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REACTIONS OF CW AGENTS HD AND GD WITH THE POLYMER FABRICS PVAM AND CHEMCAT 41

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14. ABSTRACT

Reactive fabrics were studied for the Integrated Protective Fabric System (IPFS) project. The goal of the project was to develop a protective garment that has a lower thermal burden on the wearer by allowing heat and moisture transport. The garment prevents exposure to outside chemical weapons agents (CWAs) by a combination of absorption and reaction. New methods were developed to study the reactions of CWAs with solids based on Nuclear Magnetic Resonance (NMR) and Headspace Gas Chromatography (GC). Reactive fabrics made of poly(vinylamine) (PVAM) and commercial ChemCAT 41 materials were tested by comparing several different methods to determine their reactivity. The CWAs that were used included bis(2-chloroethyl) sulfide (HD) and pinacolyl methylphosphonofluoridate (GD). At an exposure of 10 g/m^2, >90% of a CWA was destroyed by the fabrics for HD and GD. The kinetics of GD reaction were studied using Solids (HRMAS) NMR, because both reactants and products could be detected with the method. For HD, the studies were more complex because the reactions appeared to form additional products with the polymers so the products were nonvolatile and nonextractable. Methods such as Headspace GC and solvent extraction with GC–Mass Spectrometry gave consistent results regarding the destruction of HD on the fabrics.

15. SUBJECT TERMS

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REACTIONS OF CW AGENTS HD AND GD WITH THE POLYMER FABRICS PVAM AND CHEMCAT 41

ABSTRACT

Reactive fabrics were studied for the Integrated Protective Fabric System (IPFS) project. The goal of the project is to develop a protective garment that has a lower thermal burden on the wearer by allowing heat and moisture transport. The garment prevents exposure to outside chemical weapons agents (CWA) by a combination of absorption and reaction. New methods were developed to study reactions of CWA with solids based on Nuclear Magnetic Resonance (NMR) and Headspace Gas Chromatography. Reactive fabrics made of poly(vinylamine) (PVAM) and commercial ChemCAT 41 materials were tested by comparing several different methods to determine their reactivity. The CWA that were used included bis(2-chloroethyl) sulfide (HD) and pinacolyl methylphosphonofluoridate (GD). At an exposure of 10 g/m^2, >90% of the CWA was destroyed by the fabrics for HD and GD. Kinetics of GD reaction were studied using Solids (HRMAS) NMR, because both reactants and products could be detected with the method. For HD, the studies were more complex because the reactions appeared to form addition products with the polymers, so the products were nonvolatile and nonextractable. Methods including Headspace GC and solvent extraction with Gas Chromatography/Mass Spectrometry (GC/MS) gave consistent results about the destruction of HD on the fabrics.

1.0 INTRODUCTION

Reactive fabrics were studied as part of the Integrated Protective Fabric System (IPFS) project. The goal of the project is to develop a protective garment that lowers the thermal burden on the wearer by allowing heat and moisture transport from incorporation of semi-permeable materials that allow transport of water vapor or air through the material. The garment prevents exposure to outside chemical weapons agents (CWA) or biological agents (BA) by a combination of absorption and reaction.

Fabrics made of poly(vinylamine) (PVAM) and ChemCAT 41 materials were tested using several different experimental methods to determine their reactivity toward CWA. Both are commercially available materials. PVAM was purchased from Sekisui (Sekisui America, Secaucus, NJ). Majilite (Dracut, MA) is the company that laminated the PVAM to the woven liner. It was treated with benzisothiazolinone (BIT), a sulfur containing compound that is a biocide. ChemCAT 41 (STEDAIR® Chemical Active Textile) is sold by Stedfast (Stedfast, Inc., Granby, Quebec, Canada, or Stedfast USA, Piney Flats, TN).

This report includes results on the testing of PVAM and ChemCAT 41 fabrics for reactivity. Both were found to have significant reactivity toward both bis(2-chloroethyl) sulfide (mustard or HD) and pinacolyl methylphosphonofluoridate (soman or GD). The testing was done in order to meet the requirements of the kinetic determination for the IPFS Technology Transfer Agreement (TTA), shown in Table 1. While the TTA threshold/objective goals specify end-values to be met, the wording of the TTA itself specifies rate measurement and that the agents to be determined are HD and GD. The fabrics to be tested are supplied by Natick Soldier Research Engineering and Development Center (SRDEC).

PVAM is being incorporated into the Chem/Bio Combat Coverall type B garment system design.

In addition to these measurements, this report includes studies on different PVAM samples that were done during the course of the IPFS project in Section 5.0 and 6.0.

Table 1: IPFS Technology Transfer Agreement Requirement for Reactive Self-Detoxification.

Textile Properties	Current	Threshold (Acceptable)	Objective (Desired)
Self-detoxification of absorbed agent (neutralization rate)	None	50% decon at 90%RH in 24 hrs at 30°C	99% decon at 80%RH in 24 hrs at 30°C

2.0   EXPERIMENTAL

Several different experimental methods were used. Every attempt was made to do more than one kind of test on each fabric/agent combination to check for consistency of the results. In some circumstances, it was only possible to do one type of test.

2.1   Solids NMR Studies

Studies using solids (also known as High Resolution Magic Angle Spinning, HRMAS) Nuclear Magnetic Resonance Spectroscopy (NMR) were done with the procedure described in another report.[1] In summary, the following procedure was used:

1. A swatch of the fabric to be studied was humidified to the desired conditions by placing it in a bottle with the desired humidity. Water vapor was produced from a water solution of saturated NaBr or DI water. For this study, the humidities of 90-100% RH and 40-60% RH were used. The lower RH is below the specification for the objective goal of 80%. The humidity over a saturated NaBr solution is reported as 57% RH at 25°C.[2] Measurement of actual humidity with a NIST-traceable humidity meter showed that the actual humidity in the bottle was in the range of 40-60%. However, the fabric had to be removed from the bottle and exposed to ambient humidity air before analysis by NMR.
2. The fabric was cut to a size of 1.2 cm × 1.2 cm. The swatch was rolled into a tube and placed inside a solids rotor that is used for a solids NMR probe made by Doty Scientific (Columbia, SC) with a JEOL USA, Inc. (Peabody, MA) ECS-400 NMR spectrometer.
3. The fabric in the rotor was spiked with neat agent using a 5 µL syringe, the rotor was capped and sealed, and a timer was started.
4. The rotor was placed in the solids probe and spun at 1.5 KHz to 2 KHz spin rate.
5. The rotor was sealed at room temperature for at least 24 h and the reaction was monitored by P-31 NMR. Multiple NMR spectra were acquired at known time points from the same fabric sample.

6. After 24 h, the fabric swatch was removed and extracted in acetonitrile solvent by vortexing for 30 sec. The solution was analyzed by GC/MS as an independent determination of the amount of agent that remained on the fabric.

2.2 Headspace Vial-in-Vial GC Method

The method for this test was described in detail in a separate report.[3] In summary, this analytical chemistry method was developed for the IPFS project for measuring the reactivity and permeability of fabrics, films, and other solid materials. Headspace Gas Chromatography (GC) or Gas Chromatography/Mass Spectrometry (GC/MS) instrumentation is used. The method uses a small vial inside a larger headspace vial (known as the vial-in-vial method). The volatile agent is placed in a small inner vial, and the inner vial is capped with a layer of fabric or film to be tested. The agent permeates from the inner vial into an outer headspace vial by diffusion or permeation, without a pressure differential. The instrument samples the vapor in the outer vial using a syringe and injects it into the GC for analysis. The presence of agent in the outer vial indicates that it has permeated through the film. Multiple sampling can be used to determine time dependence. Solids can also be tested for reactivity in the headspace vial without the inner vial, see Section 2.3.

Spiking was typically done using dilute solutions of agent (1-5 mg/mL), although neat agent could also be used. Solvent for HD was hexane, which evaporated quickly to give a known small amount of neat agent in the inner vial. An alternate approach was to use HD in a larger amount of decane solution. This decane solvent was less volatile and provided a constant source of HD from the partial pressure of HD above the solution. The solution was used for calibration of the instrument and for exposure of a film to a constant amount of agent.

2.3 Headspace GC Single Vial Method with Extraction

A variation on the headspace method, also described in another report,[3] is to use only a single headspace vial. The material in the vial is spiked with CWA, and the headspace vapor of the CWA decreases as it reacts with the material. In summary, the following procedure is used:

1. A swatch of fabric to be studied was humidified to the desired conditions in a bottle with a water solution or DI water. Samples were cut to a size of 1 cm × 1 cm.
2. Each swatch was placed in the bottom of a headspace vial (20 mL volume).
3. The fabrics were spiked with 1 µl of neat agent using a 5 µL syringe and a timer was started.
4. Samples of vapor (0.5 mL volume) from the headspace vials were automatically removed by a CTC autosampler with a gas-tight syringe and injected into a Varian GC with a pulsed FPD detector. The GC method typically used a large split ratio during injection, since a large amount of vapor was present.
5. Calibration was done using small amounts of CW agent in empty headspace vials or with solutions of agent in decane to provide a constant partial pressure above the solution.
6. After reaction was complete or at a specified time, the fabric was extracted with a solvent, and the extract was analyzed using a liquid injection GC method.

2.4   Extraction and GC/MS Analysis

The last method that was used in the measurements was solvent extraction:

1. A swatch of fabric to be studied was humidified to the desired conditions in a bottle with a water solution or DI water. Multiple samples were cut to a size of 1 cm × 1 cm.
2. The swatches was placed in the bottom of a GC autosampler vials (1.8 mL volume).
3. The fabrics were spiked with neat agent using a 5 µL syringe and a timer was started.
4. At selected time points, one (or more) of the vials were extracted by adding 1 mL of acetonitrile to the vial, and vortexing for 30 sec. An aliquot of the solution was removed and diluted by 1:10.
5. The dilute solution was analyzed using liquid injection on an Agilent GC/MS. The instrument was calibrated by running dilute liquid calibration solutions made with the same neat agent stock.

The extraction GC/MS method is not as reliable, because there are certain drawbacks of this method. First, the extraction efficiency of agent after it is deposited on the polymer may be difficult to determine in an accurate way. For an unreactive polymer or material, if the material is spiked and the agent is recovered at 100%, then there is confidence that the extraction efficiency is high. For a reactive material, if less than 100% is recovered, it is difficult to demonstrate whether the agent has reacted or whether it is adsorbed strongly so it can't be extracted, at least with the particular solvent that is being used. It is also possible that the agent will react during the extraction process while the solution is in contact with the material.

Since PVAM is inherently reactive, there isn't a good blank material for determining the extraction efficiency. After the agent is deposited, it will react and may not be able to be extracted. Without an accurate value for the baseline extraction efficiency and extraction of products, it is not possible to calculate a mass balance.

The second drawback is that the solvent extraction is not associated with a particular type of hazard to the wearer of the garment. Vapor or contact hazards are directly relevant to the exposure to agent, but a solvent extraction is an artificial determination that may or may not be related to the actual exposure.

However, solvent extraction was used for determination of HD reactivity for reasons that are discussed later.

3.0   GD RESULTS

3.1   NMR Studies

For GD, good kinetic results were obtained by using the solids NMR method with P-31 detection. This method showed the decontamination of GD on the reactive fabric. The data points are taken from the absolute signal of the agent as it decreases in time, in arbitrary units that are determined by

the NMR software based on the signal strength for particular instrument parameters. In each case, 1 mg of GD was spiked on 1.4 cm^2 of fabric, for a dose of 7.1 g/m^2. Fabrics with two different relative humidity exposures were tested.

For the swatch of PVAM that was humidified to 90-100% relative humidity (RH), the kinetic results are shown in Figure 1. According to the TTA, the threshold goal is 50% neutralization at 90% RH in 24 h at 30°C. The probe could only perform reactions at room temperature, so the rate was not measured at 30 °C, but at 22°C. This threshold is shown by the red line in the figure. The goal is met within <20 min. after the reaction was started.

For the swatch of PVAM that was humidified to 40-60% RH, the kinetic results are shown in Figure 2. Three separate trials were done under the same conditions to determine the variability of the measurement. For the first trial, the signal decreased rapidly but leveled off, while for the second and third trials, the signal decreased more slowly and was still higher in residual GD in 24 h (1440 min.). According to the TTA, the objective is 99% neutralization at 80% RH in 24 h. The objective is shown by the red line in the figure. The goal of 99% destruction of the agent is not met, since the reaction levels off at about 90% destruction.

For the swatch of ChemCAT 41 that was humidified to 90-100% RH, the kinetic results are shown in Figure 3. According to the TTA, the threshold is 50% neutralization at 90% RH in 24 h at 30°C. The probe could only perform reactions at room temperature, so the rate was not measured at 30 °C, but at 22°C. This threshold is shown by the red line in the figure. The goal is met in 81 min. after the reaction was started.

For the swatch of ChemCAT 41 that was humidified to 40-60% RH, the kinetic results are shown in Figure 4 and 5. Three separate trials were done under the same conditions to determine the variability of the measurement. For the second trial, the signal decrease most rapidly, while for the first and third trials, the signal decreased more slowly but reached about the same amount.

According to the TTA, the objective is 99% neutralization at 80% RH in 24 h. The objective is shown by the red line in the figure. The goal of 99% destruction of the agent is not met, since the reaction reaches about 96% destruction by 24 h for trial 1. The other two trials could not be followed that long, since there were small product peaks that interfered with accurate integration of the reactant agent peaks when the reactant peaks were small.

In Figure 5, the same data is plotted on a semilog plot, normalized to the maximum intensity for each run. The results for all the ChemCAT trials show a good fit to an exponential decrease. The linearity of the data can be used to extrapolate how long it will take to reach the 99% objective. The range of time for the three trials is from 23 to 81 h, assuming the rate remains the same.
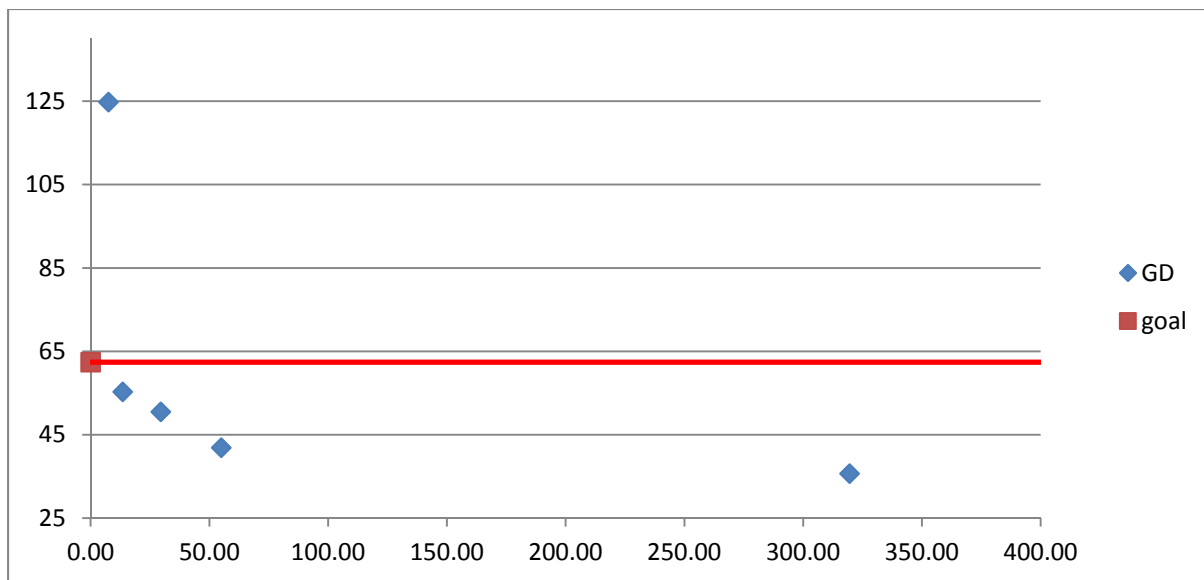
Figure 1: PVAM Humidified to 90-100% RH Reaction with GD. The time scale is in minutes.

Figure 2: PVAM Humidified to 40-60% RH Reaction with GD. The signal for the residual GD is in arbitrary units determined by the NMR. The time scale is in minutes.
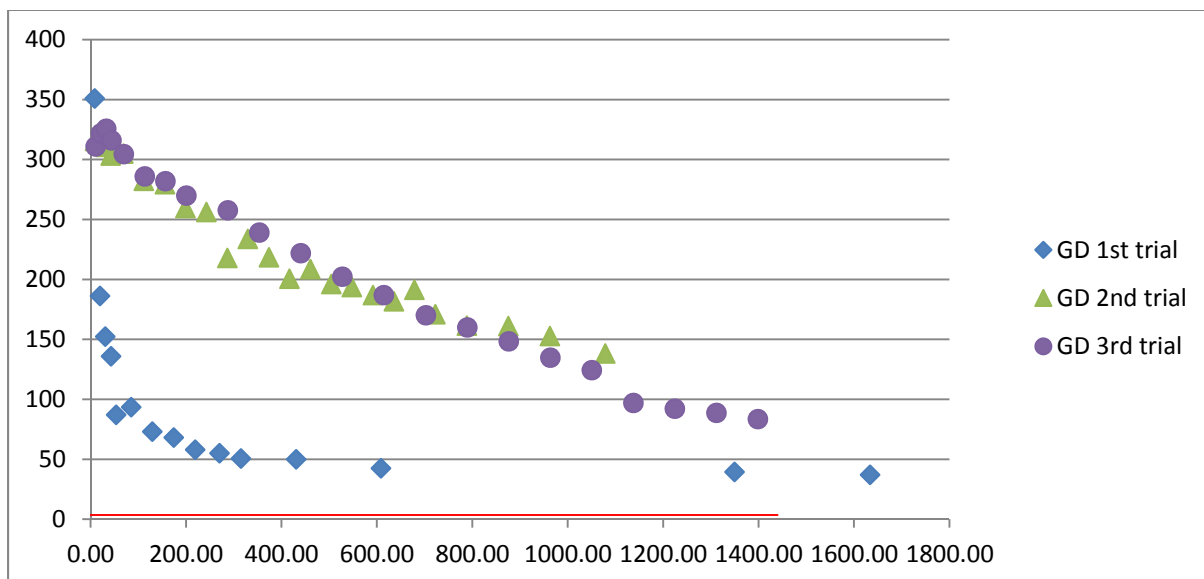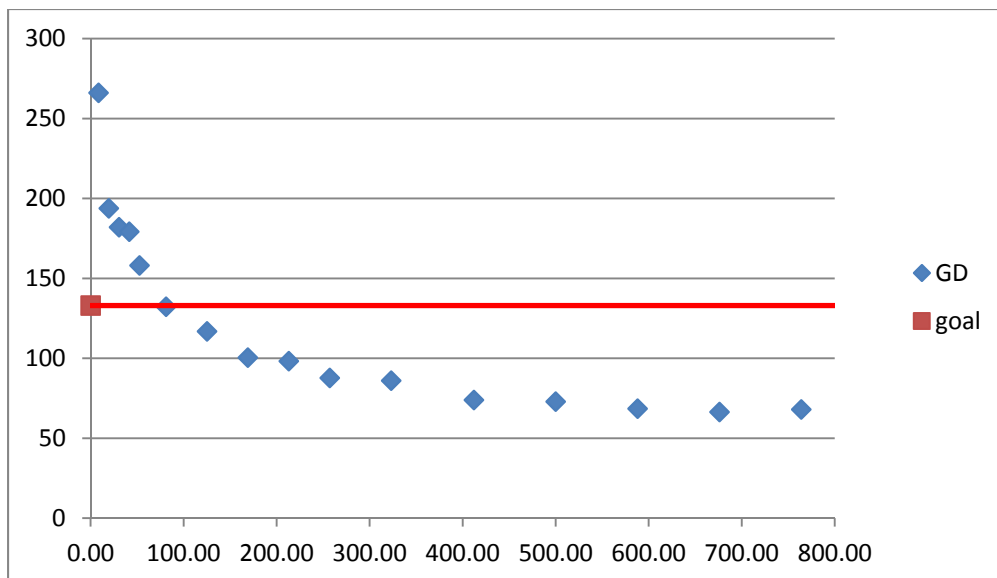
Figure 3: ChemCAT 41 Humidified to 90-100% RH Reaction with GD.
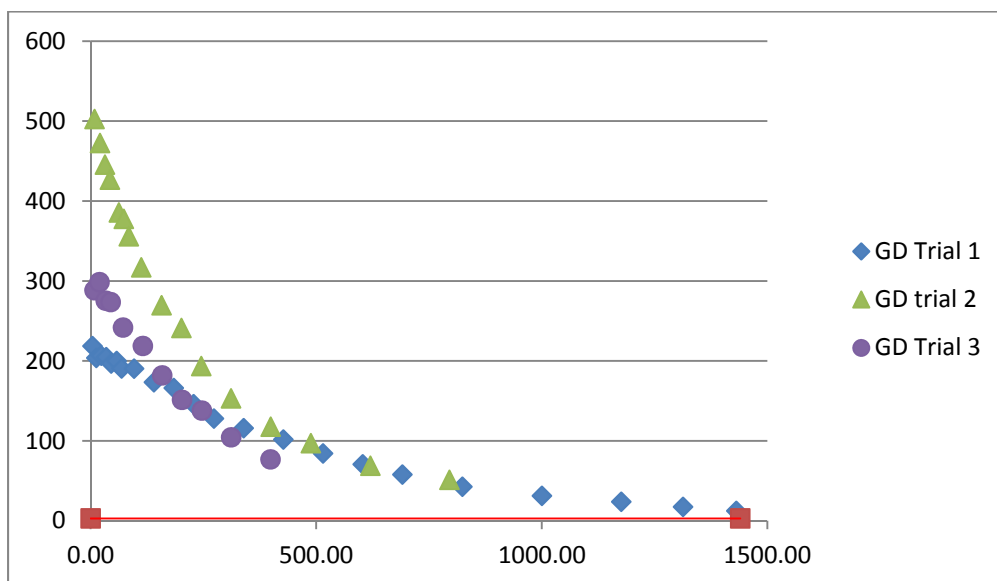
Figure 4: ChemCAT 41 Humidified to 40-60% RH Reaction with GD. The signal for the residual GD is in arbitrary linear units determined by the NMR. The time scale is in minutes.
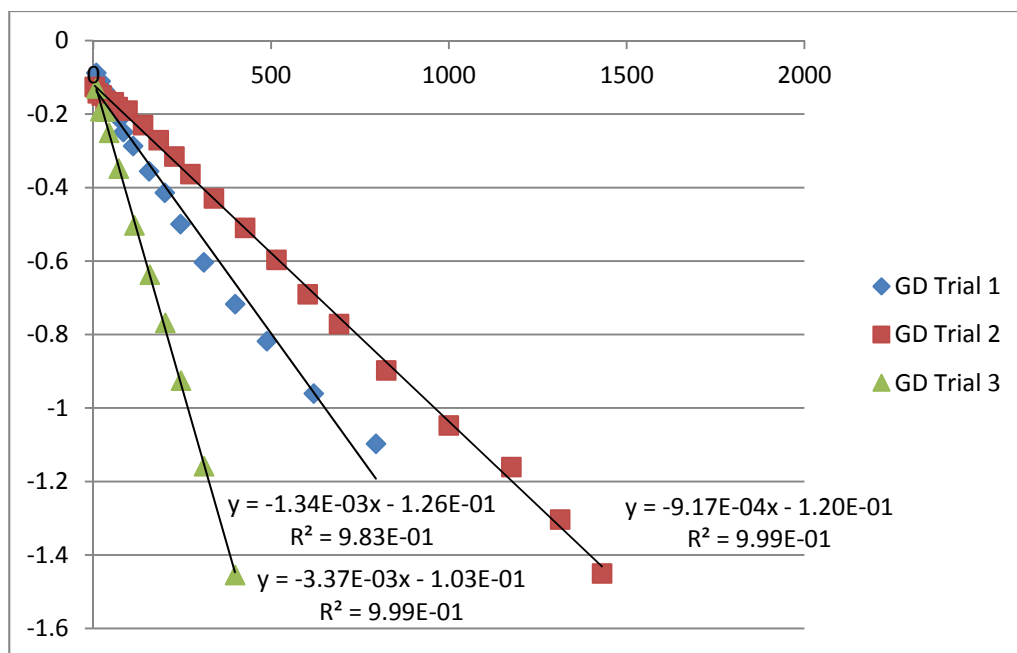
Figure 5: Kinetic Plots of ChemCAT Reactions on a Logarithmic Plot. The signal for the residual GD is in normalized natural log units. The time scale is in minutes. Best linear fit lines are shown for each trial.

There is variation for the different trials on the fabrics for both PVAM and ChemCAT. This may be due to differences in the strength of the absorption of the agent to the polymer at different locations, depending on the mobility of the GD to find reactive sites. There also could be experimental variability between the experiments. When spiking, it is difficult to distribute the agent in the same way for all the samples. A more uniform distribution of agent over the fabric may lead to faster reaction. This variability may be typical of actual field applications of the material, though, since in actual field use, the contamination will not be spread uniformly.

After the kinetic runs were completed, the fabric was extracted with acetonitrile and the solution was analyzed by GC/MS. The amount of residual agent that was recovered by this method was consistent with the NMR results. For the ChemCAT fabrics, 1-6 % of the original GD was recovered after 24 hrs. For PVAM, the amount recovered was higher, in the range of 10-30% of the original GD.

3.2   GD Chemistry

GD typically has simple chemistry, since the P-F bond is hydrolyzed to form one product, GD acid (pinacolyl methylphosphonic acid). This hydrolysis occurs much faster at high pH, but it still occurs at a slower rate near pH 7. The rate also depends on the amount of water that is absorbed into the film.

PVAM can be prepared at a range of effective pH values depending on the ionization state of the amine groups in the polymer. If the amines are free based or are associated with hydroxide anions, the polymer can be very alkaline. If the amines are associated with acid salts, they can be neutral or acidic.

For the present determinations, the polymer was tested as it was received, and no effort was made to adjust the effective pH. However, if the polymer were made more alkaline, it would react with GD much faster.

Adjusting the effective pH can change other properties of the polymer. Studies are underway for using PVAM as a hydrogel, which can increase the water permeability of the polymer. However, in designing a garment, it is important to trade off other considerations in the material properties or potential hazard to the wearer. As a result, the reactivity of the fabric wasn't optimized, and it was tested as received. There is no doubt that altering the treatment of the fabric could improve the reactivity and protection against GD as well as other G-type CW agents.

There weren't any visible incompatibility between GD and the polymer, since when the GD was deposited, it soaked into the polymer without the formation of any visible immiscible droplets.

4.0   HD RESULTS

4.1   HD Chemistry

Determination of the kinetics of HD on the fabrics was more complex than for GD. The HD reacted with the polymer to a significant extent. Unlike GD, for which one product was observed, the HD product wasn't a small molecule. Instead, it reacted with the polymer to form addition products that were nonvolatile, nonextractable, and high in molecular weight. An example of a reaction scheme is illustrated in Figure 6, but there are many possible related products, including cross-linking of the polymer chains. Similar results have been observed for HD reactions with related small molecules; for example it has been observed that HD reacts with monoethanolamine to produce N-2-hydroxyethylthiomorpholine, a cyclic addition product.[4] Preliminary results show that HD reacts with ethylenediamine, a small-molecule analog of PVAM, to form multiple products, but more work is needed to identify the products and characterize the kinetics.

The high-molecular-weight HD products were not detectable with the current methods. It wasn't possible to determine a mass balance for such products. As a result, it was necessary to measure the residual unreacted HD. The amount of unreacted HD should give an indication of the residual risk of exposure.

Most of the HD reacted quickly with the fabric, but there was a fraction of residual agent left. This may be the result of the formation of encapsulated droplets of HD that did not wet the polymer and spread out on it. It was observed that a drop of HD on the polymer didn't immediately soak in. This behavior has been observed for HD in polar or aqueous solutions, since the nonpolar HD doesn't dissolve in a polar solvent.

The experimental results that follow are interpreted in terms of this model of HD on the polymer.

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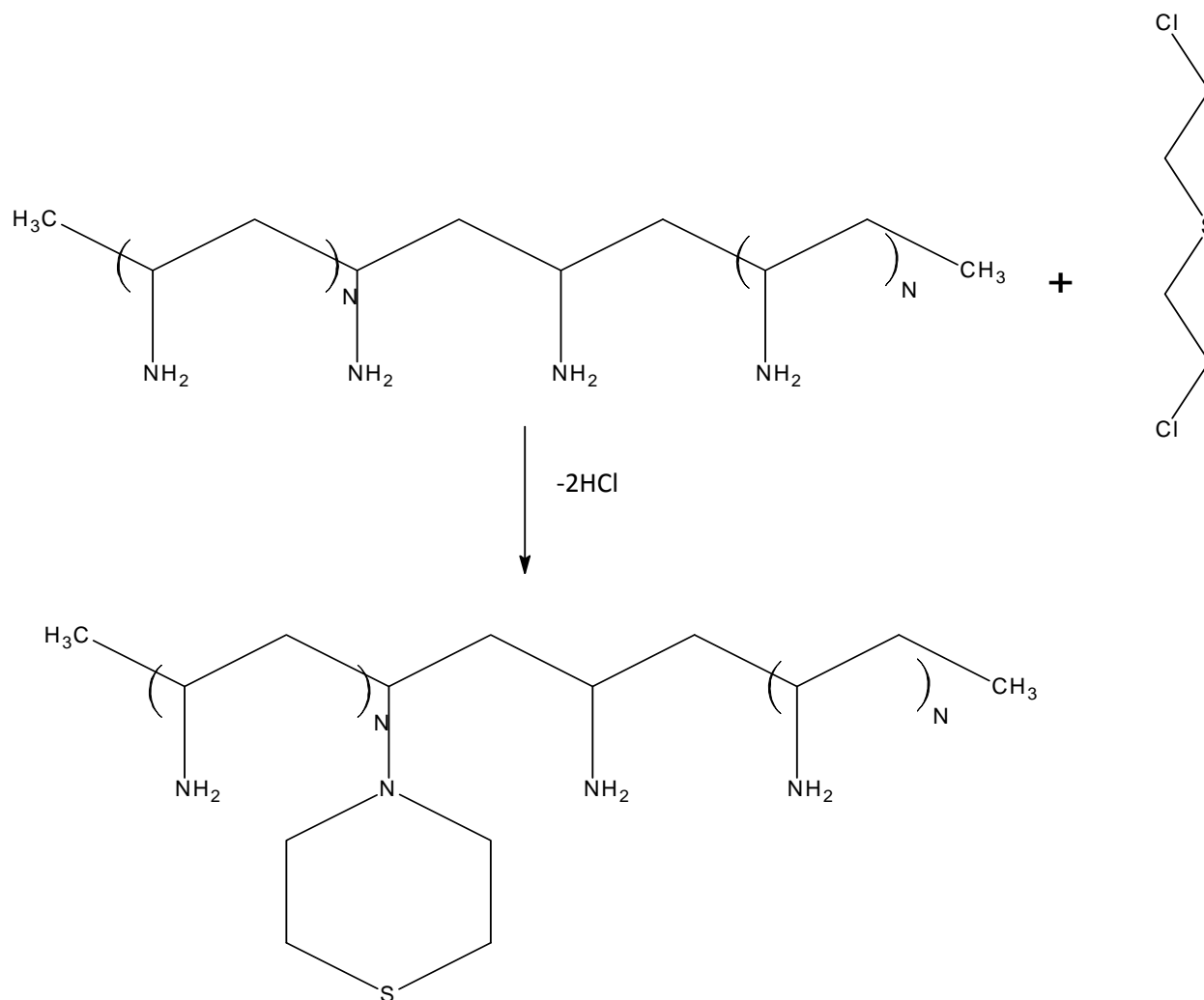
Figure 6: Example of a Reaction Scheme of HD with PVAM Polymer.

4.2   NMR Studies

Detection of HD on the fabrics was attempted using solids NMR using the same technique as was used for GD. Unfortunately, it is necessary to use either proton or C-13 detection for HD. The proton NMR lines for residual HD or possible products couldn't be resolved from the polymer background signal. The original amount of HD that was spiked on the fabric should have been detectable, but it reacted fast, forming high-molecular-weight addition product that was not simple to characterize.

Detection with C-13 NMR could assist in identifying the reaction products. However, the signal for natural abundance C-13 detection was not sufficiently large to resolve the HD from the polymer due to carbon background and because C-13 only occurs naturally at 1.1% of the amount of C-12. A way to address this problem is by making HD that is labeled with 100% C-13. Preparation of labeled HD was delayed due to the difficulty of getting custom-synthesized CW agent, and it wasn't available when this report was done.

4.3　　　　　　　　　Headspace Single Vial Measurements

　　　　　　The headspace GC method was used to obtain kinetic data. The Headspace GC single vial method with extraction was used, in which a swatch of fabric was spiked in a vial to observe the amount of HD vapor that remained. The results are shown in Figure 7. The three replicates for 60% RH PVAM give an indication of the reproducibility. The two samples from 99% RH are lower than the 60% RH samples.

　　　　　　The solid line is from multiple sequential runs for the same standard vial containing 10 µg HD in an empty vial. This amount corresponds to 1% recovery of the 1 mg HD original spike on the fabric. For the initial run, the standard corresponding to 1% recovery was higher than the signal for the spiked fabric samples. The HD vapor over the fabrics was present at <1%, implying that >99% of the HD reacted within the time that the first measurement was taken or else didn't desorb from the fabric by 1-2 h after spiking. However, multiple runs of the standard decrease in signal over time, which has been observed previously.[3] In comparison, the multiple runs for the fabric samples tended to remain stable or increase over the 24-h time span during the kinetic measurements, probably because more of the HD desorbed from the film. These results make it uncertain to accurately quantify the results. Interpreting on the conservative side, the results indicate that the reaction of HD did not reach the 99% target level for the 60% RH samples, but it is between 93-95%.
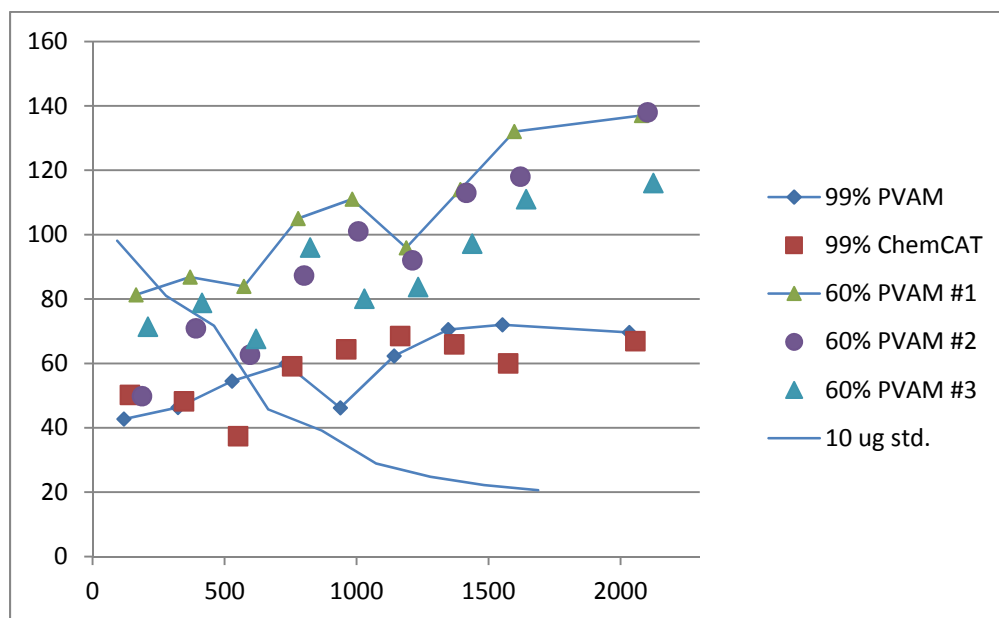

Figure 7: Headspace GC Results for 5 Vials with Fabrics, as Indicated in the Legend. The PVAM at 60% RH was three replicate samples. The signal axis is in arbitrary linear units, and the time axis is in minutes.

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4.4   Headspace Vial-in-Vial Method

The vial-in-vial method is more directly related to permeation through the film, and thus to the actual hazard. A method was used for calibration that was more stable than that shown in Figure 7. A dilute solution of 1 mg/ml HD in decane was used as a calibration standard, rather than HD in an empty vial. Over a two week trial, the signal for the standard was more stable, as shown in Figure 8, although there was still some drift in the instrument signal. Further discussion is given in another report.[3]
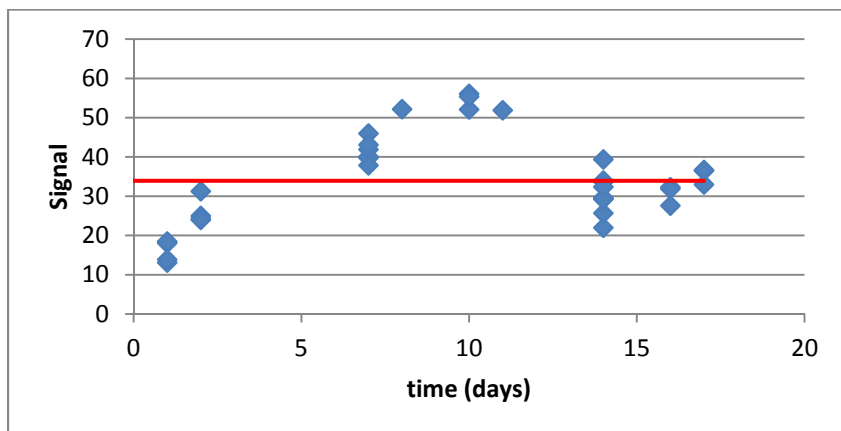
Figure 8: Plot of Pulsed FPD Signal for the Same 1 mg/mL Solution of HD in Decane, Over the Course of 17 days. The red line is the average value.

Using this calibration, two experiments were done with HD permeation through PVAM fabric: 1) a fixed amount of 30 µg of HD was added to the inner vial; and 2) a steady vapor source of HD in decane was placed in the inner vial.

Fixed Amount of HD

For this measurement, an amount of 30 µg HD (30 µL of 1 mg/mL solution) was placed in the inner vial and the solvent was evaporated. A circle of 28.3 mm^2 of fabric was placed over the inner vial and sealed. Then headspace vapor was sampled from the outer 20 mL headspace vial, using a syringe that sampled 0.5 mL of vapor. For the entire 24 h experiment, no HD was detected in the outer vial to a detection limit of 0.1 ng/injection. Since the method functionally integrates by collecting the permeated agent in the outer vial, we can assume that the entire amount of HD vapor (to the detection limit) was consumed by reaction with the PVAM fabric.

The dose of HD on the fabric for this measurement was 30 µg/28.3 mm^2, which converts to 1.1 g/m^2, which is less than the maximum target concentration of 10 g/m^2 used in the previous section. However, it can still provide protection for a range that is greater than the IDLH, 0.7 mg/m^3 for HD.

Constant Exposure Source of HD

A different scenario is that the protective garment will be exposed to a constant vapor of HD, instead of a single fixed dose. In that case, the question is, how long the protection lasts before the HD consumes the reactive capacity and permeates through the fabric. Figure 9 shows the results of the measurement. The standard used for reference is a solution of 1 mg/mL HD in decane. The solution has a calculated vapor partial pressure of 4.4 ng HD/mL in air sampled at 40°C,[5] assuming an ideal partial pressure for the solution. This amount compares to the found amount of 6.6 ng/mL (3.3 ng in the 0.5 mL injection) from the comparison to the calibration curve. The same solution is placed in the inner vial of three replicate samples, which are all plotted in the figure. The figure shows that the fabric provides protection until about 1000 min. After about 1000 min., the fabric is no longer providing protection against the HD, since the concentration of HD that has permeated into the outer vial is the same as the standard.

It is difficult to determine the reactive capacity of the fabric with this method, since it depends on the flux of agent onto the fabric surface (a conversion from the concentration per volume to a concentration per area per unit time, requiring the diffusion rate). The experiment was done with a single ply of reactive fabric. In practice, diffusion to the surface depends on the effectiveness of the shell or cover fabric from preventing diffusion. The more impermeable the shell fabric is, the less agent will diffuse to the reactive polymer, and the longer it will last. However, the choice of less permeability will also give less heat transport and less comfort to the wearer. So it is necessary to select a tradeoff of the parameters.

However, the results demonstrate that the fabric provides protection against a constant exposure of vapor.
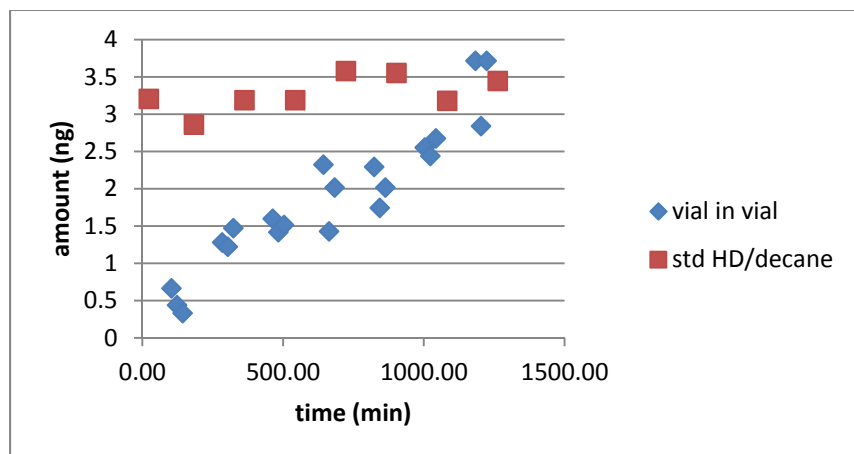

Figure 9: Plot of Permeation Through PVAM fabric with a Constant Exposure Source of HD. Three identical replicates of vial-in-vial samples are plotted relative to the standard.

4.5   Solvent Extraction Measurements

The final method was used for confirmation of the Headspace results using the spiking of liquid agent onto the fabric and solvent extracting with acetonitrile after a specified time. This method gave more scatter to the data and less uniform spiking, but it was more straightforward to calibrate the instrument. The results were generally consistent with the previous data.

For this measurement, a section of fabric was spiked with liquid neat agent, then solvent extracted at a specific time. The spike amount was 10 g/m^2, the maximum amount. Different time points were obtained using different samples. Samples were analyzed by liquid injection of the extracts on a GC/MS. A calibration curve was generated from liquid standard solutions.

For the swatch of PVAM that was humidified to 40-60% RH, the kinetic results are shown in Figure 10. For the swatch of PVAM that was humidified to 90-100%, the kinetic results are shown in Figure 11. In both cases, the results are similar. The amount of HD that can be recovered is 30% of the original spike amount within 15 min. By 24 h, the amount that can be recovered has decreased to 10-15%. The y-axis is the calibrated amount of agent as a percentage of the spike amount.

This is slightly higher than the headspace measurement, which may be due to the difference between headspace and solvent extraction, or due to the higher dose. Vapor exposure with a lower dose covers the sample uniformly, so all the reactive groups are exposed. Liquid spiking at 10 g/m^2 exposure deposits the agent on a fairly small area, which may limit the reaction to the small area rather than the entire fabric, unless the agent migrates rapidly to wet the entire available fabric. HD is nonpolar and it appeared to bead up so it doesn't migrate well. As a result, this method provides a worst-case measure of the reactivity.

According to the TTA, the threshold is 50% neutralization at 90% RH in 24 h. The objective is 99% neutralization at 80% RH in 24 h. The 50% threshold is easily met, but the 99% objective (corresponding to 1% of agent remaining) is not met for HD.
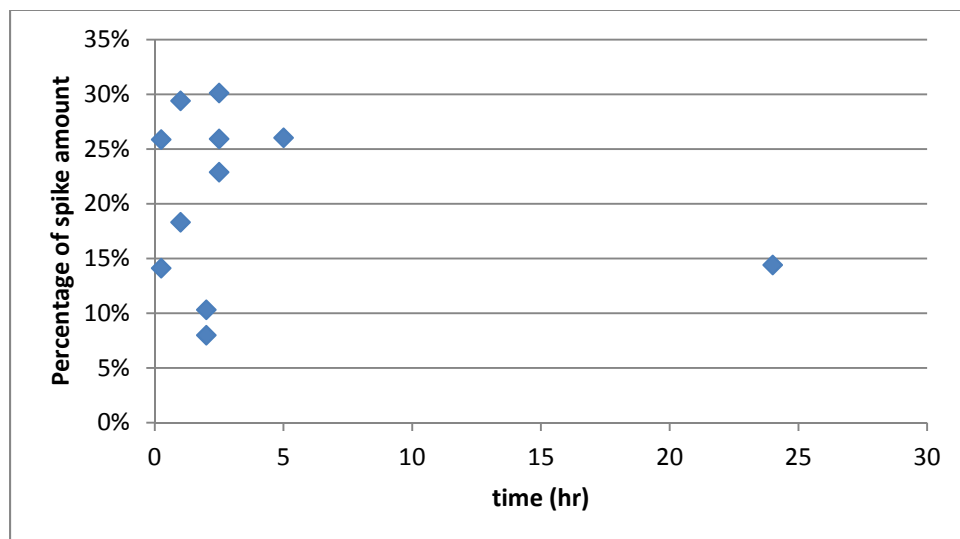

Figure 10: Recovery of HD from PVAM at 40-60% RH Using Acetonitrile Solvent Extraction.
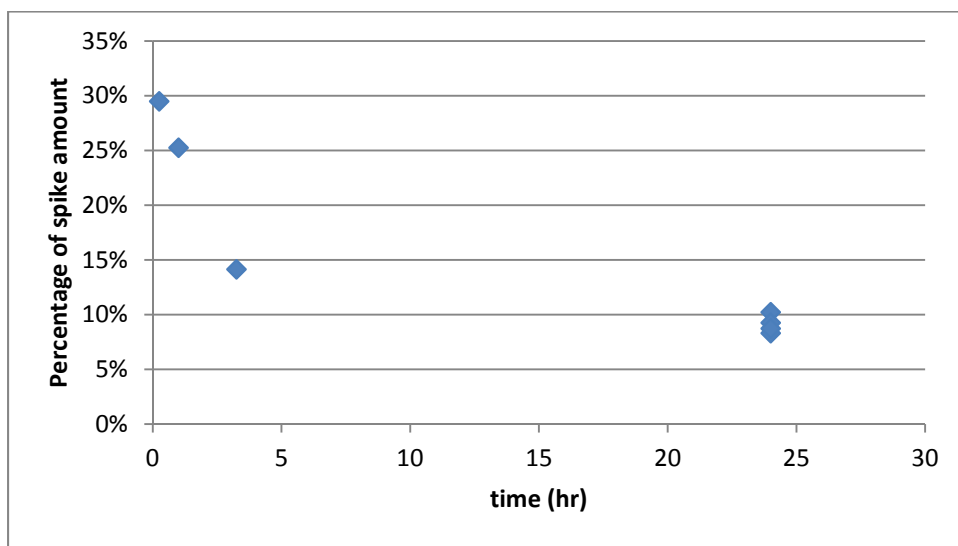
14

Figure 11: Recovery of HD from PVAM at 90% RH Using Acetonitrile Solvent Extraction.

4.6   Possible Optimization for Better HD Performance

Reaction products of HD were not observed for this reaction by any of the methods. This is explained if the HD reacts with the polymer to be bound to it as an addition product, so the product is nonvolatile and can't be extracted by the solvent. As a result, we cannot determine a mass balance for the HD reaction, because the products aren't detected. But the HD appears to be unrecoverable from the polymer and is detoxified by the polymer. The NMR results are also consistent, since the inability of the NMR to detect HD is consistent with fast reaction to a product that is difficult to identify. The results are qualitatively similar for all techniques. The results confirm the conclusion that the amount of HD that is detoxified is less than the objective of 99% agent destruction, at least for the worst case scenario of a liquid spike of 10 g/m^2.

There are some issues about the interaction of HD with the polymer that are illustrated by the following photographs. Figure 12 shows an image of a drop of HD on ChemCAT polymer. In this experiment, 2 uL of HD was deposited on a sample of ChemCAT (black side) on 2-inch glass panels. The panels were imaged at 20ºC and approx. 30% RH after 4 h. The material swells and a drop of HD can still be seen on the ChemCAT sample after 4 h. The material was extracted in acetonitrile and the extract was analyzed by GC/MS, and about 100% of the amount that was spiked was recovered. The relative humidity was low for this experiment, but a similar drop of HD was observed after exposing the polymer to higher relative humidity as well. This effect illustrates that the polymer was not readily wettable by the HD.

In another experiment, there is residual material or polymer swelling that is visible on the surface after 20 h, but no drop of liquid remains. Figure 13 illustrates that the location of the agent

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deposition is still visible. It is not known whether this residue is the agent or reaction product by this point.

These effects may depend on the relative humidity in a sensitive way. Some differences in the reactivity were observed between humidity levels. It may be valuable to obtain a humidity chamber with a more precise humidity control to study reactions at more humidity levels. More study is needed to determine the detailed effect of relative humidity on the HD reaction to identify whether there is an effect on the protection factor of the material and to determine the specifications for use of the materials.

Faster reaction might be achieved by developing a surface treatment that is wetted by the HD droplet. These polymers were purchased commercially because they were available in bulk quantities for the fabrication of garments, but they were not specifically modified for use with agent. Further studies of the surface interaction and absorption of agent may improve the performance. This type of incompatibility might be addressed by adjusting the effective pH or surface treatment of the polymer. The next sections provide experimental results using polymers from other manufacturers, but these materials are no longer commercially available.
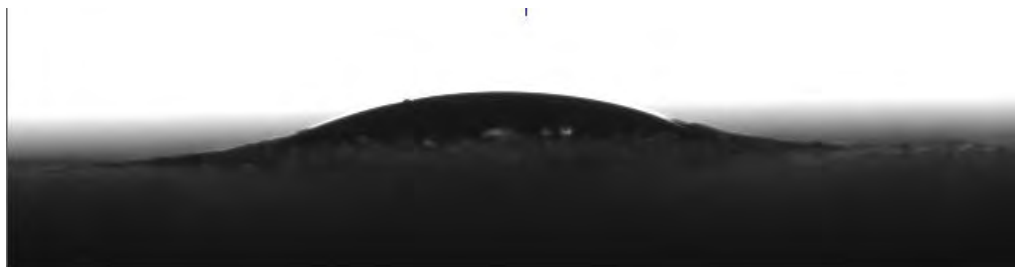
Figure 12: Side Image of a Droplet of 2 µL of HD on ChemCAT, After 4 h. The polymer swelled, and there is still a visible drop of HD.
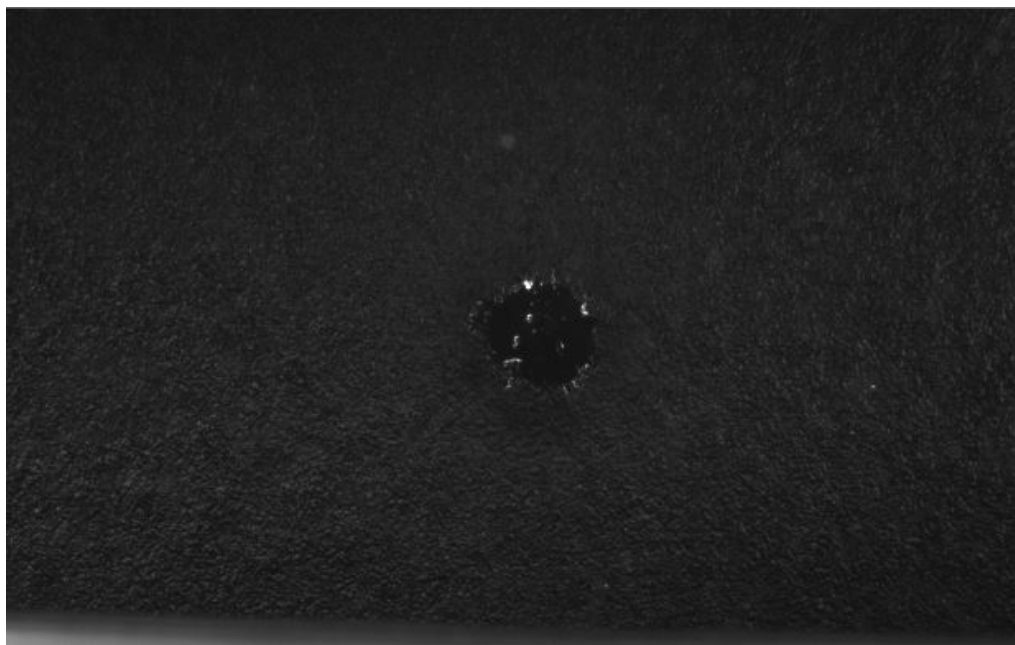

Figure 13: Top Image of Residue of 2 µL of HD on ChemCAT, After 20 h. There is still a visible area where the HD was deposited, but it is not known whether it has reacted with the polymer.

5.0 RESULTS FROM 2007 FOR SAMPLES OF PVAM

PVAM samples have been under consideration as reactive fabrics for several years. A report by Schreuder-Gibson and co-workers from 2006 summarizes early work.[6] Previous results have shown reactivity of PVAM with GD and HD, as well as simulants. The previous work was preliminary but it was used for selecting the material for final use in garment systems.

Testing of the fabric swatches focused on the reactivity of the solid materials, either at ambient humidity or exposed to high humidity in a sealed humidity chamber. Kinetic analyses of the rates of G agent decomposition were followed by the methods of solids NMR (high resolution magic angle spinning, HR-MAS). A P-31 NMR probe was employed to detect reaction products for the G agents. The NMR technique has been used to follow the reaction of the G-agent simulant diisopropyl fluorophosphate (DFP), which was used at NSRDEC as a substitute for GD.

The measurement of hydrolysis rate of DFP and GD vapor by a humidity-conditioned polyvinylamine-co-vinyl alcohol (PVAm) membrane was done using material supplied by Natick SRDEC. Exposure of the material to agent was done using a vapor exposure to test the resistance to vapor. The copolymer was commercially available from Celanese, called Erkol™ M12, and it has been under development to provide additional chemical protection within a layered protective fabric system through the ability of this copolymer to hydrolytically break down organophosphorus compounds such as pesticides and other nerve agents. The Erkol™ M12 copolymer has a composition of 12 mol% amine with a molecular weight range around 80 -140 kDa. Another copolymer available for membrane development is Erkol™ L12, or the low molecular weight copolymer of 30-35 kDa. The Erkol copolymer forms a pH 12 solution in water and functions as Lewis base when hydrated.[6]

GD and DFP Reactions

The hydrated PVAm film, containing 20% glycerol, was found to completely deplete and decompose a two-fold excess of DFP vapor (peaks -8 and -12 ppm) within 24 h, as shown in Figure 14.

For comparison, a polyvinyl alcohol film (submitted as a non-reactive control) was exposed to 10 µL of DFP, in vapor form, for three hours. Following the exposure the P-31 NMR spectrum showed 63% of the DFP remaining, while the remainder decomposed to the DFP-acid. This percentage decreased to 53% after one day, and 42% after two days. These results suggest that a nonreactive, hygroscopic polymer contains enough adsorbed water to effect a hydrolysis reaction with DFP, depleting half of the contaminant within one day of exposure.

Crosslinked PVAm (M12) film was exposed to 10 µL of the DFP, in vapor form, for 3 h. The liquid agent wasn't deposited on the polymer as liquid, but it was allowed to evaporate and react with the polymer as vapor. The initial NMR spectrum showed just 8% of the DFP remaining, and no DFP was detected after one day. A follow-up experiment 12 days after the initial exposure showed no further change in the sample. A minor unidentified phosphorus-containing product appeared at -7.8 ppm.

A crosslinked M12 film containing 20% glycerol exhibited good initial reactivity against DFP, with the first spectrum showing 12% of the DFP remaining. After an additional 2 h of reaction time the percentage had dropped to below 7%. After one day, no detectable DFP remained. This film was also exposed to GD, and showed 10% of the GD remaining after 3 h and 0% GD after 24 h.

The crosslinked M12 film was also exposed to vapor from 5 µL of GD liquid. The initial NMR spectrum (after 3 h) showed no detectable GD, and showed a strong GD-acid signal. Spiking the sample with 5 µL of a triethyl phosphate internal standard showed that 0.042 mg of GD-acid was present on the film relative to the internal standard. Only 0.8% of the liquid GD in the container had migrated as vapor to the film and been absorbed. Although this experimental method showed the film was reactive and gave promising results, this quantitative measurement indicated that the method wasn't as quantitative as other methods in terms of the amount of exposure to agent, so the method wasn't used further.
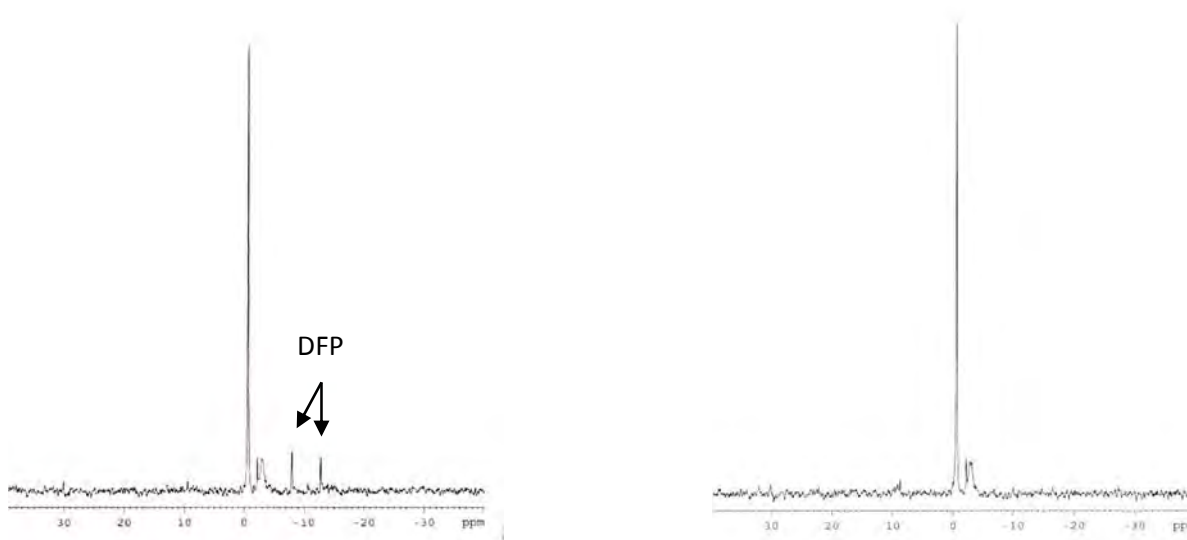

Figure 14: P-31 NMR Spectra of DFP Depletion in PVAm after 3 h (left spectrum) and DFP Depletion after 24 h (right).

HD Reactions

M12 with POM (polyoxometallate additive used as an oxidizer[7]) was tested against a direct liquid deposition of HD. No immediate reaction was noted. Over a period of days the signal decreased and broadened, but no product peaks were detected. This may indicate that either the HD or the products of a reaction of HD were tightly bound to the material, and avoiding detection by HR-MAS NMR. Thermal desorption GC-MS studies were initiated in an effort to clarify this situation.

Reactions of M-12 films with HD were studied by HR-MAS NMR. The use of C-13-labeled acetophenone as an internal standard aided the analysis, and has provided a means of tracking the amount of HD remaining and as a QC standard, without reliance on the observation of reaction products. This has helped solve a significant concern that the reaction products may be tightly bound to the solid surface, and not detectable by HR-MAS.

The spectrum in Figure 15 shows an expanded spectrum of the fully reacted material, ten days after the HD spike. The presence of overlapping peaks makes it difficult to detect small amounts of mustard in the sample, but it appears that all of the HD has reacted at this point. Similar reactivities were observed in the M12+HBP/POM material and the M12+HBP without POM. Experiments where the sample was opened to increase the amount of oxygen available to the POM did not seem to increase the reaction rate noticeably.

These results were good indications that the PVAM type of polymer could be purchased commercially which has significant reactivity toward CW agents. Additional testing of permeation with simulants was done at Natick, as well as measurement of water permeation.[6]
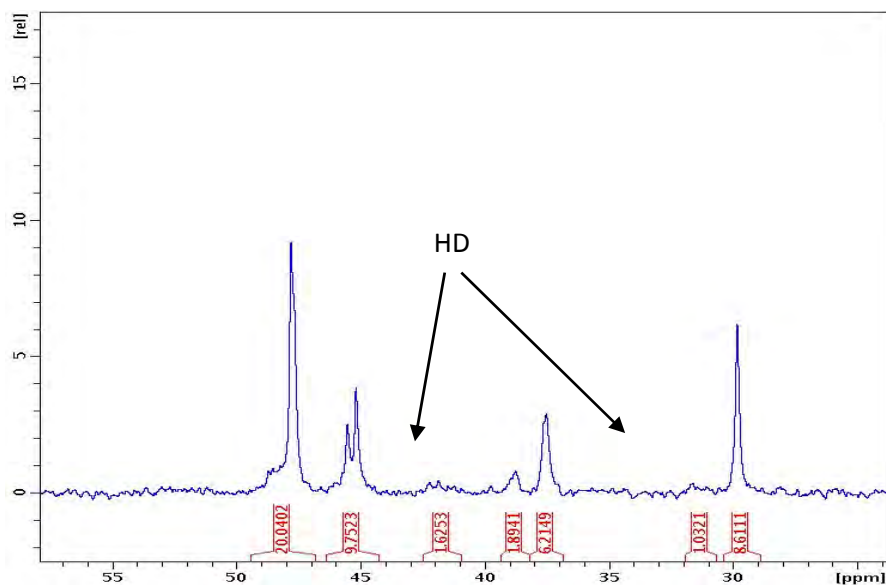

Figure 15: Final Spectrum of Reaction of HD on M12 PVAM Fabric, Showing that No HD is Remaining. Arrows indicate the expected location of HD C-13 peaks.

6.0   RESULTS FOR WICK PVAM SAMPLES

Two samples of PVAM fabric were received at ECBC from Natick on 16 Sept. 2011:

- PVAM-WickBL (PVAM-wicking fabric, black side out)
- PVAM-WickGR (PVAM-wicking fabric, gray side out)

These polymer films were obtained for an experiment to determine if there was an optimal kind of hydrophilic vs. hydrophobic surface. The surfaces were treated to produce wicking of the water to the outside of the garment. It was hypothesized that the reaction with agent would change if the water is absorbed into a particular side of the polymer, either inside toward the wearer or outside toward the environment. The difference could also affect the comfort of the wearer. The films were also used to

determine the effect of excess water compared to the films that were only humidified by water vapor exposure.

Samples were humidified at 80% relative humidity in a Thunder Scientific humidity chamber for at least overnight, until a constant weight was obtained. Some samples were analyzed as is after the humidification. Other samples received additional water, either by pipeting an extra 10 µL of liquid water, or by adding excess water until saturated, followed by blotting of the fabric with a Kimwipe paper towel to remove excess liquid. By weight, the extra water was 50 mg of water on 1.6 cm^2 (35-40 mg) of fabric.

Reactivity of the samples was measured by NMR in two ways. Selected samples were analyzed for kinetic information using solids (HRMAS) NMR. Samples of fabric with the specified amount of water were spiked with 1 µL of reagent (DFP or GD). Spectra were collected periodically to determine the amount of agent or degradation products. Samples were run on a Varian INOVA 400 narrow bore NMR using P-31 detection with a Doty HRMAS probe.

Samples from the kinetic studies, as well as other samples that reacted in the hood without kinetic studies, were extracted with solvent after a specified time. For DFP reactions, samples were extracted with DI H$_2$O after 24 h. For GD reactions, samples were extracted with methanol after 5 h. 10% D$_2$O was added as a lock solvent. Extracts were analyzed by liquids NMR on a Bruker Avance 300 NMR using P-31 detection.

DFP Results

A comparison was done between PVAM-WickBL (black side) and PVAM-WickGR (gray side) reacted with DFP at 80% RH using solids NMR. In both cases, the NMR peaks became broad in the course of 24 h reaction. It was difficult to obtain an acceptable peak integral, so kinetic data couldn't be obtained. The qualitative performance of the two samples appeared to be very similar. After 23-24 h the samples were extracted with DI water. Spectra were collected using liquids NMR. The spectra are shown in Figure 16, and the amount of reaction for the two samples is very similar.

Another comparison was done to vary the water saturation of the fabric. One sample of PVAM-WickBL (black side) was saturated with water and reacted with DFP, using solids NMR. The amount of added water was 49.2 mg on a fabric sample of 1.6 cm^2. The NMR peaks were much narrower and were easily integrated, compared to the 80% RH sample. Another sample was from 80% RH equilibrated fabric that received an additional 10 µL of liquid water (10.6 mg by weight on 1.44 cm^2). This sample was reacted at room temperature in a hood but not monitored using solids NMR. The performance of the two samples was similar. After 24.5 h, the samples were extracted with DI water. Spectra were collected using liquids NMR. The spectra are shown in Figure 17, and the amount of reaction for the two samples is very similar. Reactivity is much higher than the samples that were treated at 80% RH. Some remaining DFP can still be observed in the spectra.
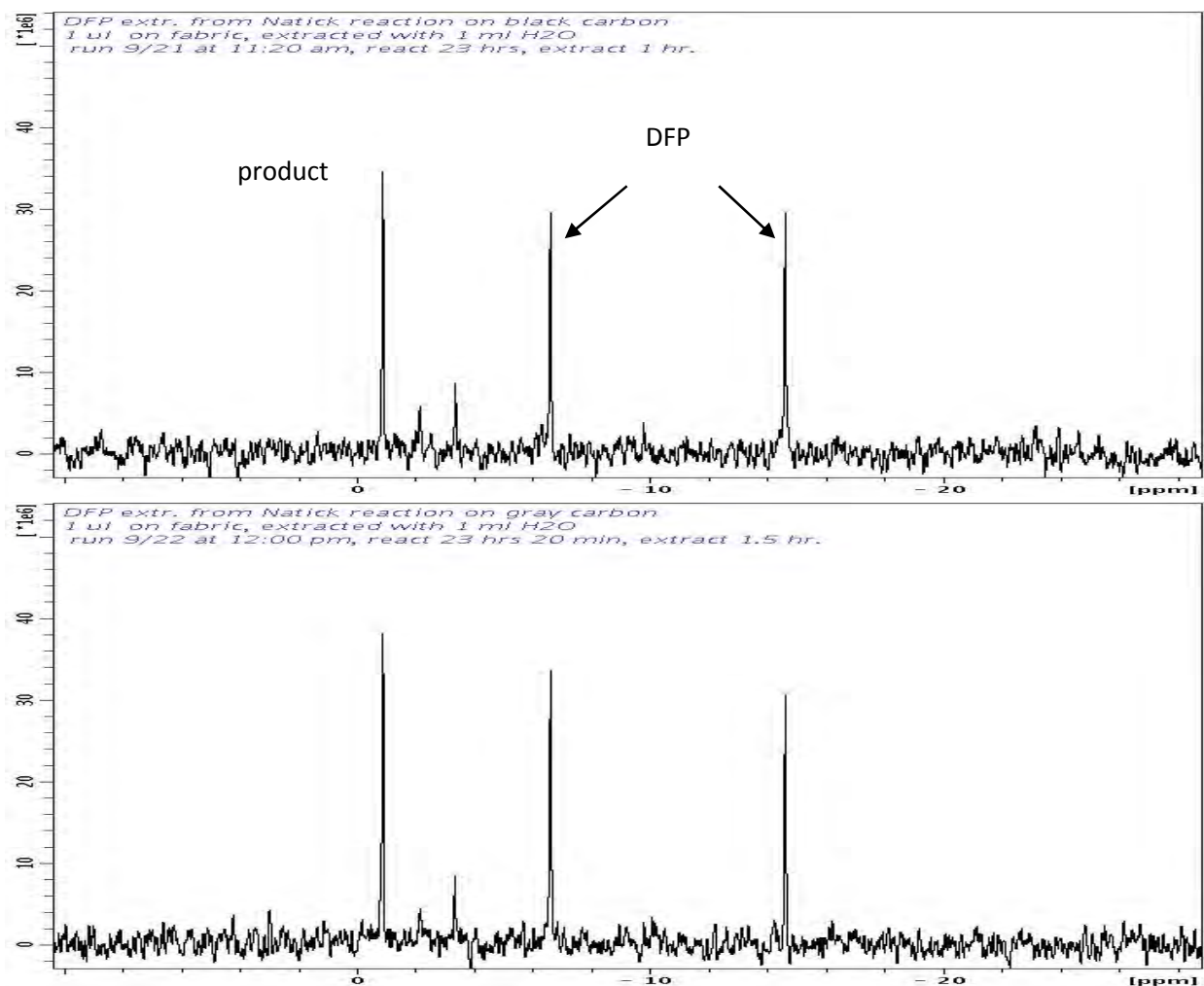
Figure 16: Comparison of Liquids NMR Spectra of Extracts of PVAM-WickBL (top panel) and PVAM-WickGR (bottom panel) After Reaction with DFP for 23 h and Extraction in DI Water. Results show the reactivity is very similar.
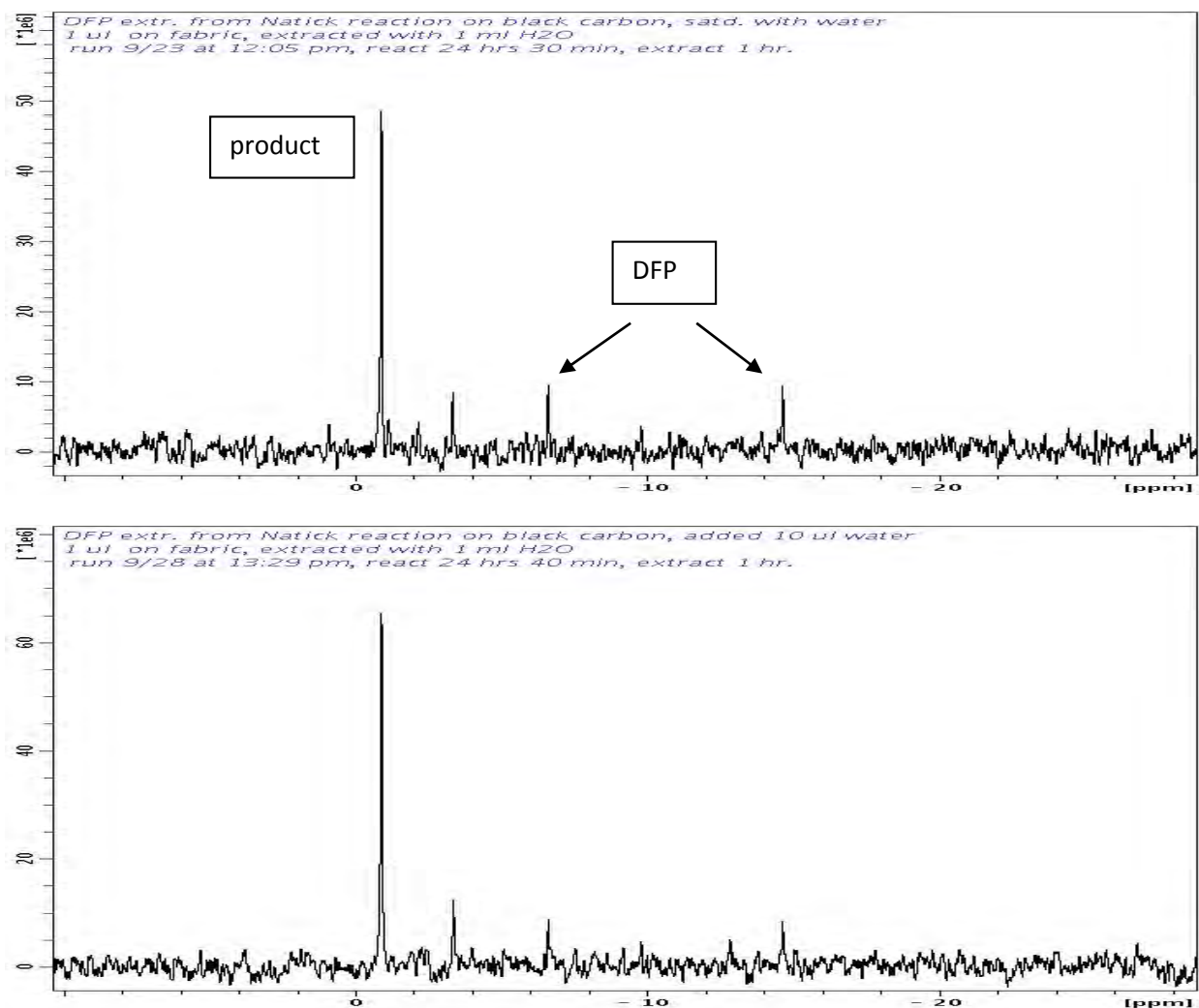
Figure 17: Comparison of Liquids NMR Spectra of PVAM-WickBL Saturated with Water (top panel) and with Only 10 µL of Added Water (bottom panel) After Reaction with DFP for 24.5 h and Extraction in DI Water.   Results show the reactivity is very similar and much higher than the samples that had 80% RH.

Another comparison was done on fabric that was saturated with DI water to fabric saturated with artificial perspiration. One sample of PVAM-WickBL (black side) was saturated with water and reacted with DFP, using solids NMR (same as shown in Figure 17). Another sample of PVAM-WickBL (black side) was saturated with artificial perspiration in the same way and reacted with DFP, using solids NMR (with 56.1 mg of liquid added to 1.4 cm^2 of fabric). The NMR peaks were easily integrated. The performance of the two samples was similar. After 24.5 h, the samples were extracted with DI water. Spectra were collected using liquids NMR. The spectrum for the water sample is shown in Figure 17, and the spectrum for the perspiration sample is shown in Figure 18. The amount of reaction

for the two samples is very similar. The kinetic plot as a function of time is shown in Figure 19. Some remaining DFP can still be observed in the spectra.
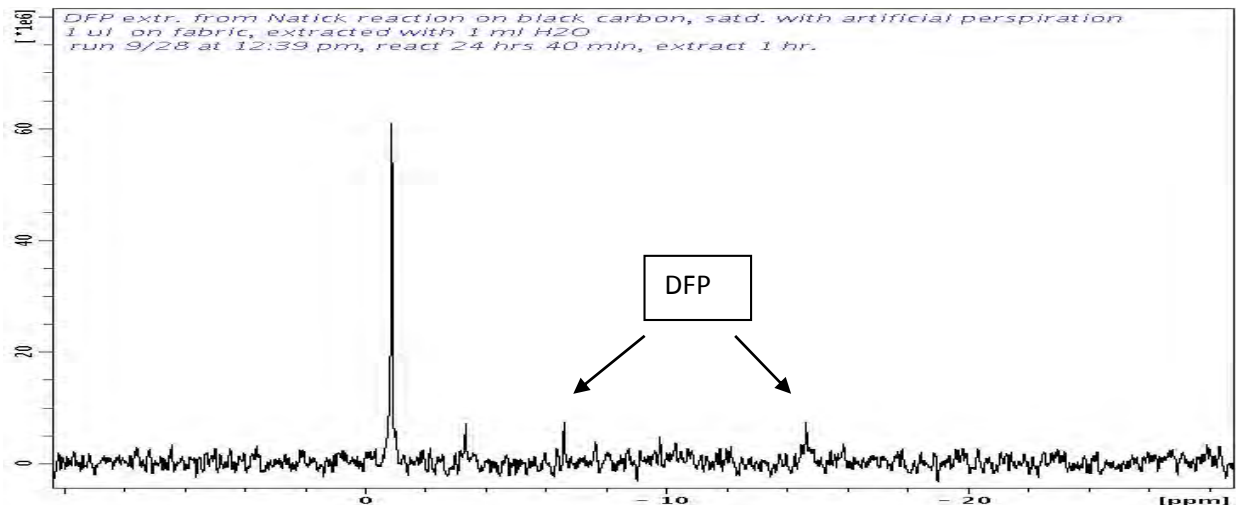

Figure 18: Liquids NMR Spectrum of PVAM-WickBL Saturated with Artificial Perspiration after Reaction with DFP for 24.5 h and Extraction in DI Water.
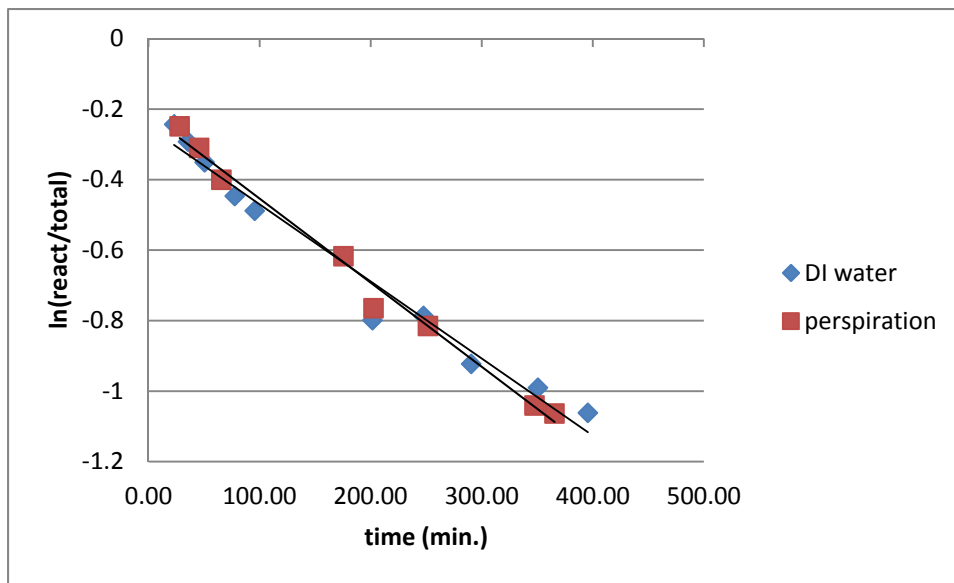

Figure 19: Comparison of the Solids NMR Kinetic Plot of PVAM-WickBL Saturated with Water vs. Perspiration During Reaction with DFP.   The reaction half life for water is 317 min.

GD Results

Another comparison was done on the reactivity of GD with varying amounts of water saturation of the fabric. One sample of PVAM-WickBL (black side) was saturated with water and reacted with GD, using solids NMR. The NMR peaks were easily integrated. The amount of added water was 48.7 mg on a fabric sample of 1.4 cm^2. Another sample was from 80% RH equilibrated fabric that received an additional 10 µL of liquid water (10.3 mg by weight on 1.4 cm^2). The third sample was equilibrated at 80% RH with no additional water. The final two samples reacted at room temperature in a hood but were not monitored using solids NMR. After 5 h, the samples were extracted with methanol. Spectra were collected using liquids NMR. The spectra are shown in Figure 20. The amount of reaction for the first two samples is very similar, but the third sample (80% RH) is slower.

Overall, the rate of reaction for GD is at least 6 times faster than for DFP under the same conditions. These films were not studied with HD.
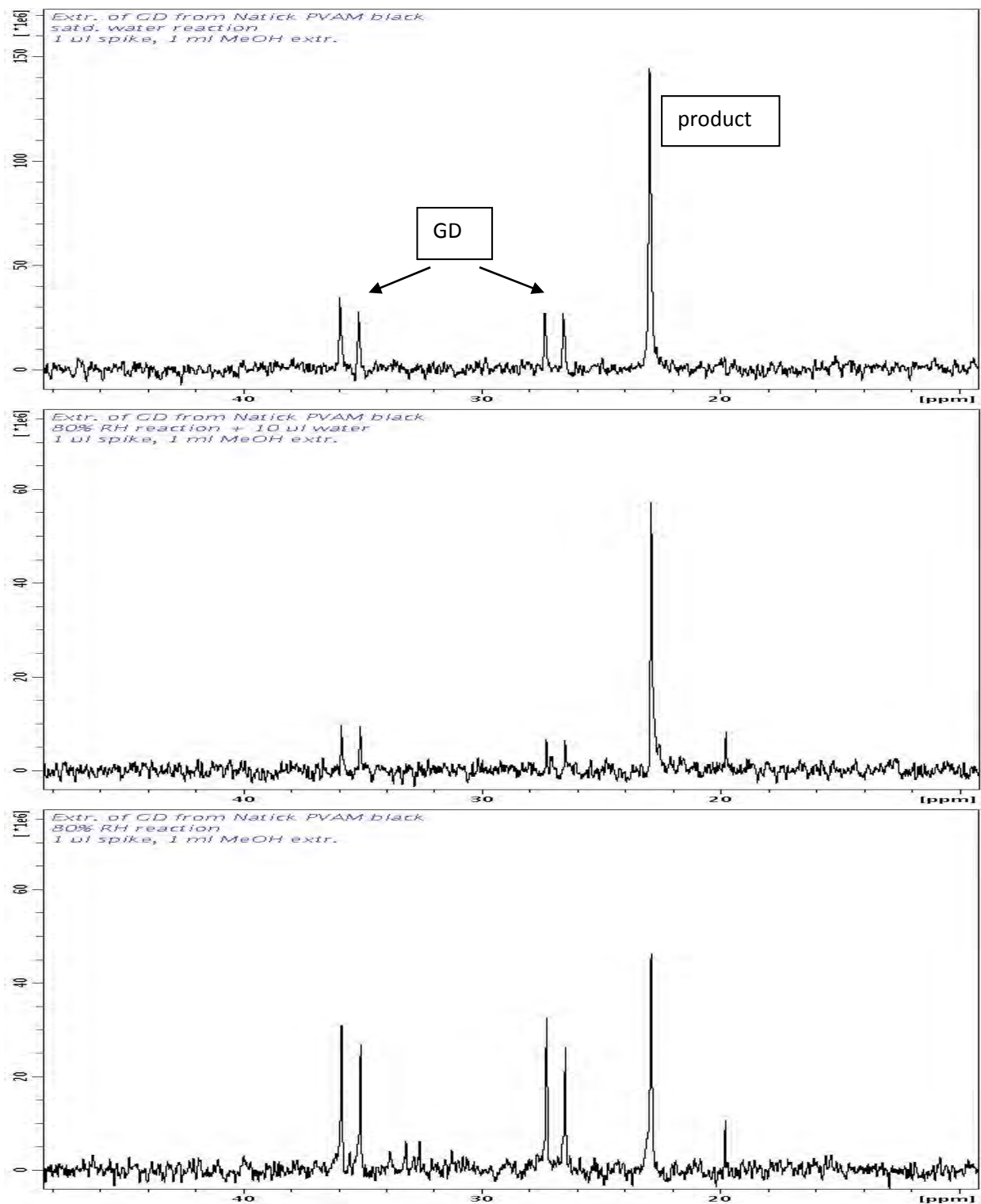
Figure 20:   Comparison of Liquids NMR Spectra of PVAM-WickBL Saturated with Water (top panel),
with 10 µL of Added Water (middle panel), and at 80% RH (bottom panel) After Reaction with GD for 5
h and Extraction in Methanol.   Results show the reactivity is slower for the samples that had 80% RH.

7.0   FUTURE STUDIES

There are some additional questions that could be studied in more detail. The reactivity of the materials with GD is well understood, because the NMR technique has allowed the reaction of GD and the products that are formed to be characterized in most cases. The results indicate that the threshold goal is easily achieved, but more work is necessary to achieve the objective goal.

The reactivity with HD is more difficult to characterize than GD because of the reaction of HD with the polymer to form high molecular weight adducts, which are difficult to detect. Some of the uncertainty about reaction kinetics can be resolved by studying the reaction with lower molecular weight analogs. This information will not resolve questions about the material interactions of HD with the polymers.

It may be helpful to develop another experimental method that can identify reaction of HD on the polymer. One possible method is Raman spectroscopy, which can probe the reactivity of material from changes of the molecular vibrational modes on the surface without the necessity of removing material from the surface. This technique may be able to observe changes in the vibrations involving the S atom after reaction.

The work that has been done on PVAM may be continued in an effort to optimize the material from a commercially available film to a custom made, optimized film. Some work that may be done in this regard includes:

- Use of PVAM as a hydrogel material such that the permeation can be changed by controlling the pH to increase the protection if a threat is detected;
- Measurement of the PVAM reactivity at low pH values;
- Chemical modification of the PVAM with other reagents to increase the reactivity or change the surface properties;
- Variation of the surface treatment to provide more wettability for HD.

8.0   REFERENCE

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