cm^2 providing surface exposure concentrations of 16.7 g/m^2 for CEES; 18.0 g/m^2 for DMMP; and 18.3 g/m^2 for MES. Polypropylene sheet type materials were evaluated in the as received density and thickness. The MultiCam NyCo fabric was of the type used in the standard combat uniform and was used as a single thickness of the fabric. For the fiber type polypropylene materials, 200 mg of the material was packed between two layers of glass fiber cloth to produce a filter (Figure 2). This filter was supported between the metal plates of the AVLAG system.

Fig. 2 — Images of 200 mg air filters prepared using the nanofiber materials between layers of glass fiber cloth. Air filters are approximately 1.8 cm in diameter and 0.4 cm thick.

RESULTS

Initially, this effort sought to determine if the polypropylene sheet type material manufactured by Apollo NanoTech (ANT) could be used as a support for the NRL-developed reactive and catalytic sorbents. On further discussion with ANT, the availability of an additional incorporation method developed by ANT was clarified. Here, we explore impact of incorporation of NRL sorbents into the ANT sheet materials using the microwave process intended for deposition of the sorbents on fabric supports. We also explore the potential application to air filtration of fiber type polypropylene materials modified using metals, mica, and organic moieties through the ANT developed incorporation process.

Modified Polypropylene Sheets.

Polypropylene (PP) sheets were modified using an ethane bridged silica sorbent material, previously published as E50 [21] The materials were then modified using meso tetra(4-carboxyphenyl) porphyrin (C$_4$TPP). Results for analysis of these materials using an Aerosol Vapor Liquid Assessment Group (AVLAG) test cell are provided in Figure 3. The method uses continuous flow with flame ionization detection (FID) under controlled temperature (40°C) and relative humidity (50%) for total exposed area of 0.64 cm^2. Figure 3 provides time-dependent FID responses for CEES, MES, and DMMP on treated and untreated PP sheets as well as on a representative fabric.

Under 2-chloroethyl ethyl sulfide (CEES) challenge (Figure 3 and Table 1), when the MultiCam fabric alone was evaluated, a peak rate of 34.5 g/h/m^2 was noted with no retention of the target (1070 µg total). By comparison, the untreated PP sheet yielded a peak rate of 39.8 g/h/m^2 with little target retention (1060 µg total). Initial target breakthrough for all materials against CEES occurred within the first minute of evaluation. The threshold for initial target breakthrough used here is based on the 1 h marginal exposure level in air (military exposure guideline, MEG). A hazard level qualified as "marginal" is defined as causing degraded mission capability or unit readiness on the basis of the proportion of the unit likely to exhibit effects, the nature of those effects, and confidence in the available data. The 1 h marginal air exposure limit for CEES is 0.1 mg/m^3. [24] Application of the porous treatment (E50) to the PP sheet resulted in reduction to the peak CEES rate of transport (17.3 g/h/m^2) with a slight reduction in the total transport of target through the fabric (1050 µg total). The sorbent utilized here has previously been shown to provide reduced CEES transport and removal of phosgene. [15, 25] The modest impact on target transport noted here was likely due to damage of the PP sheet during processing, resulting in less density in the fiber sheet. Initial deposition of sorbent utilizing the protocol designed for nylon/cotton blend fabrics resulted in a complete loss in integrity in the sheet (Figure 4). When curing and processing temperatures were reduced to a maximum of 60°C, the sheet remained intact but was more brittle than the as synthesized material. Addition of the porphyrin to the sorbent functionalized material resulted in transport behavior that was more like that of the PP sheet only. This may be a result of the hydrophilic nature of the porphyrin utilized here (C$_4$TPP) or further damage resulting from the additional processing steps during grafting of the C$_4$TPP.
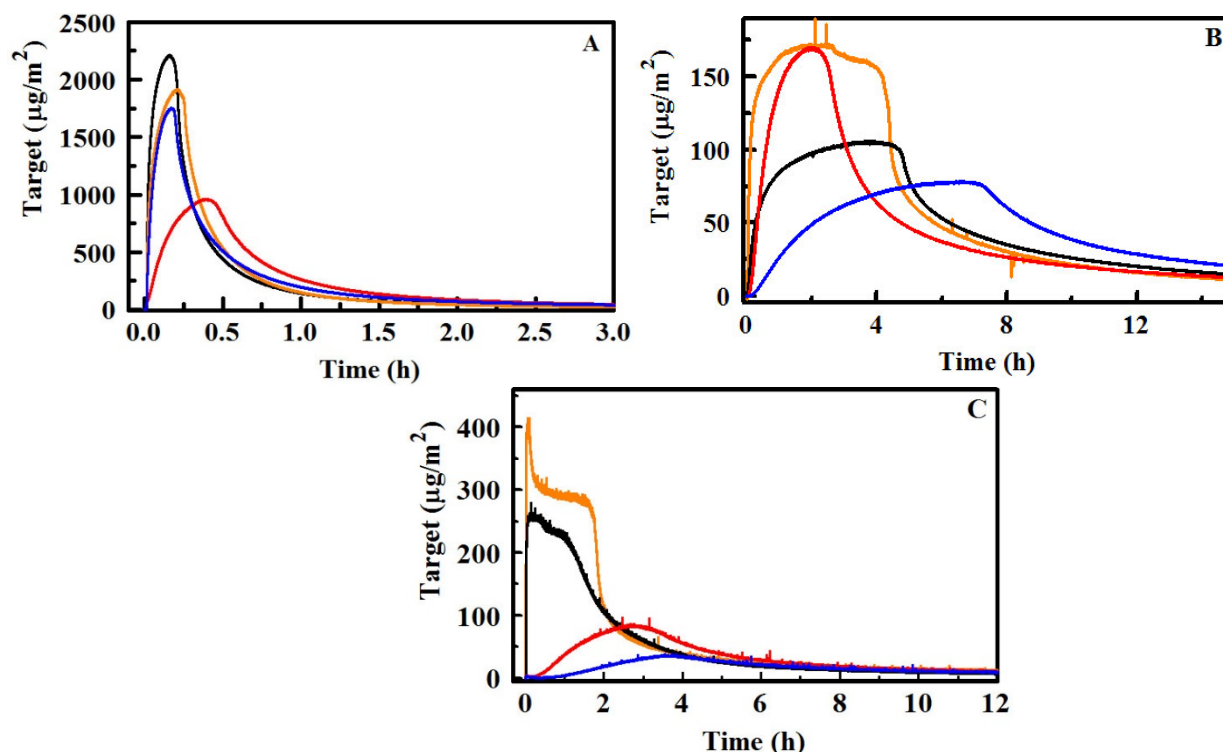

Fig. 3 — AVLAG results for analysis of polypropylene sheet materials under CEES (A), MES (B), and DMMP (C) challenge: polypropylene sheet (black), E50 on polypropylene sheet (red), C$_4$TPP on E50 polypropylene sheet (blue), MultiCam fabric (orange).

Under methyl salicylate (MES) challenge, initial breakthrough the MultiCam fabric was observed at 1.1 min. The initial period was also 1.1 min when the PP sheet alone was evaluated. The PP sheet, however, provided a reduction in the peak transport rate by 49% and the total measured target over the 1,000 min period by 23%. Functionalization of the PP sheet with the sorbent led to further extension of the time before

breakthrough to 4.5 min and reduction of total permeated target from 906 μg to 889 μg. The peak rate, however, increased from 1.9 to 3.1 $g/m^2/h$. Addition of porphyrin to the sorbent functionalized PP sheet, extended the initial breakthrough to 10.3 min with a peak rate of transport of 1.4 $g/m^2/h$ and total permeated target of 846 μg.

The 1 h marginal air exposure limit for DMMP is 500 mg/m^3; [24] none of the materials evaluated permitted target breakthrough at this rate. In order to provide a point of comparison, 5.0 mg/m^3 was used as the threshold value for DMMP. The peak DMMP rate through the MultiCam fabric was 7.5 $g/m^2/h$ with initial breakthrough at <1 min and 1020 μg recovered over the 1,000 min experiment duration. The PP sheet reduced the total target recovered to 768 μg with a peak rate of transport at 5.0 $g/m^2/h$ and initial breakthrough at 4.9 min. Addition of the sorbent to the PP sheet resulted in a significant increase in the pre-breakthrough period (>1 h) and a significant decrease in the peak rate (1.7 $g/m^2/h$) with total recovered target of 577 μg. Functionalization of the sorbent modified PP sheet using C_4TPP resulted in a further reduction in the peak transport rate to 0.7 $g/m^2/h$ and a reduction in total target recovered to 276 μg. This combination also resulted in no breakthrough rates above the threshold value of 5.0 mg/m^3.

Table 1 – AVLAG Results for Polypropylene Sheets

| Material	Initial Breakthrough (min)	Peak Rate ($g/m^2/h$)	Total (μg) over 1,000 min
2-Chloroethyl ethyl sulfide (CEES)			
PP Sheet	0.79	39.8	1060
E50 on PP Sheet	0.67	17.3	1050
C4-E50 on PP Sheet	0.64	31.5	1070
MultiCam Fabric	0.64	34.5	1070
Methyl salicylate (MES)			
PP Sheet	1.14	1.9	906
E50 on PP Sheet	4.48	3.1	889
C4-E50 on PP Sheet	10.3	1.4	846
MultiCam Fabric	1.14	3.7	1170
Dimethyl methylphosphonate (DMMP)			
PP Sheet	4.85	5.0	768
E50 on PP Sheet	61.9	1.7	510
C4-E50 on PP Sheet	--	0.7	276
MultiCam Fabric	0.62	7.5	1020
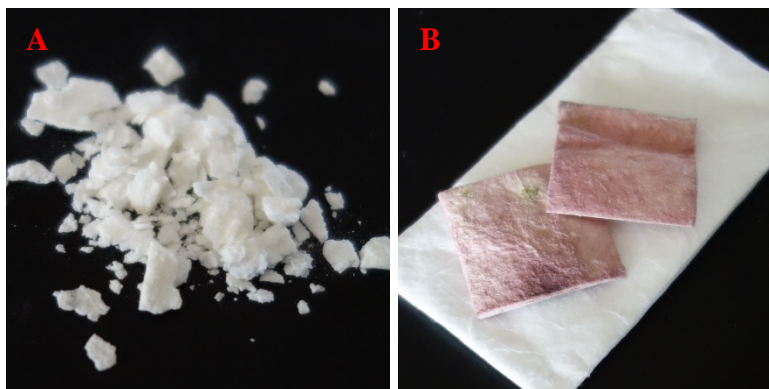
Fig. 4 — Image of polypropylene sheet following treatment using the unmodified protocol (A) and the modified polypropylene sheet utilized in these evaluations (B) shown with incorporated porphyrin and on untreated PP sheet.

Beyond evaluation of target transport across the materials, the transport of water vapor was evaluated. This type of evaluation provides information relevant to comfort in application of the polypropylene materials. If used as a barrier in clothing, for example, water vapor transport is a component of the thermal burden for the garment. In air filtration media, this evaluation can provide information on air quality following filtration. As shown in Figure 5, water vapor transport through the PP sheet was 10% lower than that through a glass fiber fabric; it was only 4% lower than that through an unbleached cotton fabric (Table 2). Modification of the PP sheet using the porphyrin-sorbent material resulted in a significant increase in water vapor transport. This is likely a result of the combination of the more hydrophilic surface and the damage done to the supporting polymer structure.

Table 2 – Water Vapor Transport

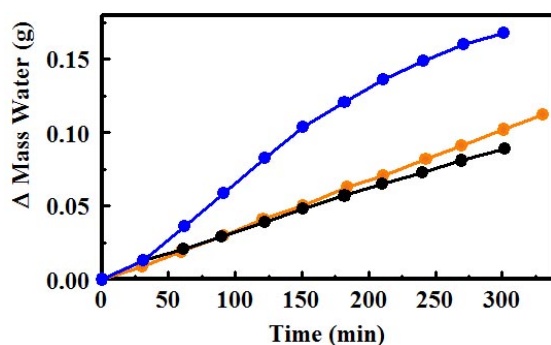| Material	Rate $(g/h/m^2)$
Glass Fiber Fabric	123
Cotton Fabric	116
Sheet Type Materials	
PP Sheet	111
C4-E50 on PP Sheet	222
Fiber Type Materials	
Hydrophobic	103
Hydrophilic	104
Mica modified PP	107
Ag/Cu modified PP	112
Crown Ether modified PP	103

Fig. 5 — Water vapor transport through the polypropylene sheet materials: PP sheet (black), C_4TPP on E50 polypropylene sheet (blue), MultiCam fabric (orange).

Polypropylene Fiber Materials.

Polypropylene fiber materials were prepared for evaluation by packing 200 mg of the appropriate material into a miniature version of an air filter with diameter 1.8 cm (Figure 2). The thickness of the resulting filter was approximately 0.4 cm with some variation resulting from the packing behavior of the different materials. For comparison, the as synthesized PP sheet was 0.15 cm thick (Figure 4). Figure 5 provides a comparison of performance for the hydrophobic and hydrophilic PP material variants to that of two layers of the glass fiber fabric under CEES, MES, and DMMP challenge in the AVLAG test cell. As in the case of the PP sheets, CEES breakthrough for all materials occurred within the first minute following exposure (Table 3). The peak rate of CEES permeation through the glass fiber cloth was 47 $g/h/m^2$ with 831 μg total target recovered over the 1,000 min experiment. The hydrophobic PP material reduced the peak rate of permeation to 6.5 $g/h/m^2$ and the total target recovered to 368 μg. By comparison, the

hydrophilic PP material reduced the peak rate to 4.5 g/h/m^2 with 209 μg recovered during the experiment. CEES is known to undergo hydrolysis on contact with water. [26] The difference in behaviors noted between the hydrophobic and hydrophilic materials maybe a result of water retained on the hydrophilic PP fiber. Modified materials were prepared using the method developed by Apollo NanoTech, providing fiber type materials incorporating mica, a combination of silver and copper, or a crown ether (12-Crown-4). These modifications had little impact on initial breakthrough or peak permeation rate for CEES (Figure 7). The mica modification did lead to less total target recovered than that observed for the hydrophobic base material.

Under methyl salicylate (MES) challenge, initial breakthrough the glass fiber fabric was observed at 1.1 min (Table 3, Figure 6). The initial period for both the hydrophobic and hydrophilic PP materials was ~30 min. The hydrophobic and hydrophilic PP materials also reduced the peak permeation rate from 8.7 g/h/m^2 to 0.5 and 0.4 g/h/m^2, respectively. The total target recovered was also reduced by more than 60% when either of these materials was used. Modification of the PP material using mica resulted in a reduction of the pre-breakthrough period to 13 min and a slight increase in peak rate (0.5 g/h/m^2) and total target recovered (310 μg; Table 3). The Ag/Cu modified PP material had performance metrics similar to that of the base material (Figure 7). Modification of the PP material using the crown ether extended the pre-breakthrough period to 78 min with little additional impact on the peak rate or the total target recovered.

As in the analysis of the PP sheets above, the breakthrough threshold for DMMP was set to 5.0 mg/m^3. Using this threshold, initial breakthrough the glass fiber material as well as the hydrophilic material occurred within the first minute following exposure. The initial breakthrough the hydrophobic PP filter occurred at 4 min. The glass fiber cloth was observed to have a peak rate of permeation at 7.7 g/h/m^2 with all of the target recovered over the 1,000 min experiment (1150 μg). The peak rate was reduced to 1.4 g/h/m^2 by the hydrophobic PP material and 2.8 g/h/m^2 by the hydrophilic PP material with total target recovered reduced by more than 60% when these materials were used. The Au/Cu and crown ether modified materials did not offer advantages in DMMP retention over the hydrophobic PP material. The mica modified material was observed to have initial breakthrough at 18 min with peak rate of transport 1.2 g/h/m^2.
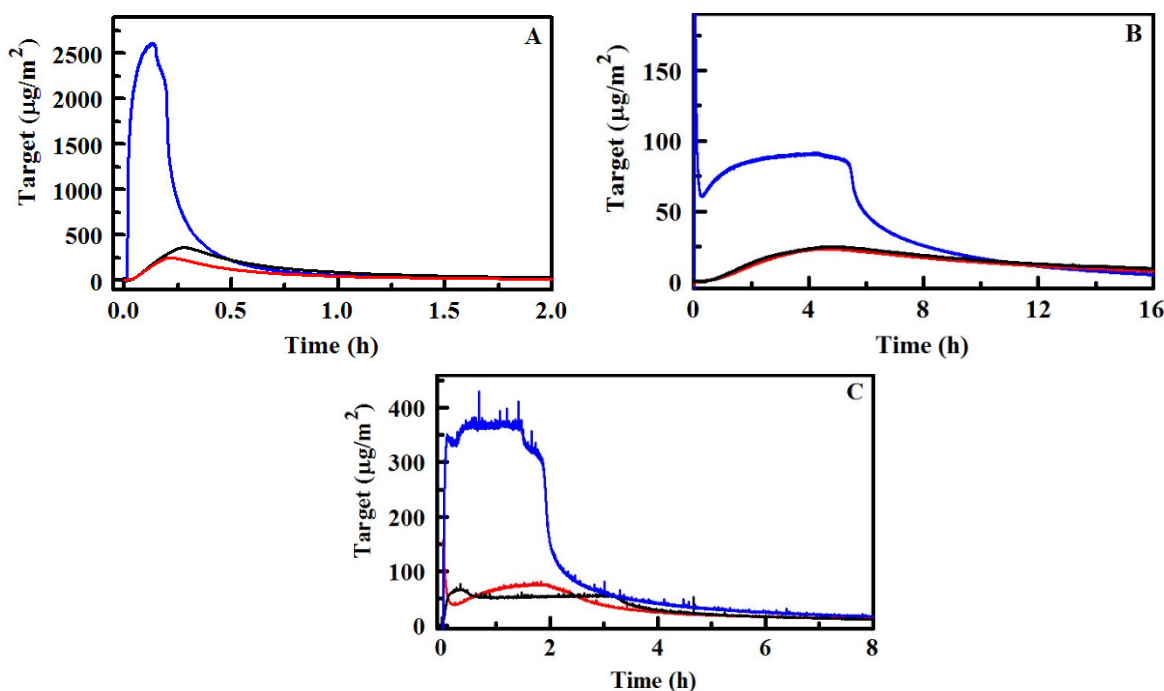
Fig. 6 — AVLAG results for analysis of polypropylene fiber materials prepared as 200 mg air filters under CEES (A), MES (B), and DMMP (C) challenge: hydrophobic polypropylene (black), hydrophilic polypropylene (red), and supporting glass fabric alone (blue).
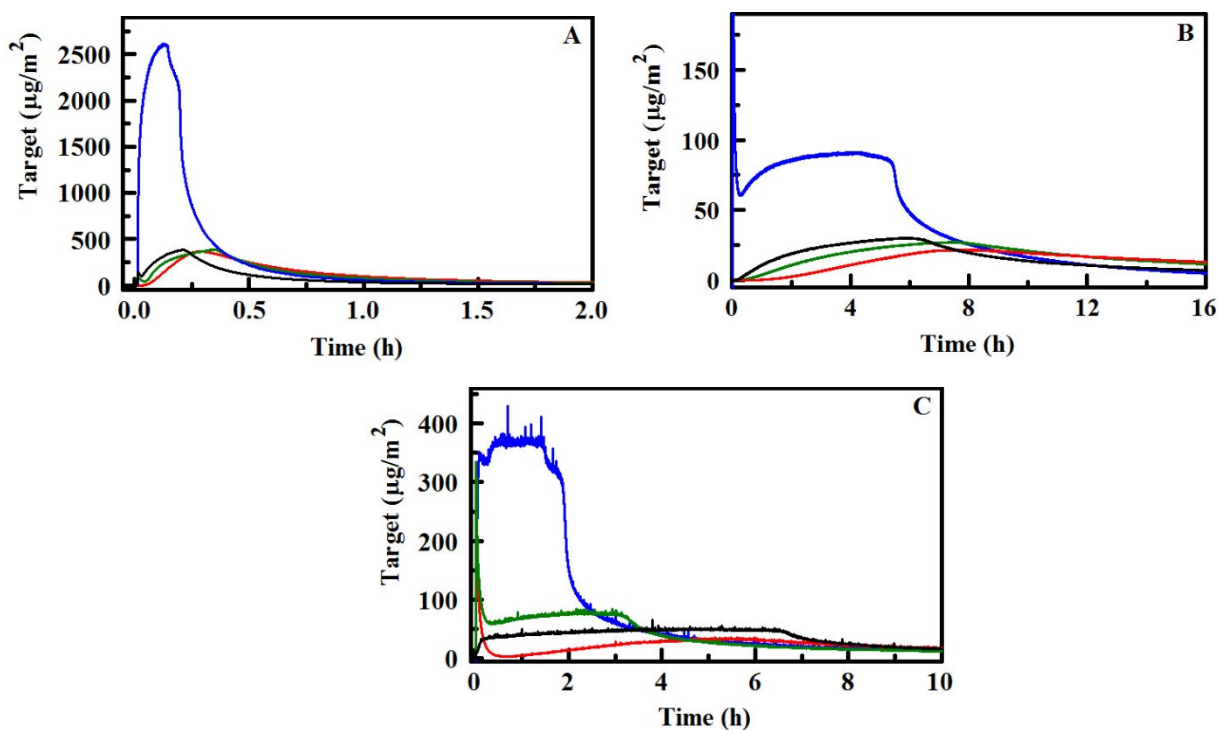

Fig. 7 — AVLAG results for analysis of polypropylene fiber materials prepared as 200 mg air filters under CEES (A), MES (B), and DMMP (C): mica modified PP (black), crown ether modified PP sheet (red), Ag/Cu modified PP sheet (green), and supporting glass fabric alone (blue).

Table 3 – AVLAG Results for Polypropylene Fiber Materials

Material	Initial Breakthrough (min)	Peak Rate (g/m²/h)	Total (µg) over 1,000 min
2-Chloroethyl ethyl sulfide (CEES)			
Glass Fiber Fabric	0.59	47.0	831
Hydrophobic PP	0.76	6.5	368
Hydrophilic PP	0.62	4.5	209
Mica modified PP	0.66	6.9	227
Ag/Cu modified PP	0.68	7.0	362
Crown Ether modified PP	0.91	6.6	375
Methyl salicylate (MES)			
Glass Fiber Fabric	1.14	8.7	772
Hydrophobic PP	31.5	0.5	285
Hydrophilic PP	29.2	0.4	257
Mica modified PP	13.3	0.5	310
Ag/Cu modified PP	23.4	0.5	330
Crown Ether modified PP	78.1	0.4	265
Dimethyl methylphosphonate (DMMP)			
Glass Fiber Fabric	0.91	7.7	1150
Hydrophobic PP	4.19	1.4	384
Hydrophilic PP	0.75	2.8	417
Mica modified PP	18.3	1.2	512
Ag/Cu modified PP	0.63	6.0	523
Crown Ether modified PP	0.94	3.7	366

Beyond evaluation of target transport across the filter material, the transport of water vapor was evaluated. Figure 8 provides a double layer of the glass fiber fabric as a point of comparison, the equivalent of the air filtration formats without a sorbent material. All of the materials in the air filter formats reduced water vapor transport between 8 and 20%. As a further comparison, a single layer of unbleached cotton fabric provides water vapor transport of 116 g/h/m². Addition of the sorbent material to the cotton fabric via the microwave process results in a 5% reduction in water vapor transport across the material.
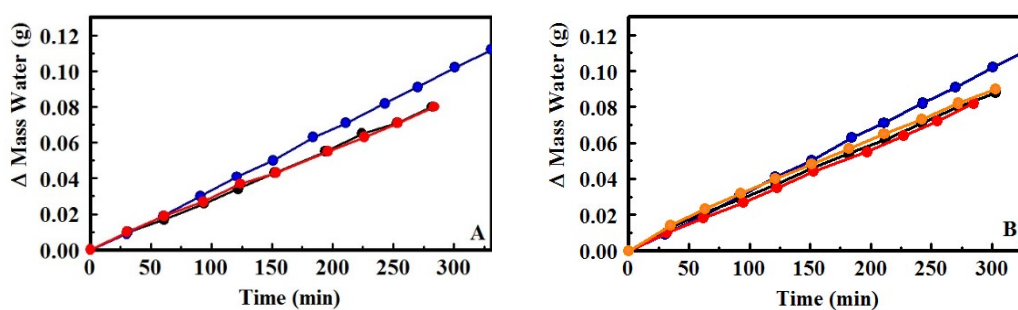

Fig. 8 — Water vapor transport through the polypropylene fiber materials in the air filter format: (A) hydrophobic PP material (black), hydrophilic PP material (red), glass fiber fabric (blue); (B) mica modified PP material (black), crown ether modified PP material (red), Ag/Cu modified PP material (orange), glass fiber fabric (blue).

CONCLUSIONS

This effort evaluated the utility of polypropylene materials in reducing the permeation of chemical threat agent simulants. The materials evaluated represented different form factors as well as differing chemical characteristics. Polypropylene sheet materials may offer an advantage in ease of handling and reduction in post synthesis processing over the batting type form factor that requires packaging of some sort for use in a filtration format. This format did not reduce target permeation as much as the batting type materials; however, the sheets were thinner than the air filter format and likely represented less packing density than those materials.

The sorbent and porphyrin modifications of the PP sheet materials led to improved barrier properties against methyl salicylate (MES, a mustard simulant) and dimethyl methylphosphonate (DMMP, a nerve agent simulant). The lack of impact on CEES permeation (a mustard simulant) could likely be addressed through changing the porphyrin used. [13] This type of change would be expected to have a positive impact on performance against MES as well. The porphyrin-sorbent combination selected for the PP sheet modification was intended to provide properties that would be useful against targets similar to DMMP. The process for incorporation, however, led to significant damage in the polymer support. The modifications used in conjunction with Apollo NanoTech's incorporation method were not identified for air filtration or barrier purposes, but did show significant advantages in some cases. Given the performance characteristics resulting from modification of the PP sheet using the sorbent and those realized for the non-optimal additives, it is likely that modification of the PP materials using the direct incorporation methods would produce a barrier material with improved properties.

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