



U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND CHEMICAL BIOLOGICAL CENTER

ABERDEEN PROVING GROUND, MD 21010-5424

DEVCOM CBC-TR-1797

Evaluation of Chemical Agent Resistance of Polysiloxane-Based Films and Coatings

**Thomas P. Pearl, Brent A. Mantooth, Janlyn H. Eikenberg,
Mark J. Varady, Anne Y. Walker
RESEARCH AND TECHNOLOGY DIRECTORATE**

**Kristian M. Van de Voorde
OAK RIDGE INSTITUTE FOR SCIENCE AND EDUCATION
Oak Ridge, TN 37830-8007**

**Erick B. Iezzi
Eugene Camerino
NAVAL RESEARCH LABORATORY
Washington, DC 20375-0001**

**Melissa L. Sweat
DEFENSE THREAT REDUCTION AGENCY
Ft. Belvoir, VA 22060-6201**

**Christopher M. Stafford, Jeremiah Woodcock
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
Gaithersburg, MD 20899-0003**

**Melissa S. Hulet
LEIDOS, INC.
Reston, VA 20190-5640**

**Adam R. Hinkle
DCS CORPORATION
Belcamp, MD 21017-1561**

October 2022

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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 h per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) XX-10-2022		2. REPORT TYPE Final		3. DATES COVERED (From - To) Oct 2019–Sep 2021	
4. TITLE AND SUBTITLE Evaluation of Chemical Agent Resistance of Polysiloxane-Based Films and Coatings				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Pearl, Thomas P.; Mantooth, Brent A.; Eikenberg, Janlyn H.; Varady, Mark J.; Walker, Anne Y. (DEVCOM CBC); Van de Voorde, Kristian M. (ORISE); Iezzi, Erick B.; Camerino, Eugene (NRL); Sweat, Melissa L. (DTRA); Stafford, Christopher M.; Woodcock, J. (NIST); Hulet, Melissa S. (Leidos); Hinkle, Adam R. (DCS)				5d. PROJECT NUMBER CB10443	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Director, DEVCOM CBC, ATTN: FCDD-CBR-PD, APG, MD 21010-5424 Oak Ridge Institute for Science and Education; 1299 Bethel Valley Road, Oak Ridge, TN 37830-8007 U.S. Naval Research Laboratory; 4555 Overlook Avenue, SW, Washington, DC 20375-0001 Defense Threat Reduction Agency; 8725 John J. Kingman Road, MSC 6201, Fort Belvoir, VA 22060-6201 National Institute of Standards and Technology; 100 Bureau Drive, Gaithersburg, MD 20899-0003 Leidos, Inc.; 11951 Freedom Drive, Reston, VA 20190-5640 DCS Corporation; 4696 Millennium Drive, Suite 450, Belcamp MD 21017-1561				8. PERFORMING ORGANIZATION REPORT DEVCOM CBC-TR-1797	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Defense Threat Reduction Agency, 8725 John J. Kingman Road, MSC 6201, Fort Belvoir, VA 22060-6201				10. SPONSOR/MONITOR'S ACRONYM(S) DTRA	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT: (Limit 200 words) Protective coatings or paints are required for all tactical U.S. Marine Corps and Army platforms including ground, aviation, and related support assets. These coatings are likely to be contaminated in a chemical warfare agent release; therefore, agent resistivity is a fundamental attribute for development of a coating system. The chemical agent resistance method (CARM) was developed to quantify agent sorption into the material. Through development of the CARM, it was recognized that multiple aspects of the coatings are not well understood, and work has now focused on understanding how coating chemistries and morphologies affect agent resistance. To better understand how to optimize coatings, researchers investigated chemical permeation and retention for coating materials using a family of polysiloxane-based coatings as a model coating system with adjustable materials properties. New techniques were implemented to quantify, understand, and control transport of chemical agents in coatings to enable the reformulation and implementation of new, superior coating systems that are applicable to topcoats or overcoat configurations. This knowledge will be used to establish a scientific basis for advancing future formulations with optimized chemical resistance.					
15. SUBJECT TERMS Polymer Coating Contamination Bis(2-chloroethyl)sulfide (HD) Chemical warfare agent Material Protection [2-(Diisopropylamino)ethyl]-O-ethyl methylphosphonothioate (VX)					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 102	19a. NAME OF RESPONSIBLE PERSON Renu B. Rastogi
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (410) 436-7545

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PREFACE

The work described in this report was authorized under project no. CB10443. The work was started in October 2019 and completed in September 2021.

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This report has been approved for public release.

Acknowledgments

The authors acknowledge the following individuals for their hard work and assistance with the execution of this technical program:

- Dr. Charles Bass and Dr. Bernadette Higgins (Defense Threat Reduction Agency Joint Science and Technology Office; Fort Belvoir, VA) and
- Members of the U.S. Army Combat Capabilities Development Command Chemical Biological Center Decontamination Sciences Branch (Aberdeen Proving Ground, MD) for their efforts in performing this study.

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EVALUATION OF CHEMICAL AGENT RESISTANCE OF POLYSILOXANE-BASED FILMS AND COATINGS

1. INTRODUCTION

The objective of this work was to quantify, understand, and control transport of chemical agents in protective coatings to enable the reformulation and implementation of new, superior coating systems that are applicable to topcoats or overcoat configurations. Several parallel efforts were undertaken to characterize chemical transport in coatings including collaborations among the U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC; Aberdeen Proving Ground, MD), the U.S. Naval Research Laboratory (NRL; Washington, DC), and the National Institute of Standards and Technology (NIST; Gaithersburg, MD). A systematic investigation was performed to elucidate the role of key coating constituents, including binders, pigments, flattening agents, and associated additives, in determining chemical resistance. Both current and upcoming coating technologies were part of this work. A set of experimental and computational tools provides information on mass transport mechanisms, spatial distribution of solids suspended in the polymer matrix, chemical interactions between coatings components and absorbed chemicals, and the role of surface and bulk layer morphology on chemical retention. The knowledge gained from these efforts is foundational for the development of new coating formulations that should generate superior chemical resistance.

To date, necessary materials characteristics are insufficiently understood to produce advanced coatings technologies with enhanced agent resistance as a function of use or application. Coatings used on military assets, primarily topcoat layers, have been shown to absorb and subsequently release contaminants (with chemical specificity as a function of coating type), which poses a challenge for hazard mitigation, including decontamination and protection. Initial efforts to improve agent resistance in coatings or overcoats have demonstrated that researchers currently lack the scientific foundation to identify and tune the system. *The key formulation or polymer interactions that influence agent resistance must first be identified to direct formulation efforts.* The goal of this work was to gain knowledge to contribute to the formulation of more resistant coatings, including topcoats or overcoat polymers. Past studies have focused primarily on paint variants across multiple formulations and pigmented systems. In this work, researchers investigated how key formulation components influence chemical or agent sorption. Ideal model polymer systems were studied to explore the ways in which the formulations could be tuned to optimize resistance properties. Model polymer composites have also been established and studied so that the role of solids suspended in polymer binders, especially the introduction of buried interfaces on mass transport and retention mechanisms, could be determined.

One initial objective was to determine the combinations of polymer binders and solids relevant to coatings that most significantly influence chemical penetrant sorption. To build the formulation rules, it was anticipated that several types of characterizations would occur, including but not limited to the following: (1) penetrant–polymer interactions (e.g., sorption into pure polymer), (2) polymer–solid interactions (e.g., how does the polymer interface to solids), and (3) penetrant–polymer–solids interactions (e.g., sorption into polymer composites). Each

interaction was probed using different techniques to elucidate the mechanisms or interactions driving the observed responses. Researchers first sought to understand how various penetrant chemicals sorbed into a pure polymer; they then analyzed how the incorporation of specific solids at different loadings influenced penetrant chemical sorption.

The principal material focus was a family of polysiloxane (PS)-based polymers developed by NRL for protective coatings formulations. Measurement of retention as a function of polymer structure, inclusion of cross-linking additives, and incorporation of solids were used to determine whether there are prevailing trends or specific types of mechanical properties and chemical interactions that need to be accounted for and controlled to promote mass transport resistance for different contaminants. This polymer system was chosen for use in protective coatings to allow for maximum synthetic flexibility and sample preparation options so that different contributors to agent retention could be assessed. Advancements in coatings formulations require collaboration with a coatings material formulator who has a perspective on how to systematically test and assess the impact of multiple interrelated effects, including the roles of binders and solids chemistry, relative abundance of ingredients, and other process factors.

2. BACKGROUND

The DEVCOM CBC Decontamination Sciences Branch (DSB) previously worked on agent retention mechanisms for paints and their constitutive polymers, particularly pertaining to polyurethane (PU)-based coatings systems.¹⁻⁷ DEVCOM CBC and the U.S. Army Research Laboratory (ARL; Aberdeen Proving Ground, MD) have collaborated on the development of methods to assess chemical resistance in parallel with exploring what critical paint material properties and components are responsible for allowing chemical ingress and retention. Although it is possible to quantify overall agent retention for materials like paint coatings (e.g., through use of the chemical agent resistance method [CARM]), the understanding necessary to formulate more resistant materials is missing. In the past, attempts to tune engineered formulations while closely adhering to comprehensive performance specifications have not been completely successful (i.e., the trade space within a coating formulation can be very limited for technologies that have multiple competing performance criteria).

The work done to date illustrates that many fundamental scientific issues must be addressed to control mass transport and retention for agents in polymeric materials, including composites. Chemical interactions with coatings materials and, therefore, resistance behaviors are typically agent-specific; certain chemicals are more difficult than others to treat. Furthermore, in some cases, inclusion of solids in polymer matrices can significantly decrease agent resistance (i.e., pure polymer can be far more resistant than polymer composite). For example, work on chemical transport in PU composites suggests that the interfaces between solids and the host binder matrix are most responsible for aggregating or facilitating chemical ingress; however, some PS systems, as reported herein, do not seem to exhibit significant changes in agent retention with the introduction of solids.

As a result of this work, DEVCOM CBC has identified the following knowledge and research capability gaps that must be addressed regarding agent retention associated with coatings materials:

- Formulation optimization rules do not exist and are necessary for producing agent-resistant protective coatings.
- A suitable polymer composite model system to represent physicochemical environments in coatings materials has not been established; therefore, the framework is not in place to make a significant technical advancement.
- Direct correlations between material properties for polymeric coatings and chemical mass uptake for agent contamination have not been established.
- Coatings formulator expertise is needed for tuning and probing chemical interactions at the surfaces and interfaces of coatings materials.

2.1 Factors Governing Mass Uptake in Paint Coatings

Agent resistance for a paint coating is represented by the retention of chemicals by the paint coating material after chemical exposure. The degree of retention can be influenced by many chemical–material interactions and mass uptake pathways, including the strength of adsorption on the material surface, the entrapment of liquid-phase chemical species in corrugated surface morphology, and the rate and extent of absorption into the material bulk. The mechanisms responsible for absorption into these coatings can include porous imbibition^{8–13} and solution-diffusion, which can be broadly classified as Fickian (controlled by rate of motion of penetrant molecules^{14,15} or non-Fickian (controlled by polymer structural relaxation).¹⁶ By measuring the absorption as a function of contamination duration, it is possible to learn the mechanisms responsible for absorption into a coating. Understanding these mechanisms is key to identifying the formulation attributes that should be optimized to minimize agent retention. The particular mechanism responsible for absorption is a function of the coating morphology, polymer properties, dispersed particle characteristics, and the way polymer structure changes with the presence of particles. The main factors for agent retention in coatings materials can be categorized as follows:

- solubility: thermodynamics of dissolution of agent tuned by polymer binder functionality (e.g., Hansen solubility, Hildebrand);
- transport rates: type and magnitude of agent diffusivity in polymer binder matrix tuned by polymer structure and cross-linking;
- permeation: contribution of polymer–solid interfaces to agent uptake or permeation, tuned by functionalization of solids to optimize interfacial binding within a composite; and
- surface adhesion: influence of material surface functionality and morphology in liquid agent adhesion and entrainment.

The overall objective of this effort was to develop a systematic understanding of the relationship between ideal polymers and polymer composites (Figure 1) that can inform how the physicochemical environment in polymer-based materials influences the absorption of penetrants or agents. Paint coatings relevant to this work are designed to achieve a wide array of performance specifications, and these criteria are met as a function of a careful balance of

polymer and solids. There is a fundamental knowledge gap in understanding how incorporation of solids influences transport in polymer composites. To overcome this knowledge gap, researchers must first investigate ideal polymers and then determine how changing the solid content, particle size, surface modification, and other characteristics change the transport properties of the overall composite to inform future coatings formulation efforts. It is anticipated that the addition of solid particles will disrupt the binder structure near the particle–binder interface, and this interface may significantly influence chemical transport. The nature and extent of the interface may be dependent on the chemical functionality of the particle, the use of surfactants, and how these interface with the binder matrix.¹⁷ Furthermore, it is recognized that percolation effects exist (i.e., critical solid–particle loading levels where transport can be significantly enhanced).¹⁸

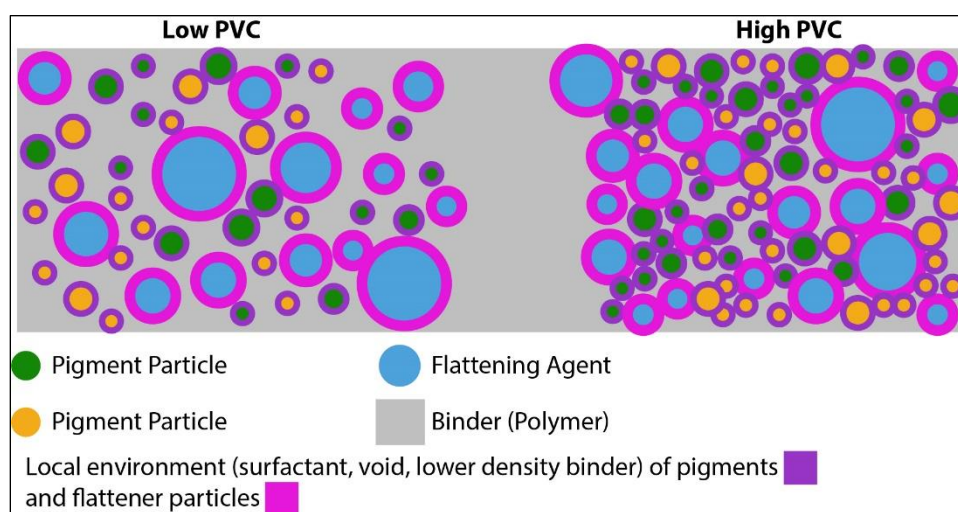


Figure 1. Example solid loading in a polymer composite. As particle loading is increased, the local interfaces may interact and influence mass transport in the composite. PVC, pigment-to-volume concentration.

Coatings are not the only technology for which the role of included solids in a polymer binder system must be considered with regard to the mass transport of penetrating chemicals. In a class of materials known as mixed-matrix membranes (MMMs), solids are incorporated to modify the permeability and chemical selectivity of a composite polymer membrane. These polymers have been studied for decades, resulting in a better understanding of chemical interactions and how solid–binder interactions influence transport.^{19–24} In these cases, the particle surface area, porosity, size, hydrophobicity, and fraction fill volume (i.e., loading) can influence the permeability of penetrant species.²⁵ The inclusion of impermeable fillers can (1) create obstructions, thereby increasing tortuosity and decreasing diffusivity or (2) induce high fractional free volumes and enhance diffusivity.¹⁹ Changes in effective permeability for MMMs can occur as a function of morphology associated with interfacial volume surrounding embedded particles.²⁰ The majority of MMM work focuses on high free-volume polymers and the permeation of small molecular weight gases (e.g., CO₂, N₂, etc.). Although this coatings work considers lower free-volume polymers and larger penetrating molecules, the physical mechanisms and trends of transport should be applicable.

As highlighted earlier, coatings require the inclusion of solids in binders to achieve all of their desired attributes. The disruption of the polymer binder by the inclusion of fillers or solids changes the local polymer properties. In the interfacial region (Figure 2), there may be enhanced segmental mobility and polymer free volume, which increases the solubility and diffusivity of penetrant chemicals. The opposite can also be the case; it is possible to have decreased segmental chain mobility at the interface compared to the bulk polymer. This indicates that it is possible to tune transport properties by tuning the polymer–particle interaction. Other additives (e.g., dispersants, anti-flocculant agents) may be influential in this interfacial zone as well. As particle loading increases, the composite polymer may become predominantly described by the interfacial region. The interplay of binder characteristics with the interface region of the solids is anticipated to be one of the primary factors for consideration in the development of agent-resistant coatings. With MMMs, some solids are much more influential toward transport than others, based on binder–particle intermolecular interactions. It will be important to identify what solids and binder interactions influence agent resistance for coatings.

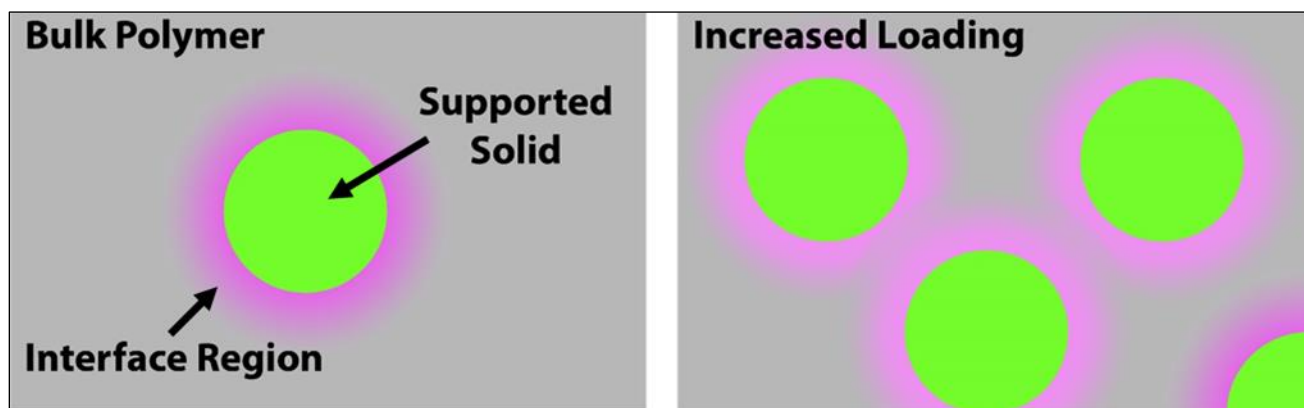


Figure 2. Illustration of solid–binder interfaces present in coating materials. With increased loading of supported solids comes the possibility of overlap of interfacial regions.

2.2 PS-Based Coatings

As part of this work, a PS-based coating developed by NRL served as a test bed for determining the relative impact of different formulation constituents and overall coatings properties on agent retention behavior. This material is part of a class of protective coatings for potential use on military assets that exhibit low gloss and adhere to other performance requirements associated with, but not limited to, corrosion resistance, color, weatherability or durability, and chemical agent resistance. An example of the structure of the organosilane polymer used in NRL’s PS coating is shown in Figure 3. Hydrolysis and condensation reactions of the polymer occur to form a cross-linked organic sol–gel network, as illustrated in Figure 4.

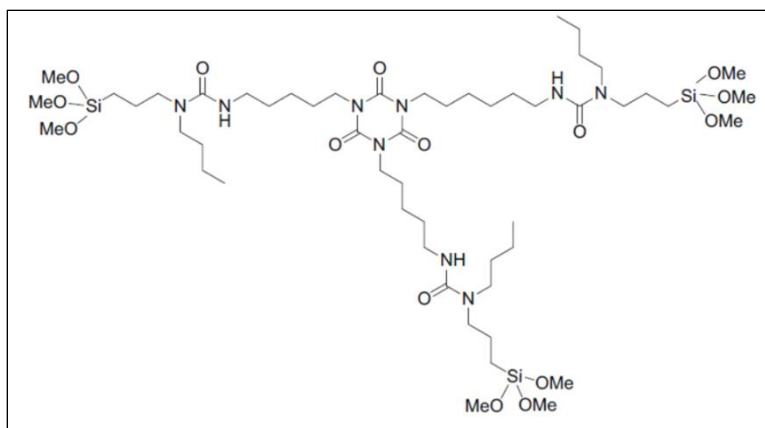


Figure 3. Structure of non-extended-chain trimethoxysilane-terminated *N*-butyl urea polymer.²⁶

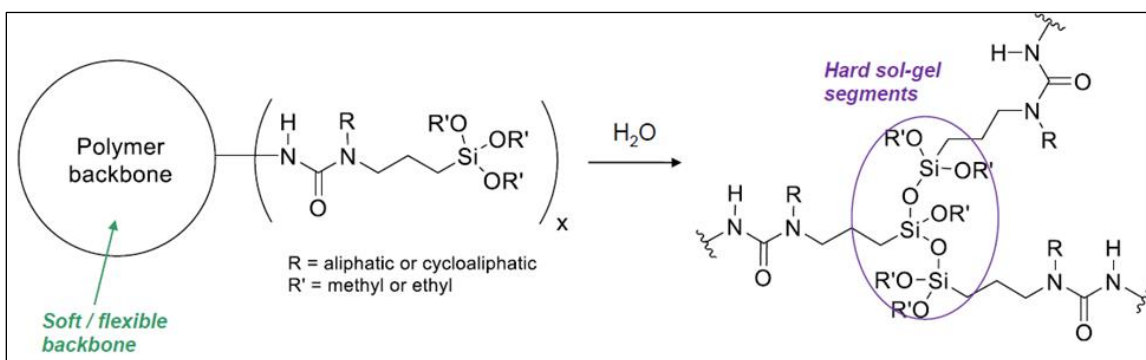


Figure 4. Generic structure for NRL's organosilane polymer and resulting network with sol-gel cross-links.

This work is not focused on comparing PS- and PU-based paint systems; however, there are advantages to using PS rather than PU in protective coating formulations:

- The Si–O bond is stronger than the C–C bonds found in all-organic coatings and improves UV oxidation and thermal stability.
- Organosilanes form sol–gel networks, which offer excellent hardness and hydrocarbon resistance.
- Processing is isocyanate-free and less hazardous or toxic.
- The chemistry of organic segments can be more easily tailored.
- NRL expertise in formulation development and polymer synthesis permits detailed investigations of agent retention as a function of material mechanical and chemical properties.

The principal reason, however, for focusing on the PS family was to leverage NRL's synthetic and formulation expertise to deconstruct an engineered paint so that the influential factors in agent retention could be explored. The objective of the work was not to optimize PS-based paint for enhanced agent resistance so much as to understand the more general formulation rules that would be important to adhere to when designing any protective coating of this type, regardless of polymer binder chemistry.

3. MATERIALS AND METHODS

3.1 Procedures for Organosilane Polymer Synthesis

3.1.1 Non-Extended Chain Polymer

An aliphatic polyisocyanate based on 1,6-hexamethylene diamine (HDI) (300.00 g, 1.554 mol isocyanate [NCO]) was added to a 4-neck 2 L, round-bottom flask under nitrogen atmosphere. This was followed by the addition of butyl acetate solvent (350.71 g) and vinyltrimethoxysilane (15.0 g) drying agent. While the solution was stirred, *N*-butyl-3-aminopropyltrimethoxysilane (369.45 g, 1.569 mol amino [NH]) was added dropwise. The temperature was kept below 60 °C. Once the addition was complete, the solution was analyzed with Fourier transform infrared (FTIR) spectroscopy to ensure all NCO (2270 cm⁻¹) was consumed. The polymer solution was 66.1 wt % solids.

3.1.2 Extended Chain Polymer

An aliphatic polyisocyanate based on HDI (400.00 g, 1.052 mol NCO) was added to a 4-neck, 2 L, round-bottom flask under nitrogen atmosphere. This was followed by the addition of butyl acetate solvent (319.81 g) and vinyltrimethoxysilane (20.0 g) drying agent. While the solution was stirred, tetraethyl 2,2'-((2-methylpentane-1,5-diyl)bis(azanediyl))disuccinate (61.54 g, 0.263 mol NH) was added dropwise, and the mixture was stirred at room temperature for 1 h. Next, *N*-butyl-3-aminopropyltrimethoxysilane (185.72 g, 0.789 mol NH) was added dropwise while the temperature was kept below 60 °C. Once the addition was complete, the solution was analyzed with FTIR spectroscopy to ensure all NCO (2270 cm⁻¹) was consumed. The polymer solution was 67.6 wt % solids.

3.2 Procedure for Formulation of Liquid Films or Coatings

Liquid films or coatings were formulated by adding the organosilane polymer to a plastic cup or metal can, followed by addition of solid particles (e.g., coloring inorganic pigments, polymeric matting agent) and subsequent high-speed mixing with a Cowles dispersion blade. The mixture was then diluted with solvent, typically butyl acetate, to form a low-viscosity formula. This was followed by the addition of additives, when applicable, including dibutyltin dilaurate as a catalyst.

3.3 Preparation of Sprayed Films for Polymers and Coatings

Materials, whether clear or filled single-component systems, were applied onto metal substrates (with or without a primer) and polyvinyl fluoride release paper to produce free films, using high-volume, low-pressure spray equipment. When materials were sprayed onto metal substrates (target thickness of 40–50 µm), either 0.5 or 2 in. diameter discs were used. Spraying on the smaller diameter discs was done using a pre-cut sheet (see Section 3.8). In other cases, polymer films were generated by spin casting onto substrates to produce very thin films (<1 µm) for quartz crystal microbalance (QCM) measurements. All polymers, associated composites, and paint formulations were produced, synthesized, and prepared by NRL.

3.4 Agent Contaminants

The agent chemical contaminants used were Chemical Agent Standard Analytical Reference Material (CASARM) grade with purity on record as obtained from either nuclear magnetic resonance (NMR) or gas chromatography/mass spectrometry (GC/MS) analysis. The chemical contaminants were obtained from the DEVCOM CBC Chemical Transfer Facility. All purity documentation was maintained by the DEVCOM CBC DSB. The agents used were GD (pinacolyl methyl phosphonofluoridate; soman), HD (bis(2-chloroethyl) sulfide; distilled mustard), and VX ((2-(diisopropylamino)ethyl)-O-ethyl methylphosphonothioate). The chemical contaminants were removed from cold storage and allowed to equilibrate to room temperature in the test location chemical surety hood immediately prior to testing. Contaminant was dispensed using a Repeater Plus pipette (Eppendorf; Enfield, CT; part number 2026020-1). Agent droplets applied to surfaces were either 1 or 2 μL for 0.5 and 2 in. panel diameters, respectively. In the case of agent vapor exposure, 5 μL droplets were used. Further details on steps for retention measurements are provided in Sections 3.5 and 3.6. To verify the mass of delivered agent for different agent droplet volumes, dose confirmation samples from repeater pipettes were collected by dispensing droplets into agent-specific extraction solvents, and agent concentration was measured by chromatography.

3.5 Agent Retention Measurements Using Direct Liquid Deposition on Surfaces

Agent retention was measured as a result of direct liquid droplet deposition on material substrates. The basic steps of the CARM are illustrated in Figure 5 for the 0.5 and 2 in. panel processes. Details associated with quantification of remaining agent (RA) are provided in Section 3.7. For 2 in. panels, a panel was placed in a plastic petri dish, and the surface of the material was exposed to a predetermined volume of liquid chemical agent. This agent-contaminated material was then covered with a plastic petri dish lid and permitted to age for a specific contamination duration under controlled temperature and relative humidity conditions. Depending on the measurement, different interaction times were used between the surface and a liquid droplet. At the end of this time, a water-rinse cycle (pre-rinse) was performed on the surface of the contaminated material (two 20 mL aliquots to the front, one 20 mL aliquot to the back), then the panel was placed in soapy water (8 mL) for 3 s followed by another water-rinse cycle (post-rinse). All water used in the rinse steps for CARM was deionized (DI) water. The soapy water solution (general purpose detergent: liquid non-ionic, water soluble, Type 1; national stock number 7930-00-282-9699) was prepared by mixing 552 μL of the soap solution per 1 L of DI water. The immersion step includes soapy water to emulate typical concept of operations (CONOPS) for pre-decontamination procedures. After the rinse steps, the panel was then extracted in 20 mL of solvent in an 8 oz glass jar with a polytetrafluoroethylene-lined cap (Scientific Specialties Service; Hanover, MD; product number 170808).

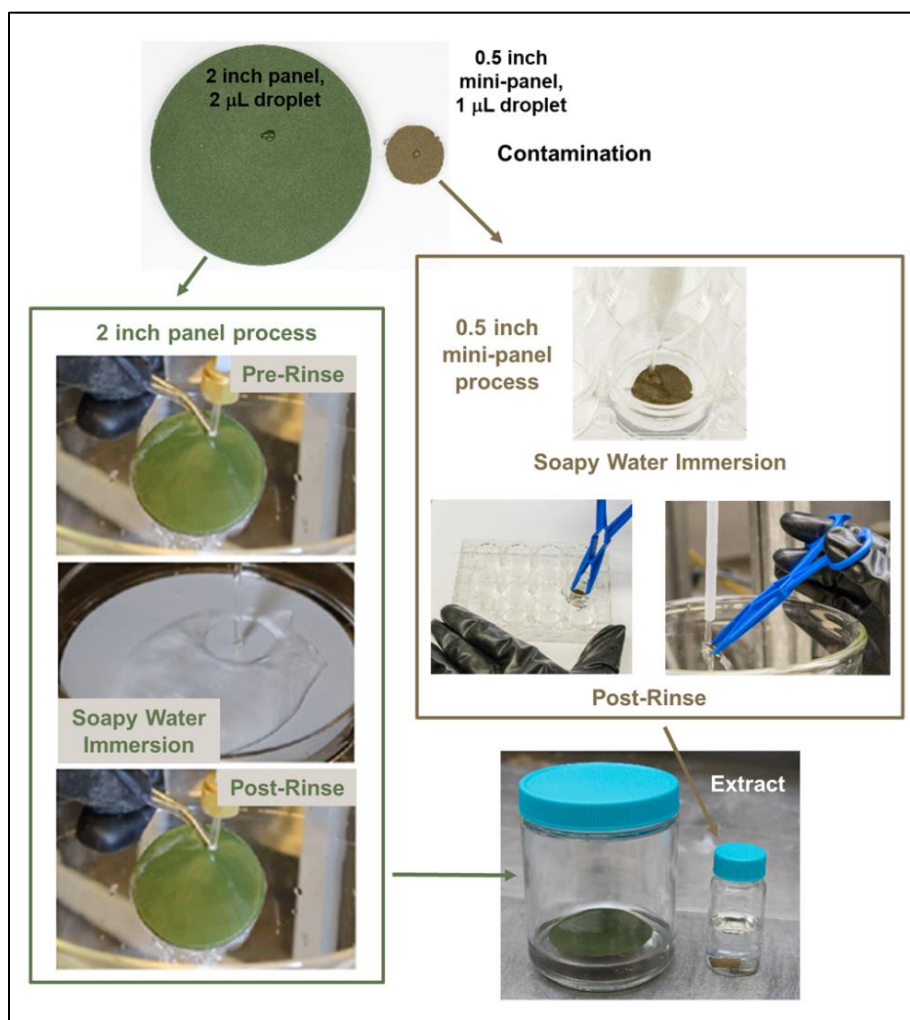


Figure 5. Steps associated with CARM for both 2 and 0.5 in. diameter panels.²⁷

For 0.5 in. diameter panels (mini-panels), certain key test parameters were modified to be close to but not necessarily to exactly match the CARM setup because the test objective was higher-throughput screening. As shown in Figure 5, for the modified version of the CARM, a 0.5 in. diameter mini-panel was placed in a polystyrene 12-position multiwell plate (Evergreen Scientific; Buffalo, NY; item number 222-8046-01F) for contamination and subsequent aging. The pre-rinse step was omitted, and 1 mL of soapy water was applied to the well containing the panel. After a few seconds of immersion in the soapy water, the panel was removed from the well, subjected to a 10 mL water post-rinse, and then was extracted in 10 mL of solvent in a 20 mL scintillation vial (Scientific Specialties Service; product number B33520). The pre-rinse step was omitted to reduce the handling burden for these panels because lifting and replacing could increase the chance of agent contamination of the storage and handling equipment. It was found that the agent was removed from non-porous materials without the pre-rinse.

3.6 Agent Retention Measurements Using Vapor Exposure to Surfaces

An alternate method of delivering agent using vapor exposure was developed to avoid the problems in parsing specific retention factors due to convolution of effects from bulk liquid exposure. Chemical mass transport from vapor exposure in polymeric thin films has been studied extensively and includes work done by the DEVCOM CBC DSB.^{3,4} For this effort, we crafted a relatively facile means of quantifying mass uptake for materials under study, specifically for the purposes of screening and performing relative comparisons, to determine whether the spectrum of material configurations would respond differently with respect to RA as a result of exposure to vapor emanating from a proximal evaporating droplet in a closed cell. This approach is similar to the measurement of water absorption in hygroscopic materials,²⁸ but instead of tracking droplet evaporation, the mass transfer to the material is measured by analysis of extraction solutions.

Figure 6 shows the key hardware and parts required to execute this measurement. Briefly, liquid contaminant droplets (5 μ L) were placed at the bottom of aluminum foil-lined wells, which were part of the base of a polystyrene well plate with an array of 12 wells. The inside of the lid of the well plate was covered in aluminum foil, and then mini-panels were affixed to the foil with a small amount of adhesive (on the uncoated side of the panel) so that the surfaces of the mini-panels faced downward, toward the bottom of each well, with lines of sight to the contaminant droplet when the well plate lid was placed on the well plate base. After the lid was placed on the base, the entire assembly was sealed with Parafilm (Bemis Company; Neenah, WI). This allowed for the collection of 12 independent vapor exposure replicates. Vapor from the evaporating droplet could adsorb and absorb into the materials coated on the mini-panels. To assess the contaminant mass uptake from vapor after exposure, the mini-panels were removed and immersed in contaminant-specific solvent. The RA mass extracted by the solvent was quantified by chromatography analysis of extraction solutions (the same processing used for CARM-style measurements for RA analysis). This method eliminates two factors that can complicate interpretation of RA results: liquid spreading and wetting effects at contamination; and variable efficacy in removal of surface-bound bulk liquid via water rinse prior to solvent extraction. A number of assumptions are built into this measurement that must be addressed if more than relative comparisons of agent absorption are to be made between materials for the same contaminant.

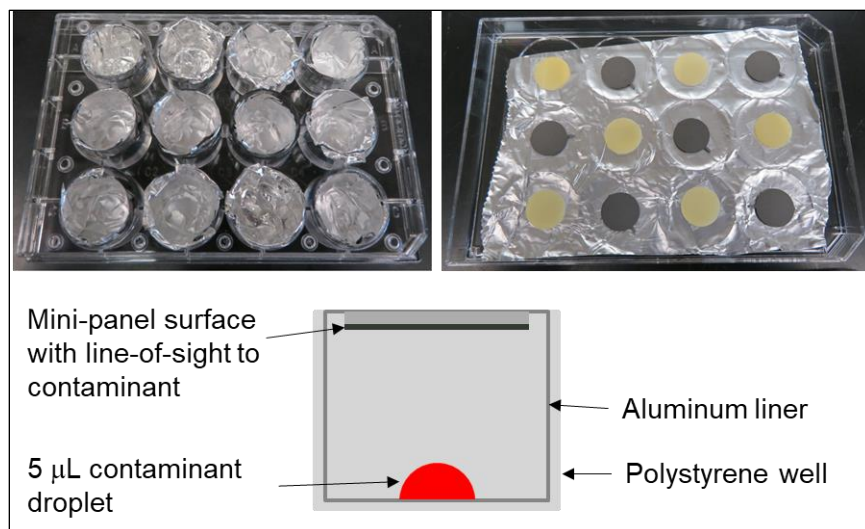


Figure 6. Execution of vapor exposure experiment for mini-panel materials. Top left: the base of a polystyrene well plate with aluminum liners; top right: the well plate lid with mini-panels affixed to aluminum foil (other side of foil is attached to inside surface of lid). Bottom: side-view schematic of mini-panels positioned above liquid contaminant in the wells of the well plate when the lid is placed on the base.

3.7 Analytical Chromatography for Agent Mass

Regardless of the exposure type, the mass of agent retained by materials was quantified using analytical chromatography. Liquid-phase extraction solutions were analyzed to evaluate material retention of chemical species. Extraction solution samples were diluted, and the analytes were quantified using GC for HD and GD (a model 6890/7890 GC system equipped with a model 5975 mass selective detector [Agilent Technologies; Santa Clara, CA]) and using liquid chromatography (LC) with MS for VX (an Agilent 1200/1290 series LC system and an Applied Biosystems [Carlsbad, CA] API 5000/5500 triple-quadrupole mass spectrometer equipped with a Turbo V ion source). Details on the use of the chromatography platforms are published elsewhere.²⁹

3.8 Utilization of Mini-Panel Sheets

The ability to generate many small panels facilitates faster screening of coatings formulations so trends in agent resistance can be evaluated. The viability of using 0.5 in. diameter panels (i.e., mini-panels) instead of 2 in. panels for higher-throughput screening was previously documented in work that stemmed from a collaboration between DEVCOM CBC and Clear Scientific (Cambridge, MA).²⁷ In that work, which sought to optimize a temporary overcoat to enhance chemical resistance for paint materials, 0.5 in. metal discs were mounted individually on a large backing material to allow for production of painted panels. Although this approach for mini-panel production ultimately met the needs of that particular program, it was evident that alternatives would be worth pursuing for future coatings work.

High-throughput screening methods are needed to facilitate the development of coatings materials designed to enhance the protection of military assets from chemical warfare agent contamination. CARM was established to evaluate chemical agent-resistant coatings used on tactical equipment. CARM quantifies the mass of agent retained by a material after a mild treatment process in which agent-resistant materials should retain minimal agent mass. Because of the form factor of the materials used and the test parameters established for evaluations, CARM is not amenable to high-throughput measurements that limit the number of materials that can be screened, especially in formulation efforts. The work that provided the rationale for fabricating sheets of mini-panels is based on the development of a method (derived from CARM) for evaluating chemical resistance for coatings-related materials. The modified CARM uses different material geometries and contamination conditions that permit a significant increase in sample throughput while producing data that can be correlated to formal CARM results. A case study involving the optimization of proprietary overcoat technologies from Clear Scientific was used to illustrate the utility of this CARM-based screening methodology.²⁷

To promote more efficient screening investigations for material development programs associated with chemical agent resistance, DEVCOM CBC produced an array of suspended, or pre-mounted but easily removable, metal discs in a fashion that was deemed to be most amenable to coating by spraying. Briefly, 1/32 in. thick cold-rolled steel was laser cut and surface orbital sanded (for deburring and minimizing sharp edges) to produce 3 × 5 in. sheets of 20 mini-panels held in place by two 0.020 in. wide stems (Figure 7). These sheets were produced by the DEVCOM CBC Advanced Design and Manufacturing, Engineering Design and Analysis Branch. The substrate cost for the mini-panels was ~\$14/sheet (\$0.70/panel, uncoated) in comparison to ~\$20/panel for 2 in. diameter panels. These sheets can be treated with a zinc phosphate conversion coating to prevent corrosion for storage or for cases where weathering testing is involved. Corrosion was still observed in some cases during the testing process, even with the conversion coating; therefore, the substrate was changed to 1/32 in. thick aluminum that did not require a conversion coating and did not exhibit corrosion for the test conditions considered here.

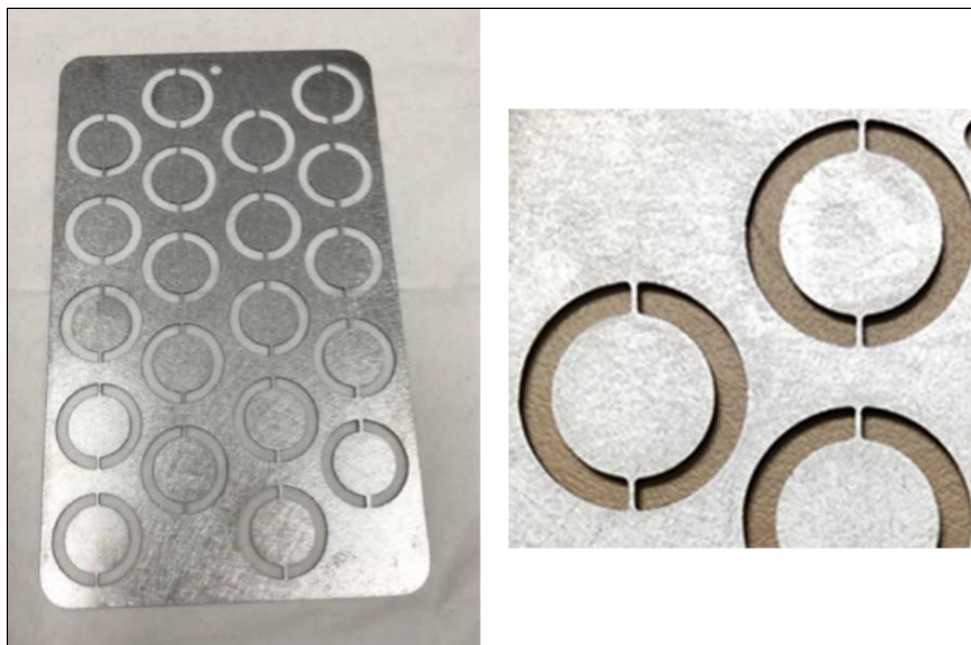


Figure 7. Left: full sheet of mini-panels (3 × 5 in. with 20 mini-panels in each sheet). Each mini-panel is 0.5 in. in diameter, and the thin supports are 0.020 in. so that they can be easily cut with a handheld tool. Right: close-up view of mini-panels in the sheet.

The use of mini-panels for evaluation of chemical resistance has had a significant impact on multiple coatings programs, including this effort. The drastic increase in throughput has enabled evaluations that were previously inconceivable because of the significant cost and time that would have been required. The cost reductions include laboratory resources for execution of agent-resistance tests and production of coatings samples. This is especially true with formulation efforts for which only small quantities of a given formulation may be generated, but many samples are required for analysis. The impacts of and opportunities provided by mini-panel technique and geometry are anticipated to extend to hazard mitigation evaluations.

3.9 Mechanical Properties and Chemical Interactions Associated with Polymeric Materials

The ability to characterize chemical transport in military-relevant polymer systems for the purpose of advancing hazard mitigation has improved significantly in recent years. Multiple experimental techniques are required to better understand how to control agent resistance. CARM provides information about how much agent is retained, but it does not provide good time resolution (i.e., dynamics), which hinders delineation of different transport mechanisms, and it focuses on only three penetrant chemical species (i.e., GD, HD, and VX). Although the chromatography used in the CARM provides superior chemical specificity, this approach requires cumbersome extraction and chromatography methods. To better understand penetrant–polymer interactions (e.g., why HD tends to be sorptive in coatings), multiple penetrant chemicals must be investigated. Multiple programs, including work at DEVCOM CBC, have implemented characterization techniques such as scanning electron microscopy–

energy-dispersive X-ray spectroscopy (SEM–EDS) to provide elemental mapping;¹ QCM to characterize mass uptake;^{3,4} various forms of FTIR spectroscopy, including attenuated total reflectance flow cells, to characterize absorption and desorption dynamics;^{3,30,31} Raman chemical imaging to track chemical gradients and fronts; and UV absorption flow cells to characterize single- and multi-component diffusion.^{3,4} Coupled with molecular dynamics and continuum modeling, these techniques have been used to understand transport in various silicone³² and PU systems.^{3,4} These techniques, a subset of which are highlighted in Figure 8, have enabled characterization of transport mechanisms and molecular interactions that govern transport in polymer systems. The overall approach has been to understand mass transport in polymer composites by addressing relationships between coatings’ mechanical responses and morphology and time-resolved chemical absorption and concentration gradients.

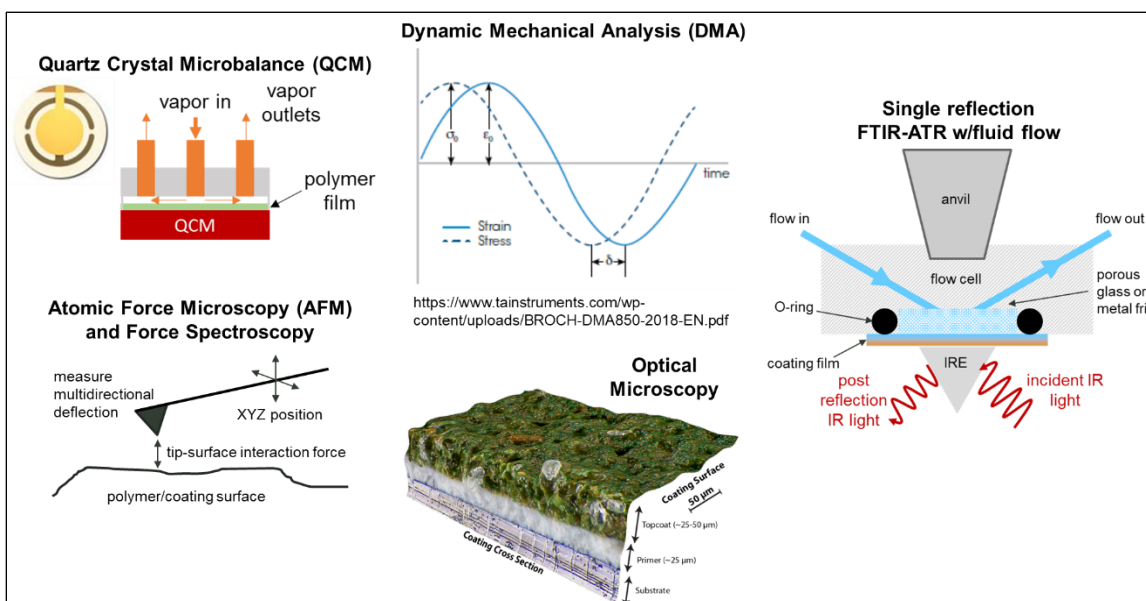


Figure 8. Complementary experimental tool set for interrogating roles of material mechanical properties and morphology in transport of chemicals in coatings materials. Tools include QCM, atomic force microscopy (AFM) and spectroscopy, dynamic mechanical analysis (DMA), optical microscopy, and Fourier transform infrared-attenuated total reflectance (FTIR-ATR).

The following sections detail additional key pieces for achieving the requisite scientific foundation for development of formulation optimization rules to produce resistive coatings.

3.9.1 Mechanical Properties of Contaminated Materials

Related work conducted on pure PU polymer has demonstrated how much affinity penetrant or agent functional groups have for polymer and how the free volume of the polymer can accommodate the agent molecules.³⁻⁵ Factors such as cross-linking also influence how much the polymer can swell to accommodate the absorbing molecules. The swelling of the polymer network upon chemical sorption determines how much the diffusivity increases, which also factors into overall agent resistance. As a result, tuning polymers for chemical resistance results

in tradeoffs in desirable polymer properties. From a chemical resistance perspective, it is good to have a highly cross-linked, glassy polymer. But other required properties, such as toughness, suffer (e.g., polymer becomes more brittle), and it may be difficult to incorporate solids into a stiff polymer network. The objectives of this program are to better understand how polymer characteristics are affected by the presence of penetrant or agent chemicals and learn how to tune the polymer and polymer composite (i.e., binder and solids) to resist penetrant chemicals while meeting other performance requirements.³³ Many of these properties are manifested in the mechanical characteristics of the polymer (e.g., glass transition temperature [T_g], storage modulus, loss modulus, etc.) that can be characterized using DMA and QCM. The relaxation dynamics can also play a key role in the diffusion rate for non-Fickian transport, which can be studied using both DMA and QCM. Part of this work has explored the use of new tools to evaluate how materials change as a function of contamination with respect to facilitating or resisting further chemical mass transport. Techniques such as QCM with dissipation (QCM-D) make it possible to measure dynamics via mass loading without chromatography techniques; an example of a vapor exposure profile is shown in Figure 9. This makes it much easier to characterize multiple probe chemicals with high time resolution.

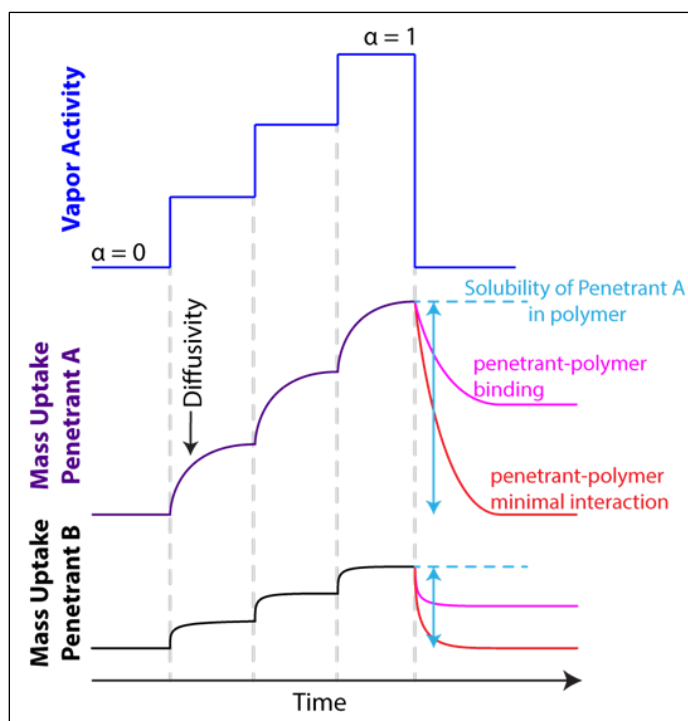


Figure 9. Vapor exposure and QCM output of mass uptake.

QCM-D may also be able to indicate whether a penetrant chemical changes the polymer's mechanical properties during the exposure; such a change would indicate strong penetrant-polymer interactions. Measurement of desorption can also indicate whether there is binding between the penetrant and polymer. We have previously implemented QCM to characterize penetrant-polymer interactions,^{3,4} and a key objective of this work has been to establish the ability to resolve viscoelastic properties of materials as a function of chemical exposure with QCM-D.

3.9.2 Interrogating Polymer–Solid Interfaces

The inclusion of solids in a host polymer matrix creates a distribution of chemical environments and interfaces (between solids and polymer) that are difficult to characterize but critical to understand. Alternate measurement tools (e.g., neutron and X-ray scattering and reflectivity) that are capable of revealing details associated with bulk physicochemical environments are necessary. DEVCOM CBC is collaborating with NIST to obtain measurements on coatings-related materials, specifically polymer–solid interfaces, that can provide insight into the role of bulk polymer composite structure in determining the nature of chemical mass transport.

3.9.3 Chemical-Specific Retention Trends

The smaller molecular weight, linear shape, lower dipole moment (i.e., less polar), and chemical functionality of HD are assumed to be responsible for its high sorption into polymers of interest. And although the HD molecule is nonpolar overall, the electron-rich Cl atoms at its ends may be particularly influential with regard to solubility of HD in a polymer. Previous investigations have focused on testing specific molecules (e.g., HD, GD, VX, and limited simulants like methyl salicylate), but addressing chemical trends for retention requires understanding how chemical functionality relates to chemical sorption as tested by multiple probe chemicals. Concepts of agent resistance for coatings share similarities to transport in other composites ranging from protective materials (e.g., gloves) to permselective membranes, where materials are specifically developed to enable or prevent transport of specific molecules through the materials. For example, solubility parameters (e.g., Hansen) have been used to characterize and develop materials specifically for chemical resistance-like applications.^{18,34–39} Using a solubility parameter approach, polymer composites can be developed and characterized with mass uptake, swelling, and DMA measurements using a range of probe molecules to understand how modification of polymers and solids influences chemical retention across a range of chemistries. Although this route of investigation does not account for the presence of polymer-supported solids and interfaces, we anticipate this will provide insights into how binder chemistry and the addition of solids influence how probe chemicals absorb into composite polymers. This approach aims to provide insight in how to tune coating resistance for HD and improve understanding of agent to simulant relationships.

3.9.4 Retention Measurements Beyond CARM

Multiple experimental techniques will be required to better understand how to control agent resistance. CARM provides information about how much agent is retained, but it does not provide good time resolution (i.e., dynamics), and it focuses on only three penetrant chemical species (GD, HD, and VX). Although the chromatography used in CARM provides superior chemical specificity, this approach requires cumbersome extraction and chromatography methods. Multiple penetrant chemicals must be probed so penetrant–polymer interactions (e.g., why HD tends to be sorptive in coatings) can be better understood. Techniques such as QCM-D make it possible to measure dynamics via mass loading without chromatography techniques; an example of a vapor exposure profile is shown in Figure 9. This makes it much easier to characterize multiple probe chemicals with high time resolution. Researchers are actively

working to establish other means of differentiating between sources of RA signal by using a combination of liquid- and vapor-phase exposure to specific classes of materials. Section 4.2.7 provides details on method development. This work will allow for a discrimination of effects present in polymer films using vapor-phase exposure that can then inform the configuration of coatings materials that would be evaluated using liquid-phase exposure CARM.

3.10 Advancement of Experimental Capabilities for Polymeric Coatings Research

As part of this effort, DMA and QCM measurements were obtained to assess properties of coatings-related materials as a function of polymer structure, additives, dopants, and solids in different chemical environments. These tools are intended to work in conjunction with RA measurements to reveal the specific ways in which material properties and chemical interactions between penetrants and polymer matrices are responsible for mass transport behavior.

QCM and DMA have been used in concert, in particular to show how QCM outputs can be directly related to DMA results.^{40,41} QCM is a high-frequency measurement (megahertz level; sensitive to short time-scale changes) that is performed on thin films in isothermal conditions within a controllable chemical environment. QCM can be used to assess changes in viscoelastic behavior for thin films as a function of polymer structure and solid loadings in simple composites in a limited temperature range. DMA is a low-frequency (<100 Hz) measurement performed on bulk films at variable temperatures; however, there are more limitations on the chemical environment. For future work combining QCM measurements with DMA, we envision using QCM to inform the tuning of bulk films measured by DMA en route to overall chemical resistance measurements (e.g., CARM).

3.10.1 DMA Instrumentation Development

Central to this work is how the experimental tools complement one another with regard to drawing out the correlations between mechanical properties and chemical mass transport in polymeric thin films like coatings. For example, QCM and DMA (as well as AFM) are capable of resolving changes in mechanical properties as a function of chemical absorption. Each of these tools is best suited as a function of film composition and sample construction. FTIR, confocal Raman imaging, SEM-EDS, optical microscopy, and neutron or X-ray scattering provide information about transport behavior such as what contributors from the chemical environment are presented at surfaces and interfaces, including in bulk layers. A DMA instrument capable of performing measurements as a function of chemical exposure to materials was acquired (TA Instruments; New Castle, DE; DMA 850). As described in Section 1, it is imperative that we understand the relationship between mechanical properties of coatings materials and their contamination susceptibility to propel formulation optimization or discovery of governing factors for dramatically enhanced chemical resistance.

The focus of the instrument use was characterization of samples provided by NRL. The film and fiber clamp were used, and the emphasis was on characterization of the system's crystalline and amorphous character. Additionally, the DMA measurements were intended to elucidate key polymer properties such as thermal transitions, viscoelastic behavior,

molecular weight between cross-links, and the overall material changes with changes in system chemistry and filler type or ratio. This information allows for correlation of the DMA with results gathered through other techniques (e.g., QCM and RA measurements from liquid or vapor exposure) and provides an understanding of how polymer properties, namely T_g , cross-link character, filler density and type, and chain structure, affect penetrant–matrix interaction. System confinement effects and interfacial effects can also be determined by pairing DMA data with rheological and differential scanning calorimetry data.

3.10.2 Multichannel QCM-D Measurement Capability

An instrument setup involving a multichannel quartz crystal microbalance (QCM-I; Gamry Instruments; Warminster, PA, in conjunction with MicroVacuum, LTD; Budapest, Hungary) coupled to a custom-built vapor delivery manifold was constructed for this work on polymer-based coatings. Briefly, two independent QCM cells capable of measuring and fitting the impedance signal that results from driving a quartz crystal and any loaded mass into resonance were installed into a temperature-controlled chamber. The quartz crystals used in this study were coated with Au electrodes and had an unloaded resonance frequency of nominally 5 MHz. Polymer films of interest were spin cast onto the sensors using a WS-650 spin coater (Laurell Technologies; North Wales, PA) and cured; details are provided in subsequent sections. The baseline unloaded resonance frequency for each crystal was measured as a reference prior to any film deposition. The measurement cells permit fluid flow to the sensor so that time-resolved measurements of mass uptake and changes in mechanical properties of films spin cast onto the quartz crystals could be measured. For the purposes of this work, one cell typically had a polymer-coated crystal, and the other cell had an uncoated crystal as a control. Both cells were equilibrated to the same temperature and exposed to the same chemical exposure via gas flow. The spectral characteristics of the fundamental and associated harmonics for the impedance signal were a function of mass load on the sensor, including differential mass, but also the mechanical properties of the load (e.g., from rigid to viscoelastic film responses), as evidenced by the nature of the resonant shear wave propagation. Details on the use of QCM for this purpose have been published elsewhere.^{40–47} Details on the vapor manifold design used in the DSB have also been provided in past work.^{3,4}

A chemical fume hood in the DSB laboratories was selected for use with this program. An incubator (Torrey Pines Scientific; Carlsbad, CA; IN45 programmable chilling and heating incubator) was installed in the hood so that environmental control of the QCM as well as all necessary gas flow control equipment (e.g., saturator cells) could be maintained. Considerations were made for proper operator access and use of key hardware. Experiments in this configuration are run isothermally between the vapor source and QCM flow cell; details on the use of this type of vapor generator in combination with analytical instruments are published elsewhere.^{3,4}

Initial measurements involved spin cast films of PU and polydimethylsiloxane (PDMS) exposed to methanol (MeOH) as a probe molecule. PU and PDMS were chosen because both materials were readily available, and internal knowledge existed to ensure the creation of useful films. MeOH was chosen because of its lower molecular weight; small molecules are more likely to facilitate a rapid experiment.

As an initial example of chemical uptake into a model spin cast polymer film, Figure 10 shows the results for the shift in frequency (Δf_n) and half-width at half maximum (Γ_n) for both $n = 1$ and 3 (fundamental frequency and third harmonic) for MeOH exposed to PU. The initial baseline depicts the film as it exists in an inert nitrogen environment. The quartz crystals used for this work have a fundamental resonance frequency at 5 MHz. The addition of mass to the crystal due to polymer film deposition or chemical absorption results in a decrease in the resonance frequency (assuming other key material properties remain constant). Based on the decrease in resonance frequency for f_1 for the uncontaminated PU film on the quartz surface, which was approximately $\Delta f_1 = 9000$ Hz, the Sauerbrey rigid film limit calculation of film thickness, (d_{polymer}) corresponds to approximately 1.3 μm , calculated as

$$\Delta f_n = \frac{-2nf_1^2}{\sqrt{\rho_q \mu_q}} \rho_{\text{polymer}} d_{\text{polymer}} \quad (1)$$

where

- ρ_q is quartz density (2.648 g cm⁻³);
- μ_q is quartz shear modulus, 2.947×10^{11} g cm⁻¹ s⁻²;
- f_1 is resonance of fundamental mode (5 MHz);
- Δf_n is change in frequency of n th overtone;
- ρ_{polymer} is polymer density (nominally 1.2 g cm⁻³); and
- d_{polymer} is polymer film thickness.

This expression holds in the limit where there is no significant loss in shear wave transmission with mass attached to quartz and mass loading corresponds to <2% of the resonance frequency of the unloaded crystal. Figure 10 shows the absolute value of the magnitude of the frequency shift, which corresponds to a decrease in resonance frequencies as a function of mass loading (i.e., greater values of Δf_n correspond to lower frequencies). At approximately 200 s, MeOH was introduced to the system by flowing a stream of nitrogen saturated with MeOH over the sample at a rate of 100 cm³/min with vapor activity set to 1 (value simply chosen to ensure rapid signal given the training environment). A maximum was reached within approximately 10 s, after which time the absorbed mass decreased slightly until the MeOH flow was stopped (~500 s). From the time the MeOH was turned off, the film required a little less than 40 s for 90% of the MeOH to desorb. Ultimately, some MeOH remained absorbed in the PU film through the remainder of this (short) training evaluation. Numerous reasons exist for the lack of complete desorption of MeOH from the PU film, including chemical binding and the amount of time required for vapor to be transported from within the film to the film surface for desorption.

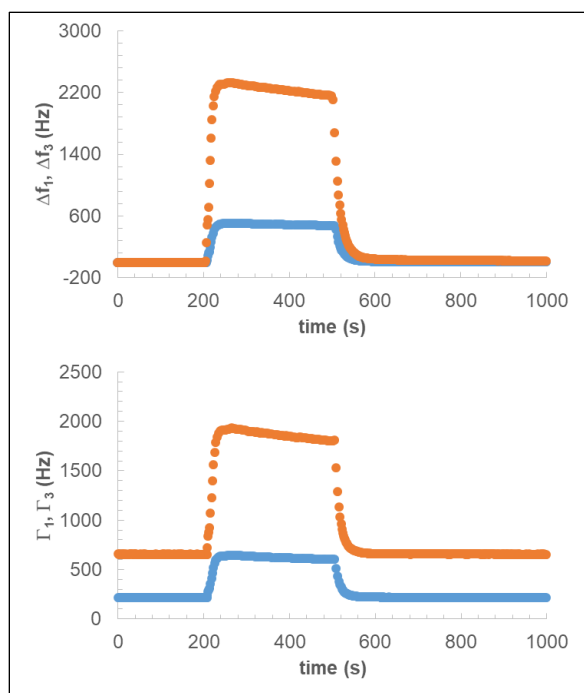


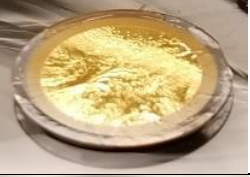
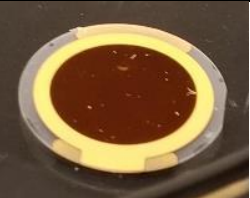
Figure 10. QCM measurements for absolute value of Δf (top) and Γ_n (bottom) for the fundamental ($n = 1$, blue) and third harmonic ($n = 3$, orange) for MeOH vapor exposed to PU.

The difference in mode-normalized frequency shifts was examined (i.e., $\Delta f_1/1$ was compared with $\Delta f_3/3$ at the point of MeOH uptake equilibrium), and the magnitude of this difference was determined to be >250 Hz, whereas a rigid film would have roughly had a difference of <10 Hz. By measuring the mass uptake at multiple frequencies, it is possible to determine whether and to what extent the film is exhibiting viscoelastic behavior. The measurement of shifts in the conductance peak position, Δf_n , and Γ_n at multiple modes or resonances (n) can be used to feed mechanical models to extract information regarding swelling, hardness, and viscoelasticity. *This capability is made possible through this particular QCM instrumentation and will serve as a critical measurement approach for assessing changes in mechanical properties for thin films as a function of chemical exposure and permeability for both pure and simple polymer composites.*

PU sourced from Sigma-Aldrich (St. Louis, MO) was anticipated to be the target polymer of choice for initial QCM studies. However, the T_g of this PU was determined to be too low, and it existed in a rubbery state at room temperature. Because the target polymer films developed by NRL will be glassy at room temperature, the decision was made to instead use poly(methyl methacrylate) (PMMA) as a test bed for the refinement of experimental procedures and approaches. Accordingly, a fair amount of experimentation was required to appropriately dissolve the PMMA into a solvent that would facilitate smooth spin casting of the PMMA onto the QCM crystals. Unfortunately, obtaining films of adequate quality and thickness proved to be a challenge, and the decision was made to switch to glassy PU sourced from ARL for use moving forward. One of the most significant difficulties was establishing QCM signal stability for extended periods of time (multiple hours) for the deposited films as a function of chemical exposure to solvent vapor such as MeOH or isopropanol (IPA).

Because film thickness is critical to achieving good results in the QCM, film casting procedures must be adjustable to ensure sufficient film thickness. In the case of the targeted glassy polymers, a film thickness of approximately 1 μm is necessary for mass uptake experimentation, whereas a 5–10 μm thickness is more optimal to measure viscoelastic effects, at least for an uncontaminated glassy polymer film. Depending on the impact of chemical absorption as well as the specific composition of the materials under study as a function of both polymer structure and solids inclusion, the film thickness needs to be optimized to allow for viscoelastic phenomena to be robustly accessible. White-light thin-film reflectometers were used to independently measure thickness of spin cast clear polymer films; however, these types of spectrometers are insufficient to evaluate opaque films, and methods are being discussed to evaluate the cross section of the filled polymers to provide the necessary film thickness information for QCM experimentation. Some examples of the film types that may be created through spin casting are presented in Table 1. Here, four films of glassy PU were cast onto QCM crystals using four similar techniques. Past work on spin casting PU on different form factor surfaces (e.g., other QCM and FTIR-ATR crystals) served as the starting point for the preparation of these films (spin casting nominally at 1000 revolutions per minute (rpm) for 2 min). Two polymer solutions were considered (PU dissolved in cyclopentanone and chloroform), and the amount of solution was varied (1–2 drops at various volumes). In addition, some of the crystals were pretreated with cyclopentanone to facilitate spread of the polymer solution across the film surface. As shown, each of these variables can create a significantly different film; therefore, sample preparation must be considered carefully. High film quality and robust adhesion to the Au-coated quartz QCM crystals are imperative for chemical exposure measurements.

Table 1. Examination of the Effect of Spin Casting Parameters on QCM Thin Film Quality for PU

Photograph	PU Polymer Solution Concentration (mg/mL)	Solvent Pretreatment of Gold Surface	Deposited Polymer Solution Volume (μL)	Notes
	75	10 μL cyclopentanone	1 $\times$ 40	Very clean surface
	105	10 μL cyclopentanone	1 $\times$ 40	Surface covered in moderate features; crackly appearance
	105	None	2 $\times$ 15	Significant surface crackling; solvent clearly evaporated unevenly, leaving a highly irregular, rough film
	105	20 μL cyclopentanone	1 $\times$ 20	Very smooth surface

The initial studies have achieved a variety of “soft” goals. Stress testing was performed so that the instrument limitations could be observed, specifically with regard to data acquisition for multiple frequencies over extended time periods, which is necessary for many of the stepwise vapor-exposure experiments with slow penetration (low diffusivity) of penetrants into glassy polymers. IPA was chosen to probe polymer films, but in a thinner film limit ($\sim 1 \mu\text{m}$ thick), with the expectation of measuring mass uptake as a function of vapor activity exposure so that chemical interaction (e.g., Flory parameters) could ultimately be quantified. IPA is one of several chemicals under consideration for probing the penetration of chemical vapors into NRL polymer films, so this setup could provide a good baseline for comparison with future studies. This technique is a continuing work in progress, and the near-term efforts will be crucial in identifying the steps required to perform successful experiments on the QCM. The troubleshooting steps required are already underway to ensure successful evaluations once the target films are generated in collaboration with NRL. In addition, the initial studies were intended to provide a good understanding of the amount of time required to observe material uptake, as well as the amount of time required for desorption of the penetrant material. Future

polymer evaluations will be made as a function of both the fundamental frequencies and associated higher-order harmonic frequencies.

An example of mass uptake evaluated as a function of vapor activity is illustrated in Figure 11. Here, the mass uptake of IPA into glassy PU measured by QCM is shown for activity values of 0.6 to 1. Decreasing activity values (e.g., when the gas flowing over the QCM crystal is less than 0.5 activity for IPA) led to drastically increased absorption times, so the decision was made to start the evaluation at 0.6 activity for IPA. As shown, even this simplified test required more than 90 h (nearly 4 days) to complete. However, the rapid response of the QCM to the introduction of IPA to the PU film can be easily observed here. The vapor activity changes almost instantaneously, and the film responds accordingly. Although some film–penetrant combinations may respond differently, this provides confidence that the instrument is responding appropriately.

Penetrant–polymer binding is also indicated by the non-sharp decrease in mass as IPA was driven out of the film after 40 h.

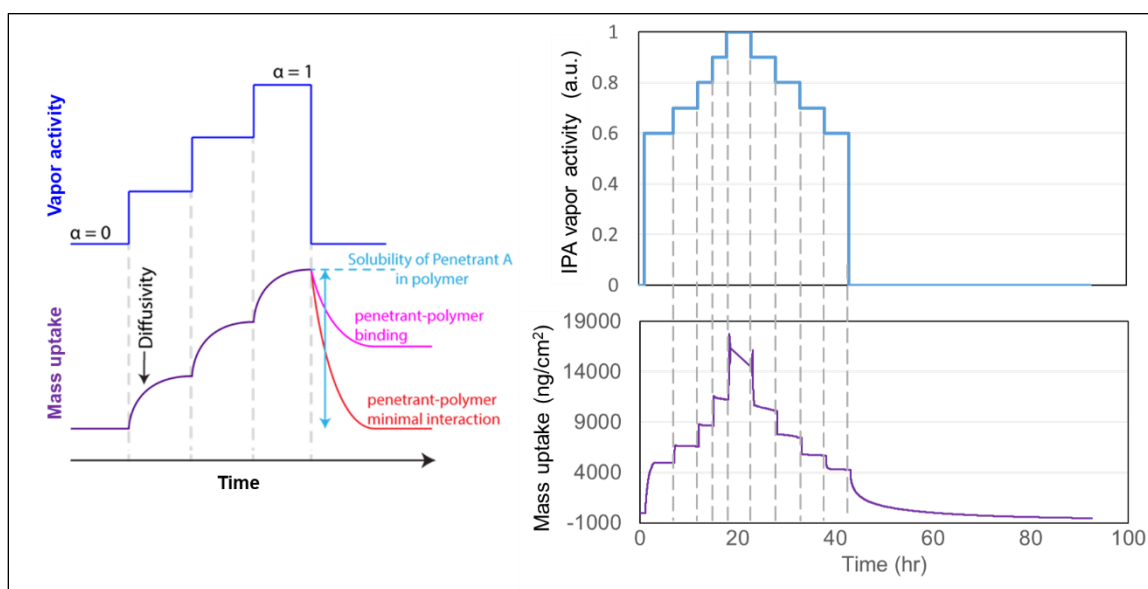


Figure 11. QCM data collection concept (left) and experiment for IPA exposed to PU (right). The time-dependent mass-uptake profile and equilibrium mass absorbed at each vapor activity step provide insight into the penetrant–polymer interactions.

Two main types of QCM measurements will be used to determine the key factors that drive chemical retention in polymers and select composites. The first is the measurement of mass uptake and chemical volume fraction as a function of chemical exposure, as shown in Figure 11. We will be able to evaluate the proclivity for absorption for different probe molecules into polymer films in a thin rigid-film limit. By measuring mass uptake as a function of vapor activity exposed to the polymer film, it will be possible to evaluate the chemical-specific equilibrium volume fraction, which in turn will allow for the calculation of single-component

interaction Flory parameters and polymer cross-link density. This analysis quantifies the degree of chemical interaction between chemical penetrant and polymer matrix as a function of polymer chemical structure.

The second type of measurement is associated with changes in mechanical properties, including manifestation of viscoelastic effects, in polymer films as a function of chemical exposure. Key to this work is the use of analysis tools that combine QCM observables with mechanical models that describe frequency dependence of shear wave propagation in solids. The Shull Group at Northwestern University (<https://shullgroup.northwestern.edu/>; Evanston, IL) has published analysis code for the evaluation of mechanical properties as measured by QCM (RheoQCM).^{41,44,45} The main inputs to the code are frequency and conductance peak width for the fundamental resonance and multiple harmonics, which are used to calculate mechanical characteristics of the polymer as a function of exposure to the penetrant species. The overall objective is to use QCM to measure Δf_n and Γ_n to feed mechanical response models that will generate $d\rho$ (e.g., swelling), ρG_n^* (e.g., hardness), and ϕ_n (e.g., viscoelasticity) as a function of chemical exposure conditions. The following are key notes for QCM-based determination of factors that drive chemical resistance in polymers and composites for this work, which is focused on organosilane materials, and future efforts:

- The core need for the program is an understanding of how specific types of molecules transport through organosilane-based polymer and polymer composite networks.
- Fundamentally, if a penetrant is capable of significantly modifying the mechanical state of a polymer or polymer composite, then enhanced transport and retention is possible.
- It is necessary to understand how penetrant–polymer interactions drive viscoelastic diffusion effects.
- We need to assess what factors matter with respect to molecular penetrant properties and penetrant–polymer interactions for mass uptake in the context of the specific class of polymer matrices synthesized by NRL.
- While we have a certain degree of freedom with respect to polymer structure, the base organosilane polymer used by NRL is **not** a completely adjustable parameter; it needs to remain amenable to serving as a host matrix for solids to comprise a polymer composite coating.
- In general, we do not have well-established means of describing what happens to materials during and after contamination. We have only recently started to account for the effect of not only heterogeneous structure in polymer composite coatings on transport and retention but also the influence of changes to materials as a function of contamination (i.e., introduction of viscoelasticity).
- There is an opportunity to use QCM with dissipation to assess mass uptake to feed viscoelastic diffusion models, including volume fraction ($\phi_{c,m}$).
- Calculations beyond the rigid film limit must be considered to accurately assess mass uptake in the limit of penetrant-induced viscoelastic effects.⁴
- We must determine what penetrant–polymer interactions are principally responsible for affecting transport behavior and driving the increase in impact

of viscoelasticity; *decreases in T_g and modulus, as well as increases in viscoelastic phase angle are all hypothesized to correlate with decreased chemical resistance.*

Initial viscoelastic property evaluations for the QCM were qualitative and were intended to provide confidence in the ability of the instrument to produce reasonable results consistent with published values for the materials of interest. As noted above, the viscoelastic properties of materials are determined based on QCM measurements by collecting multiple harmonics for shear-wave propagation and fitting those resonance peak positions and widths to appropriate mechanical models. The following example demonstrates how the density and shear modulus of PMMA was experimentally calculated for an $\sim 5\ \mu\text{m}$ thick PMMA film with no chemical exposure. Following the procedure outlined by the Shull Group, the normalized frequency and Γ shifts for the fundamental and third harmonic resonances from QCM were analyzed.⁴² From there, ρd and $|G_n^*|$ were calculated, where ρ is the film density, d is the film thickness (here, measured as $5.7\ \mu\text{m}$), and $|G_n^*|$ is the shear modulus. The data for ρd and $|G_n^*|$ are shown in Figure 12. Averaging across the measured timeframe provides density and shear modulus values of $1.19\ \text{g/cm}^3$ and $1.88 \times 10^8\ \text{Pa}$, respectively. Literature values for the density and shear modulus for PMMA are $1.18\ \text{g/cm}^3$ and between 2×10^8 and $2 \times 10^9\ \text{Pa}$ (depending on the molecular weight of the polymer). Our experimental results are reasonable and provide confidence in the ability of the QCM to perform the necessary viscoelastic measurements. Resolution of viscoelastic effects by QCM depends on both polymer physical state and film thickness.

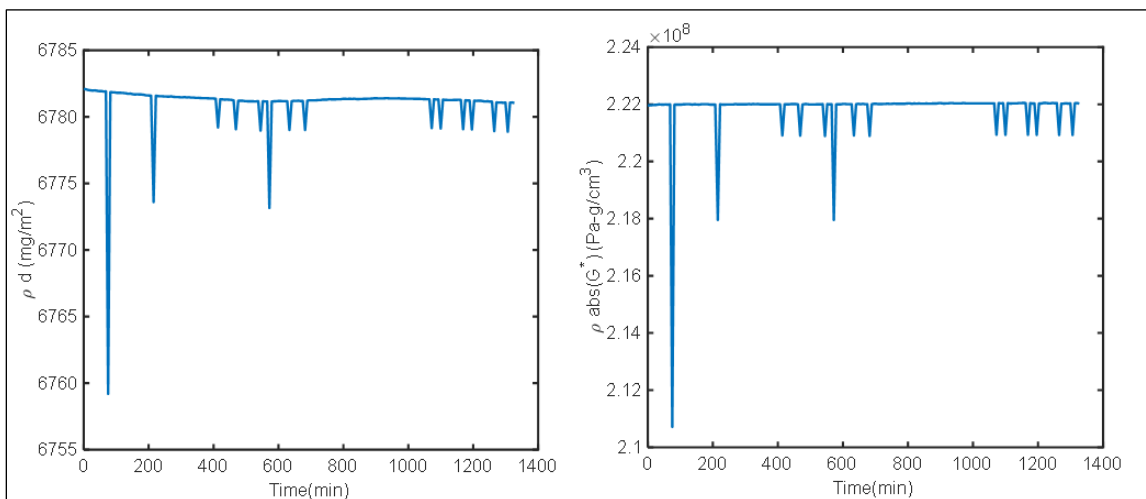


Figure 12. QCM data for PMMA in the presence of nitrogen only (no penetrant chemicals) to show viscoelastic evaluation. Data shown for the ρd (left), and $\rho|G_n^*|$ (right), as a result of analyzing the characteristics of the fundamental frequency and third harmonic resonances for an $\sim 5\ \mu\text{m}$ thick PMMA film as a function of time.

4. RESULTS

4.1 Baseline Retention Measurements for Paint Systems

As a starting point, the agent retention of three variations of full formulations of PS-based coatings was compared to that of a PU paint coating that meets similar performance requirements. The PU paint example is only a representative coating from that polymer class and is not a universal paint sample for all PU-based coatings. However, most of the DSB's work with protective paint systems has included the use of PU-based materials. For an investigation circumscribed to PS-based coatings and the associated polymer binders, it was necessary to first assess the difference in RA response between the two material types with representative materials. Figure 13 shows the variation in RA as a function of age time, or interaction time between a liquid agent droplet and a surface. The evaluated materials are low-gloss paints that all adhere to the same specification. The three varieties of NRL materials had similar responses across all three agents, but C responded somewhat differently than A and B. For reference, NRL-A and -B were based on the non-extended chain *N*-butyl urea silane polymer, whereas NRL-C was produced commercially (specific PS-based polymer structure is not known). For both PU and PS-based coatings types, HD retention was distinctly different than that for GD or VX.

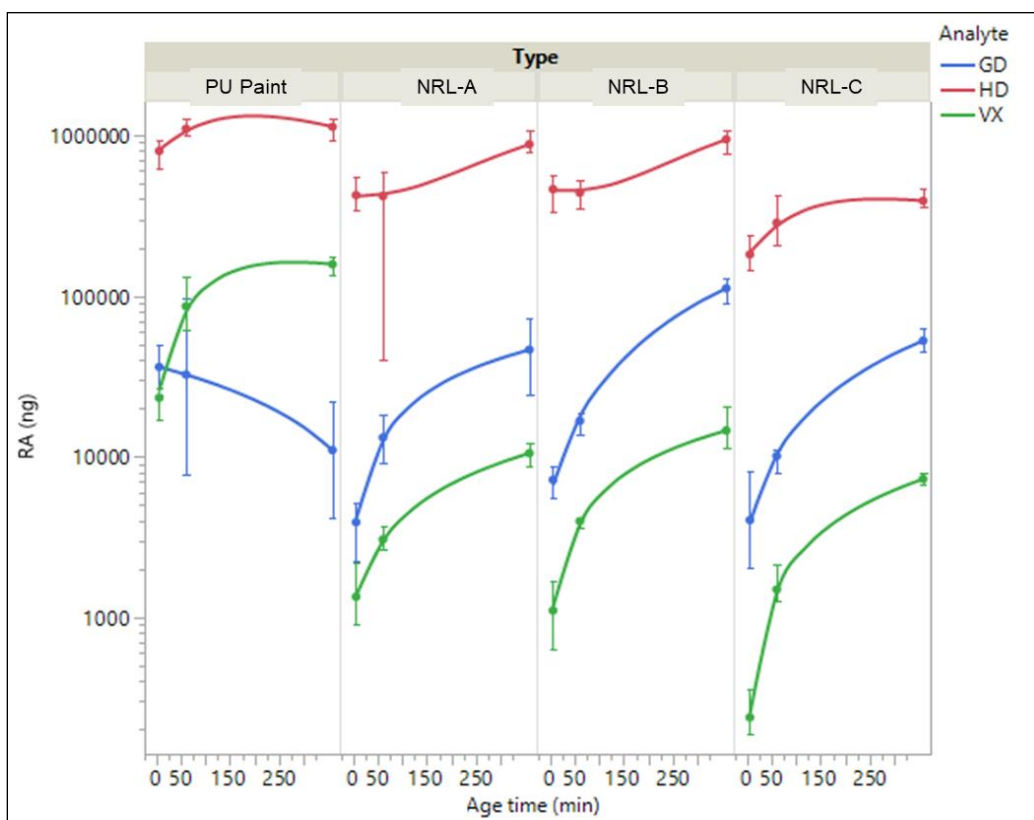


Figure 13. Comparison of RA mass between PU-based paint and three different varieties of PS-based paint from NRL of the same pigmentation. In all cases, 2 μ L droplets were applied to 2 in. diameter panels. RA measurements were performed on different panels with 5, 60, and 360 min interaction times with deposited liquid agent.

The spreading behavior of agent liquids on the surfaces of PS coatings was significantly different than on PU, as shown in Figure 14. By and large, all three agent liquids spread on the PU coating surfaces, whereas the same volume droplets on PS coating surfaces remained sessile. As documented in past work,⁶ liquid wetting behavior on these materials is not directly or uniquely indicative of retention (i.e., contamination via absorption into the bulk is not solely a function of liquid spreading at the surface).

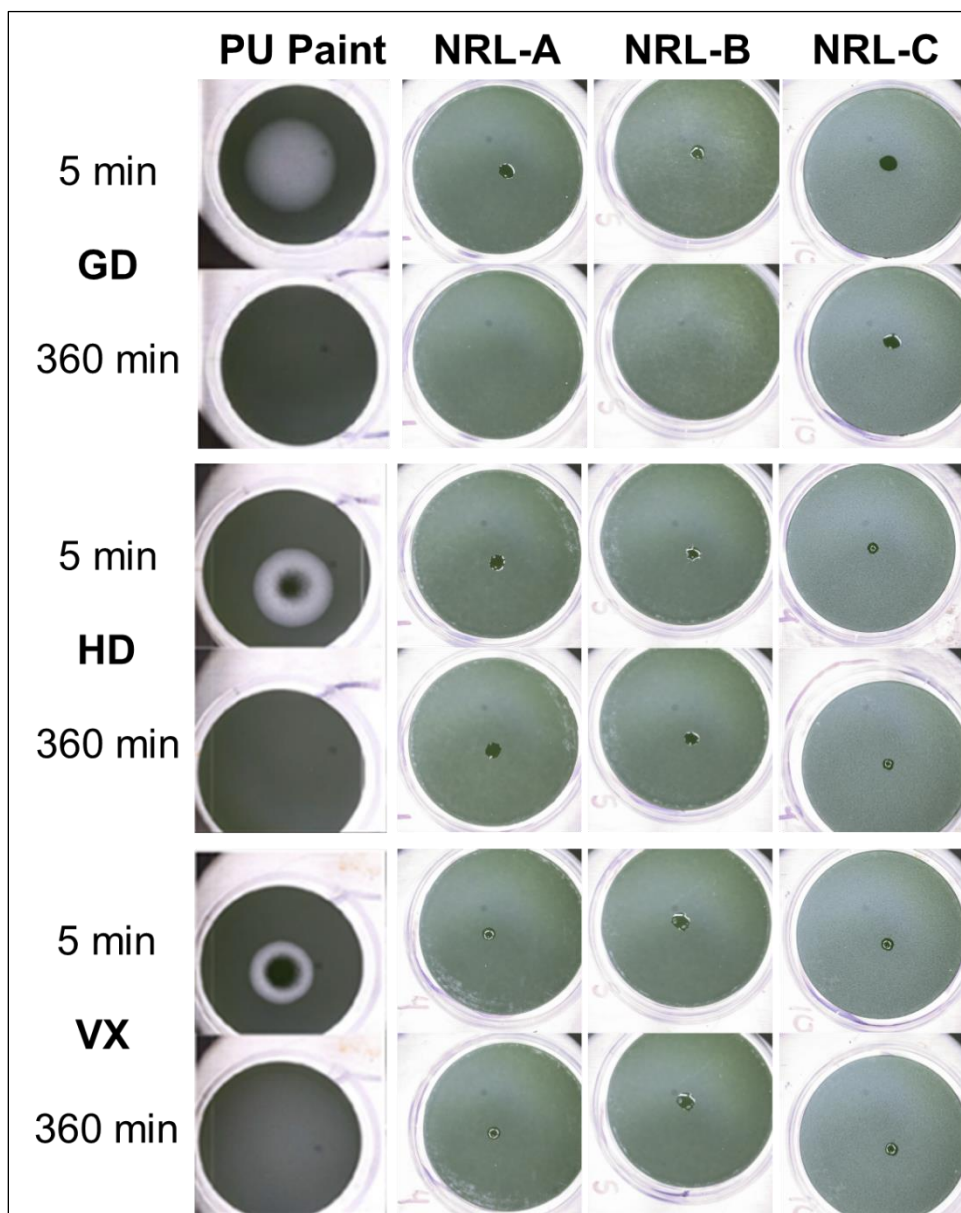


Figure 14. Comparison of liquid droplet spreading behavior among PU-based paint and three different varieties of PS-based paint of the same pigmentation from NRL. Photographs show the panels at 5 and 360 min time points after deposition of a single 2 μ L droplet.

4.2 Evaluation of NRL PS-Based Materials

4.2.1 Initial Screening Study

Initial samples incorporated typical coatings solids (i.e., pigment and matting agents), one solid at a time, into a set of PS-based binders for a range of loading levels. Polymer structures were chosen to span cross-link density, T_g , and flexibility. Agent resistance measurements were obtained using mini-panels so it could be determined what principal polymer–solid combinations and what loading levels had the strongest influence and therefore warranted further investigation. The objective of this test was to determine whether certain solids, loadings, and additives influenced agent retention. This work was started with two different polymer variations to serve as a sensitivity analysis of how solids influence agent resistance. The screening hypothesis was that particles that integrate well with the polymer will decrease permeability, and particles that disrupt the polymer interface will increase permeability. Polymer structures initially considered spanned both flexible and inflexible backbones, in the form of extended and non-extended PS-based chemistries, respectively. Along the lines of positing that the interfacial region is an important consideration in the generation of chemical mass transport routes, the flexibility of the polymer chain in terms of being conformal to dispersed solids can be very important. Different solids that are commonly integrated into these types of coatings were the focus, specifically TiO_2 pigment particles and a fluorinated alkoxysilane additive. We anticipated that the influence of specific solids on overall chemical resistance would be variable. Table 2 delineates the formulation variations produced.

Table 2. Materials Produced by NRL for Initial Testing*

NRL Sample Identifier	Polymer Binder Chemistry	Polymer Binder Structure	Solids or Additive	Loading (vol %)	Description
007A	None	None	None	0	Primer [†] only
007B	1 (<i>N</i> -butyl urea silane)	Non-extended	0	0	Primer with non-extended polymer
007C	1 (<i>N</i> -butyl urea silane)	Non-extended	TiO ₂	7.75	Primer with non-extended polymer and low loading of TiO ₂
007D	1 (<i>N</i> -butyl urea silane)	Non-extended	TiO ₂	15	Primer with non-extended polymer and high loading of TiO ₂
007E	1 (<i>N</i> -butyl urea silane)	Non-extended	Fluorinated alkoxysilane additive	4	Primer with non-extended polymer and low loading of fluorinated alkoxysilane additive
007F	1 (<i>N</i> -butyl urea silane)	Non-extended	Fluorinated alkoxysilane additive	7.75	Primer with non-extended polymer and low loading of fluorinated alkoxysilane additive
007G	2 (extended <i>N</i> -butyl urea silane)	Extended	0	0	Primer with extended polymer
007H	2 (extended <i>N</i> -butyl urea silane)	Extended	TiO ₂	7.75	Primer with extended polymer and low loading of TiO ₂
007I	2 (extended <i>N</i> -butyl urea silane)	Extended	TiO ₂	15	Primer with extended polymer and high loading of TiO ₂
007J	2 (extended <i>N</i> -butyl urea silane)	Extended	Fluorinated alkoxysilane additive	4	Primer with extended polymer and low loading of fluorinated alkoxysilane additive
007K	2 (extended <i>N</i> -butyl urea silane)	Extended	Fluorinated alkoxysilane additive	7.75	Primer with non-extended polymer and low loading of fluorinated alkoxysilane additive
007L	1 (<i>N</i> -butyl urea silane)	Non-extended	None	0	Non-extended polymer (no primer)
007M	2 (extended <i>N</i> -butyl urea silane)	Extended	TiO ₂	15	Extended polymer with high loading of TiO ₂ (no primer)

*Polymer binder chemistry refers to a specific PS-based chemistry under exploration by NRL, which can be synthesized in a non-extended or extended backbone array.

[†]A military specification primer used for these types of coatings.

The first screening-level test was used to identify and address technical challenges and any optimizations that need to occur with sample preparation and testing before further samples were generated. The following questions had to be addressed because this work involved new sample preparation methods:

- Are there any challenges associated with chromatography interference testing for these specific polymers and polymer–particle combinations?
- Are solid loadings at appropriate levels to probe a dynamic range of RA response?
- Is primer needed in all cases to test topcoats, as evidenced by film stability (e.g., resistance to delamination)?
- Is the coating uniform across the mini-panel sheet?
- Are there challenges associated with spray coating the mini-panel sheets?
- Are the applied coatings homogeneous with respect to solid dispersion (e.g., particle agglomeration, particle settling)?
- Are single solid loadings appropriate for these binders or are additives required to make homogeneous films?

Optical microscopy was performed at DEVCOM CBC for all of the materials produced by NRL to assist with sample production optimization. Any variations in film texture or uniformity, any defects, and any possible failure modes for the materials when the mini-panels were removed from the mini-panel sheets were noted. Mini-panels were successfully removed from the sheets without damage to the films except in the immediate vicinity of the cuts on the tabs. There was no widespread compromise to film integrity in the removal. Figure 15 shows a mini-panel that was removed from a mini-panel sheet produced for this screening-level study.

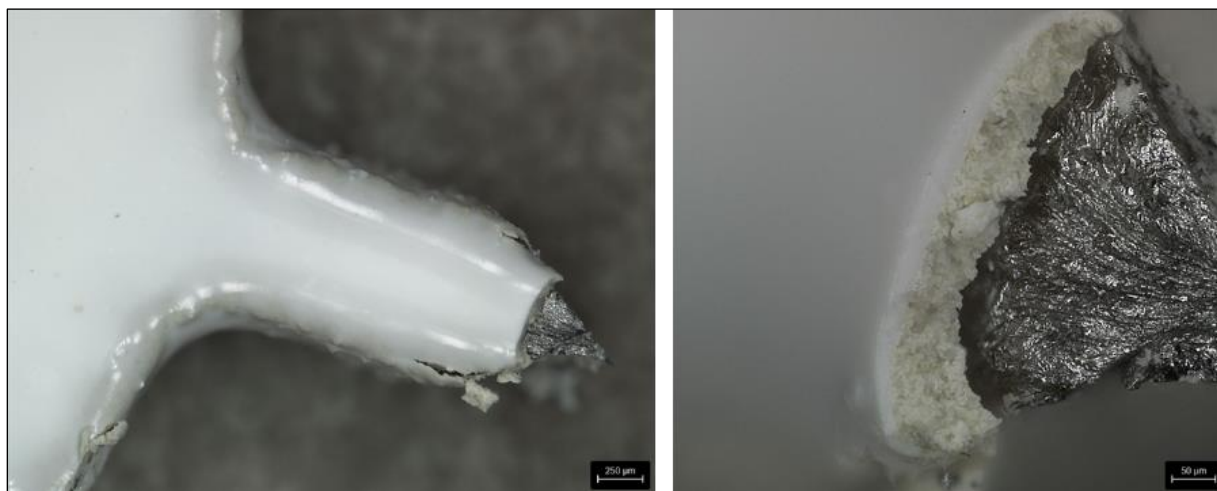


Figure 15. Optical microscopy for a coated mini-panel that was removed from a mini-panel sheet (sample 007C: primer with *N*-butyl urea silane and 7.75 vol % TiO₂). Left: clear coverage to all of the edges (scale bar, 250 μm). Right: distinct topcoat and primer layers along with some film damage only in the vicinity of the cut on the support tab (scale bar, 50 μm).

Initial observations of the films also revealed various textures and defect densities (Figure 16). These coatings were designed to characterize specific chemical functionality and did not include additives to facilitate optimal film formulation (which could interfere with the test objective). As a result, some films were very smooth, whereas others exhibited pit defects. These pit defects could possibly influence CARM results because the liquid agent could be retained in the pits and not be removed by the treatment process. However, after analysis of the RA results, no qualitative correlations with the presence of pit defects were found. Pit defects did not seem to be retaining significant quantities of agent liquid.

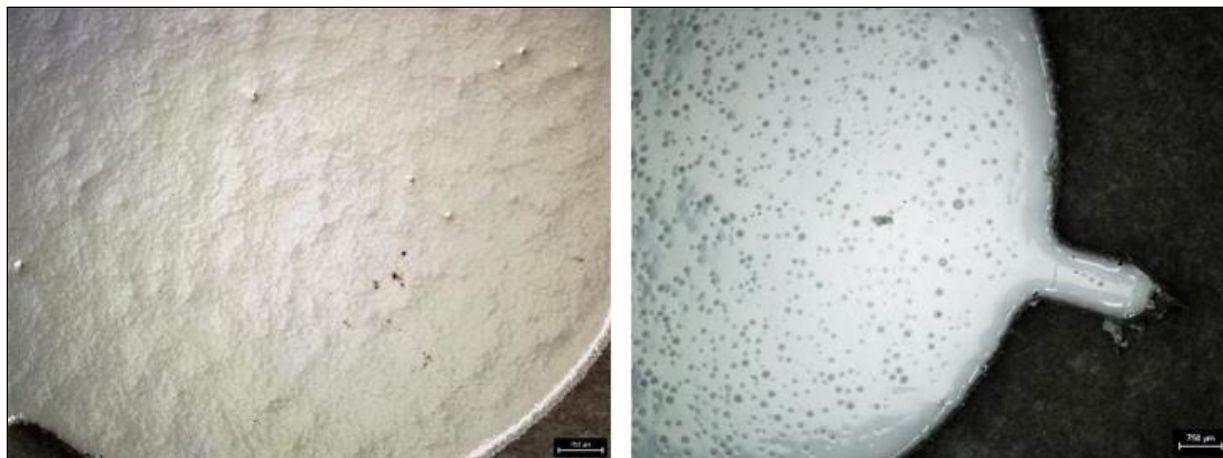


Figure 16. Optical microscopy of various films; (left) showing some pit defects, and (right) a much higher density of pit defects.

Agent-resistance measurements were performed for HD and VX. Droplets (1 μL) were deposited for a 240 min contamination duration to elucidate trends as a function of coating variant, including polymer structure and solid type and loading, as well as trends with respect to agent. The analysis tracks RA versus loading for each polymer–solid combination for each agent to identify influential trends. This analysis also involved evaluating whether the effect of a given solid was different across the polymers tested. The results are shown in Figure 17 for the effect of the different additives (fluorinated alkoxy silane and TiO_2) included in two different polymer structures (i.e., non-extended or extended chains). In the case of HD, the non-extended version of the polymer structure (designated by circles in the figure) was more resistant than the extended variety (designated by triangles). Regardless of the additive or solid loading level, the RA was higher for films based on the extended structure. Increasing the fluorinated alkoxy silane level slightly improved agent resistance, whereas TiO_2 was not influential on RA. For VX, RA was similar for both polymer structures, and increasing fluorinated alkoxy silane additive seemed to have more impact on decreasing RA, whereas TiO_2 was not a significant factor. It should be noted that the overall retention for HD was approximately an order of magnitude higher than for VX, and that there were more instances of greater data spread for VX as compared to HD. There is a clearer distinction in overall RA for extended structures in contrast to non-extended structures for HD.

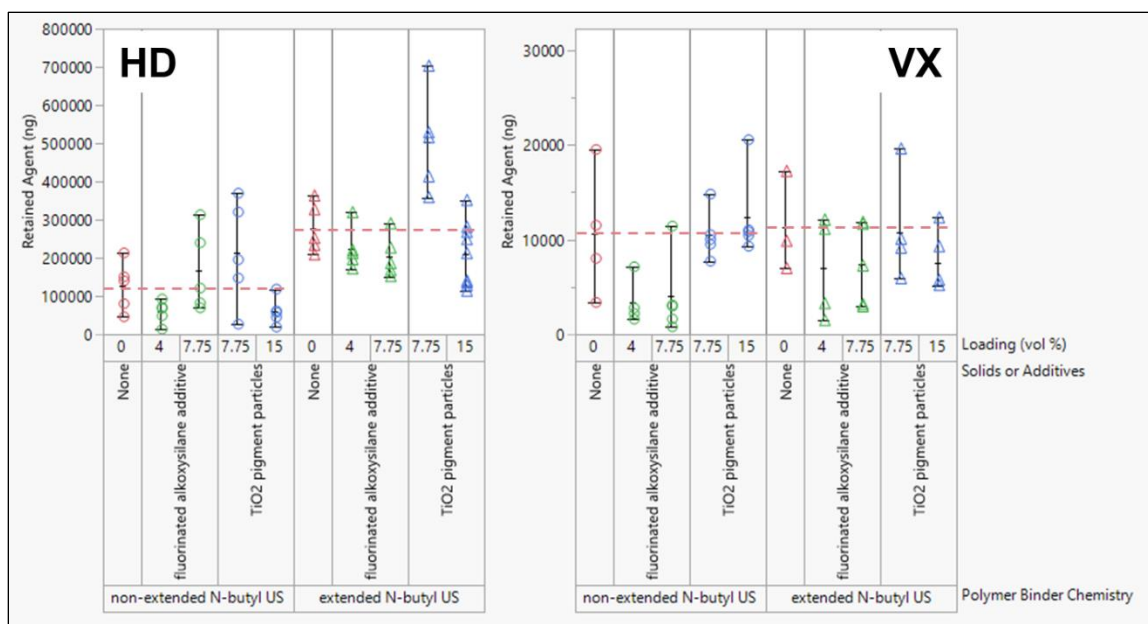


Figure 17. Retained agent measurements for HD (left) and VX (right) as a function of fluorinated alkoxy silane and TiO₂ levels. Dashed red lines correspond to the mean value of cases with no additives or solids.

4.2.2 RA Trends due to Presence of Solids, Dopants, and Hydrogen Bonding

The next test addressed the roles of solids, dopants, and hydrogen bonding. The results showed that TiO₂ loading was not influential on RA; therefore, it was not considered in this evaluation. Furthermore, the results showed that extended chain polymer structures were likely to cause increases in RA most prominently for HD; therefore, non-extended structures were exclusively tested in this materials set. The fact that an extended structure resulted in increased retention suggests that increased free volume for the polymer with less tight packing because of a bulkier backbone structure gives rise to enhanced chemical penetration. This will need to be evaluated with dedicated rheological measurements. All evaluations were performed with 1 μ L droplets (nominally 1 mg) with a single 4 h contamination duration. Table 3 specifies the functional groups included on the polymer backbone, and Figure 18 shows the base structure of the non-extended polymer for which the R-group was varied.

Table 3. R-Group Substitutions for the PS Structure Shown in Figure 18

R-Functionalization	Hypothesis
<i>N</i> -methyl	Less steric hindrance on urea, leading to more hydrogen bonding
<i>N</i> - <i>tert</i> -butyl	Increased hindrance
<i>N</i> -cyclohexyl	Most steric hindrance on urea, leading to less hydrogen bonding

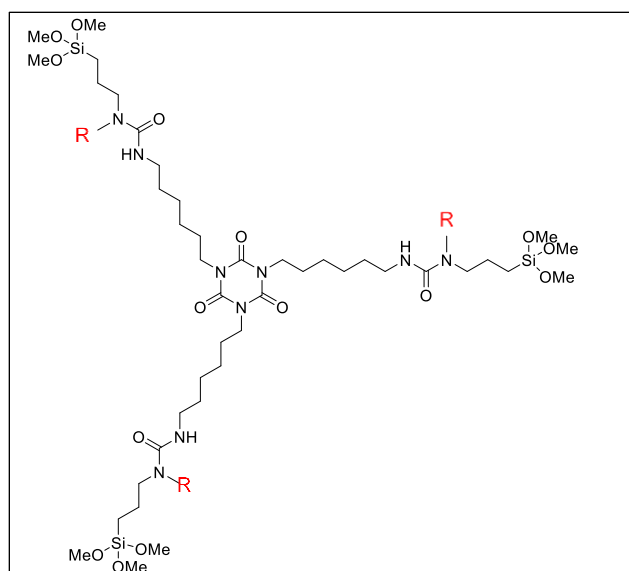


Figure 18. Base PS structure with R-substitutions of methyl, *tert*-butyl, and cyclohexyl groups on the non-extended backbone to promote more to less hydrogen bonding interactions, respectively.

The major variations studied included modification of the R-groups, as described in Table 3, and the inclusion of various additives tested at three concentration levels, as described in Table 4. NRL produced clear, filled, and doped cross-linked networks using a non-extended base PS structure, which can be synthesized with N-substituted urea linkages. The chemical functionalization substitution modulates the degree of promoted hydrogen bonding within the polymer, which in turn presents variable chemical environment and polymer chain mobility for diffusing contaminants. Past work on transport in PU films has shown that availability and competition for hydrogen bonding sites on polymer backbones influences diffusivity for chemical penetrants. Additives such as the fluorinated alkoxy silane or octadecyltrimethoxysilane (ODTMS) are agent-phobic moieties that cross-link at the alkoxy silane groups of the polymer and showed some response in the initial screening.

Table 4. Additives Included in Each of the Polymers Listed in Table 3
(Corresponds to NRL Sample Sets 015 and 022)

Solid or Additive	Loading (vol %)	Polymer type	NRL Sample Identifier	Description
Fluorinated alkyl silane	0, 4, 7.7	<i>N</i> -methyl urea silane (MUS)	015 A/B/C	Agent phobic additive cross-links at the alkoxy silane groups of the polymer
		<i>N</i> - <i>tert</i> -Butyl urea silane	015 D/E/F	
		<i>N</i> -Cyclohexyl urea silane	015 G/H/I	
ODTMS	5, 11	<i>N</i> -MUS	022 A/B	Additive that cross-links at the alkoxy silane groups of the polymer
		<i>N</i> - <i>tert</i> -Butyl urea silane	022 E/F	
		<i>N</i> -Cyclohexyl urea silane	022 I/J	
Polypropylene matting agent	10, 20	<i>N</i> -MUS	022 C/D	PP beads that disrupt polymer matrix and create polymer-particle interface
		<i>N</i> - <i>tert</i> -Butyl urea silane	022 G/H	
		<i>N</i> -Cyclohexyl urea silane	022 K/L	

RA measurements for the materials specified in Table 4 are shown in Figures 19–21 for GD, HD, and VX, respectively. Across all three contaminants, the variance in RA response as a function of loading in all three polymer structures was not as significant as hypothesized. Also, in most cases, the additive had similar influence across the different polymers (i.e., variation in steric hindrance or hydrogen bonding did not affect the additive loading on RA), with the fluorinated silane presenting the greatest difference for the case of the extended chain structure.

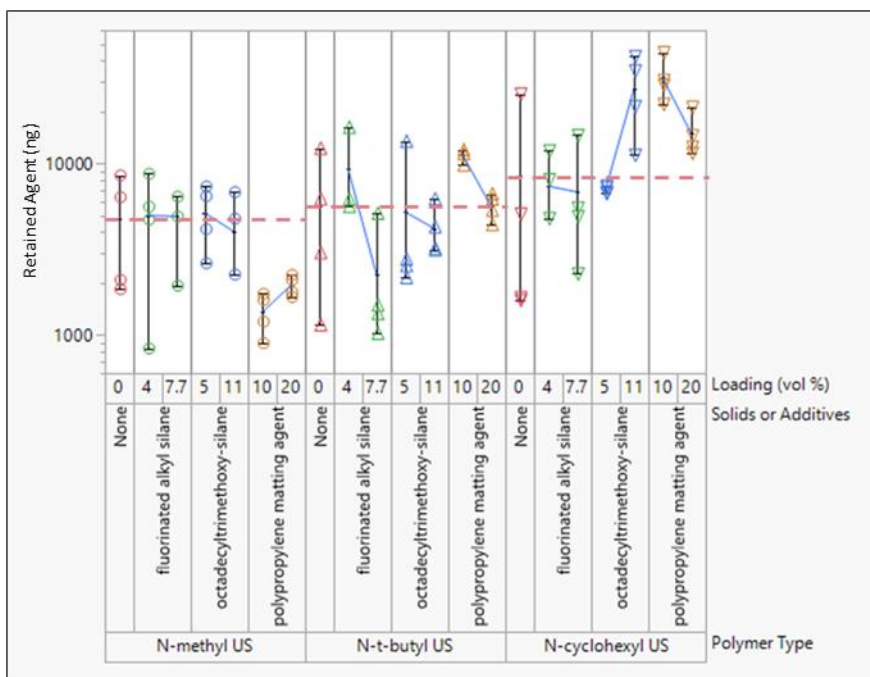


Figure 19. RA results for GD across the polymers and additives tested. Level corresponds to volume loading percentage. Dashed red lines correspond to the mean of cases with no additives or solids.

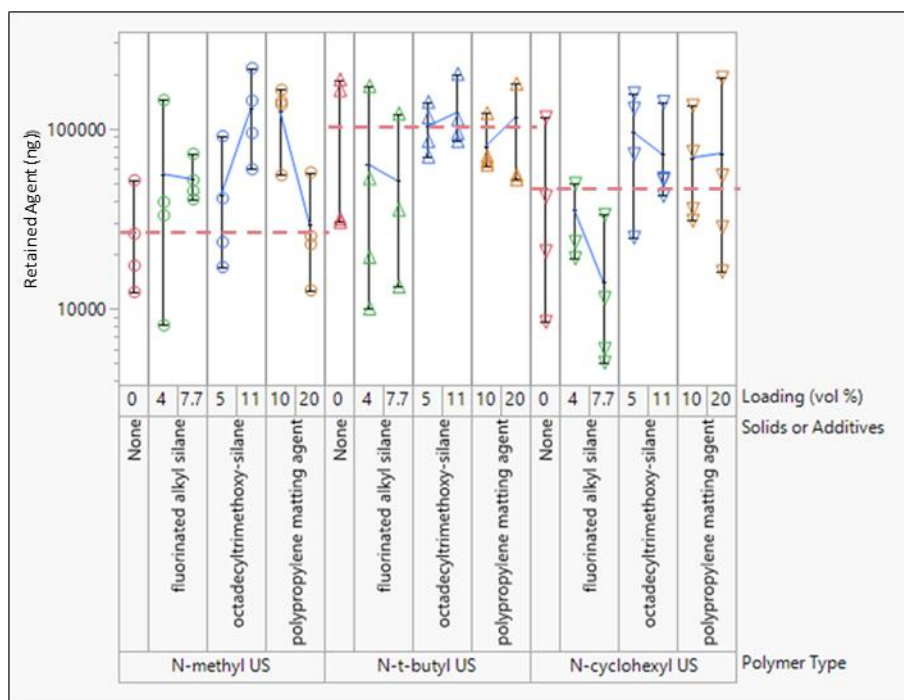


Figure 20. RA results for HD across the polymers and additives tested. Level corresponds to volume loading percentage. Dashed red lines correspond to the mean of cases with no additives or solids.

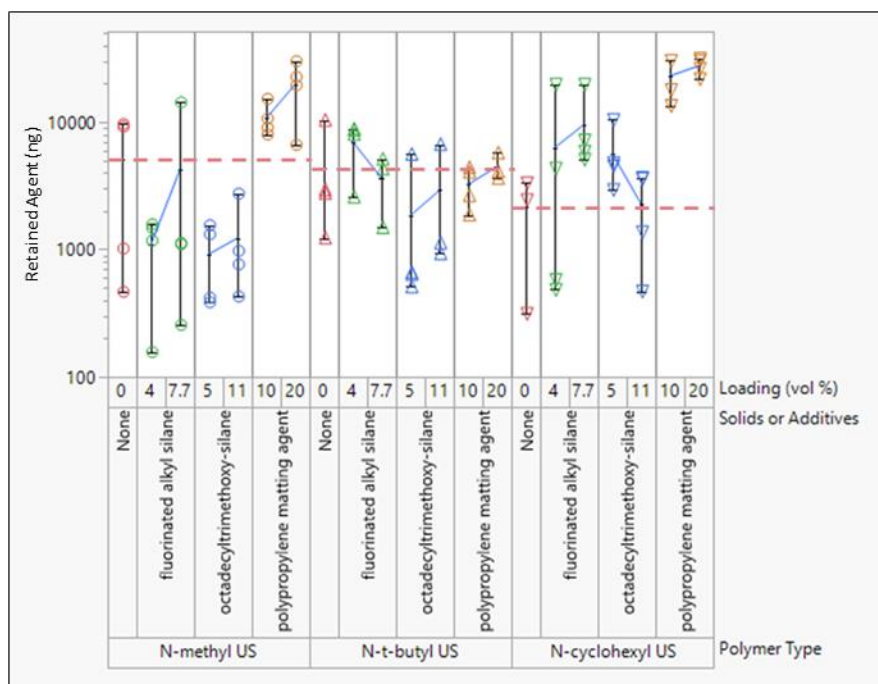


Figure 21. RA results for VX across the polymers and additives tested. Level corresponds to volume loading percentage. Dashed red lines correspond to the mean of cases with no additives or solids.

4.2.3 Optical Microscopy Observations for Sprayed Films

There are many potential pitfalls in a deconstruction-style investigation such as this, where the constituents of integrated materials systems are treated in isolation. The level of impact on different measurements as a function of sample preparation effects was tracked in this work. All NRL materials were sprayed on primed mini-panels, and the resultant films exhibited a wide range of defects, textures, and variations in morphology. The degree to which these film preparations for different types of materials significantly influence RA measurements using liquid deposition is unclear. The following questions may need to be addressed in future work:

- Is the lack of signal due to the influence of the components chosen, or is it more a function of the sample preparation, including the use of mini-panel substrates?
- Can we independently but efficiently test different hypotheses to check for systemic trends in RA evaluations?
- What are the other options for sample preparation that would permit sufficiently high throughput?
- Are there any complications with regard to how these types of films are sprayed due to the variations in solid loadings and types?

Optical microscopy images of the polymer films described in Table 3 are provided in Figure 22. There is variation in the material as a function of the polymer for the sprayed films; however, it is not clear what causes the apparent defects (e.g., surface or subsurface bubbles) or whether there is a significant influence on RA. Optical microscopy was also used to characterize how the additives influenced the coating morphology (Figure 23). The inclusion of an additive can influence polymer composite film surface texture or morphology; furthermore, depending on the type of additive, there can be varying levels of inhomogeneity with regard to additive distribution, which can result in domains or clustering. The influence of these morphology effects is not directly integrated into the RA analysis but provides context as to which film characteristics may be relevant to track as new samples are tested.

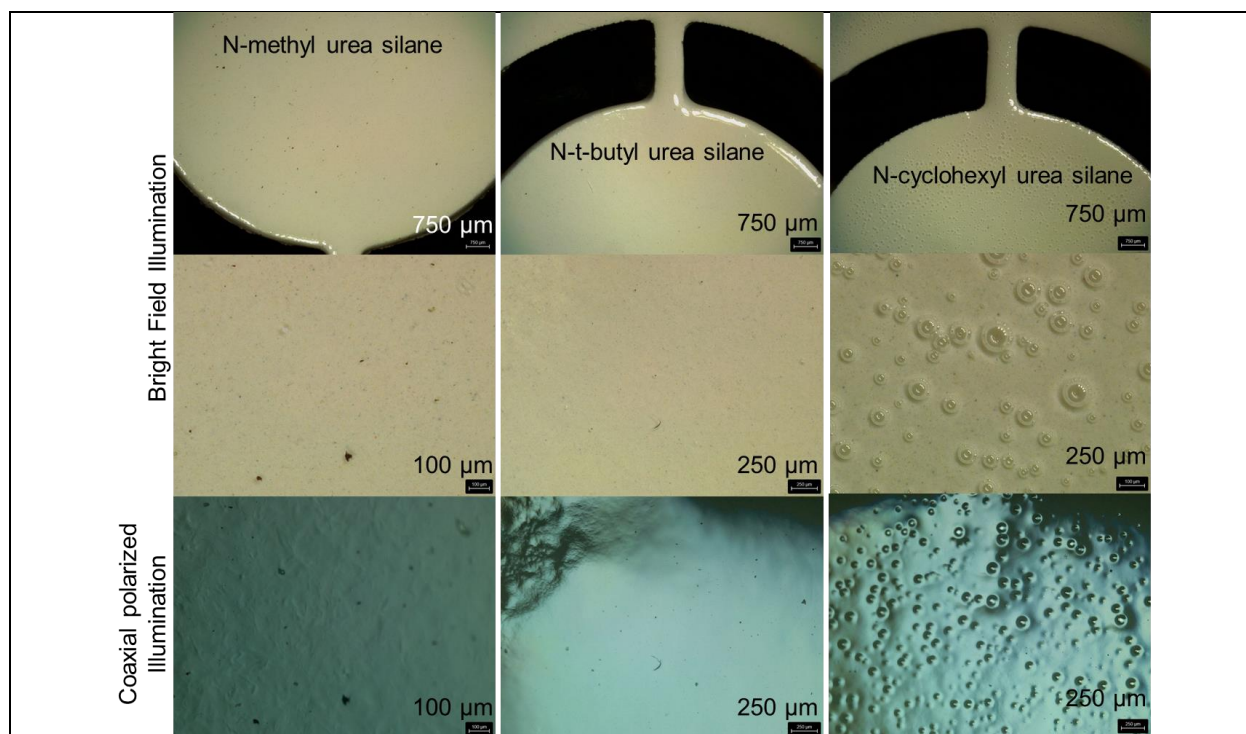


Figure 22. Optical microscopy images of the pure polymers showing surface textures and defects. Coaxial illumination was between 6 and 11° off normal incidence to highlight surface texture.

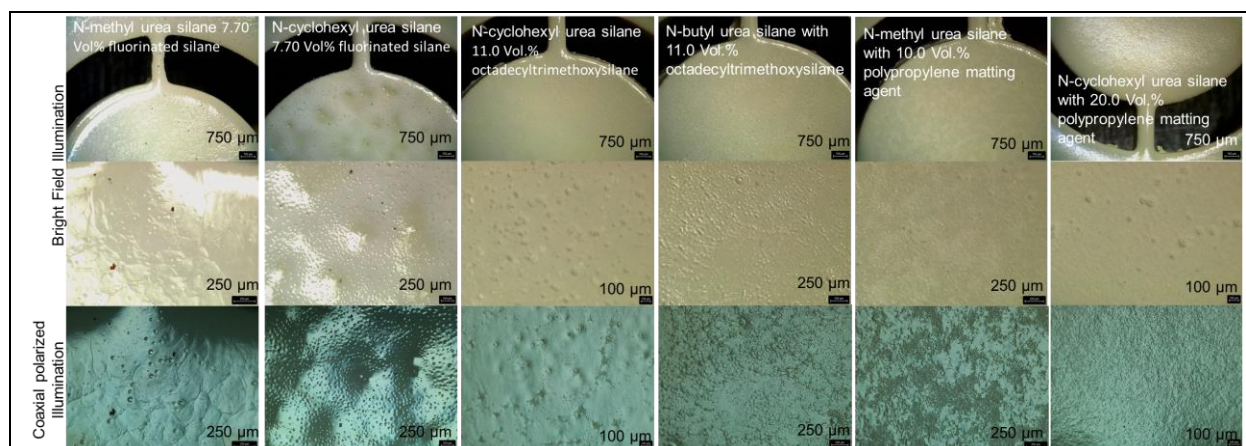


Figure 23. Optical microscopy of select samples including additives. Coaxial and bright-field illumination was between 6 and 11° off normal incidence to highlight surface texture. The images in the middle and bottom rows shows the same sample area recorded with different illumination/contrast.

The polymers generated for testing need to be characterized so that confident correlations can be drawn between polymer structure and agent resistance. This is particularly important during this phase of testing, in which the strongest influences on contaminant retention for the class of coatings under investigation are being uncovered.

The following questions and topics, some of which have been addressed in the past, might be worth revisiting:

- What can we learn about the chemical resistance of fully formulated systems by studying simpler versions consisting of one or two solid additives at a time? To support paint formulation optimization, where does this type of simplification succeed and where might it fail?
- From NRL's perspective, for the formulation of paint, what needs to be considered when separating the paint formulation into its constitutive components? Or, to rephrase, what are the scientific pitfalls in creating model systems with polymer binders and single types of dispersed solids?
- What are the synthetic limitations? This topic has been covered in the past, but a revisit is warranted regarding preparation options for different types of samples. The biggest challenge is controlling the size of the solids relative to the film thickness. This is an important consideration for measurements where film thickness is a limitation, such as QCM and FTIR; it is not as much of an issue for DMA.

4.2.4 RA Trends due to Inclusion of Cross-Linking Agents

To probe the effect of specific cross-linking additives at higher loadings on agent retention, a set of materials (Table 5) was produced with additives containing thiol or amine functionality. Higher loadings were considered in this sample set to push the bounds for what might be necessary to observe an RA response.

Table 5. NRL 039 Sample Set to Evaluate the Effect of Including a Cross-Linking Additive with Variable Functionality*

NRL Sample Identifier	Chemical Functionalization Substitution, Base Polymer	Additive	Loading (vol %)	Data Use
039A	N-MUS	None	0	Primer and non-extended polymer with functionalization substitution to promote higher hydrogen bonding within polymer
039B		3-Mercaptopropyl-trimethoxysilane (MPTMS)	10	039A and cross-linking additive with thiol functional group
039C		Tetraethyl orthosilicate (TEOS)	20	039A with high loading of cross-linking additive (no fluorine, sulfur, or nitrogen-based functionalities)
039D		3-Aminopropyl-trimethoxysilane (APTMS)	10	039A and cross-linking additive with amino functional group at lower loading
039E		APTMS	20	039A and cross-linking additive with amino functional group at higher loading
039F	N-Cyclohexyl urea silane	None	0	Primer and non-extended polymer with functionalization substitution to promote lower hydrogen bonding within polymer
039G		MPTMS	10	039A and cross-linking additive with thiol functional group
039H		TEOS	20	039A with high loading of cross-linking additive (no fluorine, sulfur, or nitrogen-based functionalities)
039I		APTMS	10	039A and cross-linking additive with amino functional group at lower loading
039J		APTMS	20	039A and cross-linking additive with amino functional group at higher loading

*For example, inclusion of thiol or amino groups or neither (see Figure 24). Base polymers are at two ends of the spectrum with regard to promoted hydrogen bonding.

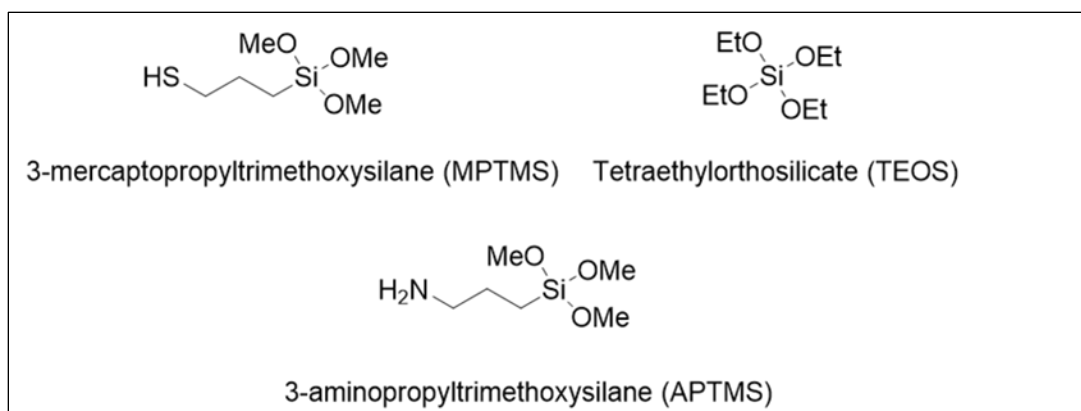


Figure 24. Chemical structures of additives explored by NRL with urea silane-based polymers.

Figure 25 shows a summary of additive (chemical structures shown in Figure 24) impact on RA as measured by liquid exposure for two different base polymers across GD, HD, and VX. This dataset also highlights the translation of APTMS's impact on full formulations. In most cases, APTMS reduces agent retention. Addition of APTMS to *N*-cyclohexyl urea silane reduced agent retention to levels similar to those for *N*-methyl urea silane (*N*-MUS), whereas MPTMS had no effect or increased agent retention. TEOS had no effect or reduced agent retention. *N*-Cyclohexyl urea silane was more influenced by additives than was *N*-MUS.

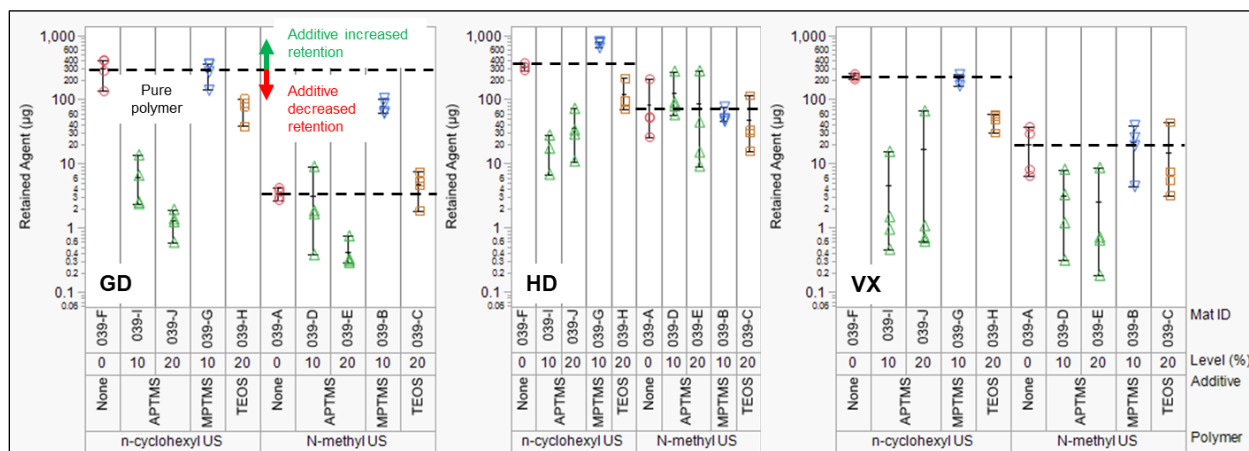


Figure 25. Liquid contamination (240 min duration) on two different polymers, *N*-methyl and *N*-cyclohexyl urea silane (US), with varying additives sprayed onto primed substrates for GD, HD, and VX. Dashed lines indicate baseline (no additive) polymer responses for each polymer-agent combination.

The RA data displayed in Figure 26 show a lack of differentiation in RA response from CARM mini-panel measurements for HD compared to those for VX for the same base polymer as a function of additives used for promoting cross-linking (Table 5; designated by the red box in Figure 26) as a well as a solid (polypropylene matting agent; the blue box in the figure) that was previously hypothesized to be an example of a major contributor to RA. Dashed

lines correspond to the polymer baseline mean RA response for each agent. Modifications to the *N*-MUS polymer were more effective in lowering RA with respect to the baseline as compared to the same variations for HD.

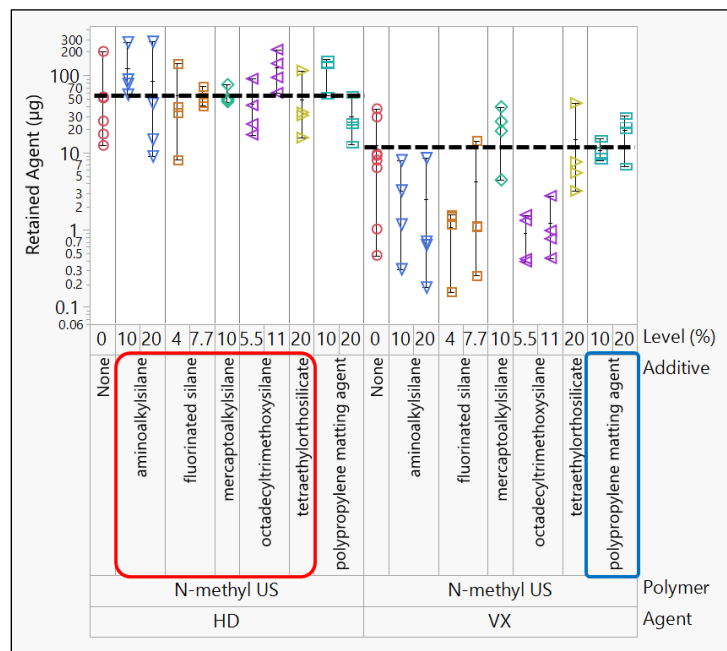


Figure 26. HD and VX RA data for NRL sample set 039 with a focus on the *N*-MUS polymer (see Table 5).

4.2.5 Challenges with Liquid-Phase Exposure RA Measurements for Polymers

The agent retention results for the pure polymers and the samples with different additives and solids are provided in Figures 27–29 for GD, HD, and VX, respectively, as a function of polymer structure, additive type, and additive loading level. Included for comparison are measurements for materials from NRL sample sets 007, 015, 022, and 039 as well as PU-based coatings of three different pigmentations: black, green, and tan. Overall, for the baseline pure polymer cases, no significant differences in agent retention were observed across the polymer functionalization, with the potential exception of *N*-cyclohexyl urea silane providing lower retention for VX. Increasing or promoting hydrogen bonding interactions via substitution of the functional groups on the chosen polymer backbones did not impact RA. As indicated previously, the extended chain polymer had higher retention for HD and VX relative to its non-extended counterpart. Based on past work with polymer composites, specifically for coatings materials,¹ the pure polymer cases presented the lowest RA and set the lower bound of the dynamic range for RA.

Variations in solid loadings from the base materials (i.e., the designation of low- and high-volume percentages) did not result in more than a 1 log difference (LD) between levels. The mini-panel RA results for these polymer systems had a greater data variance than occurred in previous results for fully formulated coatings, which made it more difficult to identify the influence of the additives. The same personnel and procedures were used in this

work as in previous studies; the variability was likely attributable to how the agents and the treatment processes interacted with these polymers. There was also limited dynamic range for the RA measurements considering that the baseline, pure polymer conditions were within factors of 10–100 of the dose mass. Additionally, the lack of differentiation within the RA data for these investigations indicates the necessity for other types of measurements that can resolve specific influences of chemical environment and film morphology on penetrant transport and retention.

As part of the comparisons shown in Figures 27–29, an *N*-cyclohexyl urea silane polymer baseline repeat with no additive loading was included (compare material identifiers 015G and 039F). It is unclear why there was a significant variance in the RA among the polymer films across all three agents. Many different reasons were investigated, including whether the sprayed films for 039F had a significantly higher defect density to permit liquid permeation and whether there was a difference in chemical identity at the surface. Optical microscopy imaging was relatively inconclusive; both films were very similar. However, vibrational absorption bands in the FTIR-ATR spectrum for the 039F surface were broader than for 015G, which indicates that a degree of chemical degradation had occurred for the films. It is possible that the polymer structure of the 039F films was different from and more heterogeneous than that of the 015G films and permitted increased liquid retention. This disparity in film response highlights the need for careful consideration of baseline responses, especially for materials evaluated out of context from use in an engineered coating system. Both baselines are included in the dataset because materials that were generated from both baseline solutions were included in the comparison.

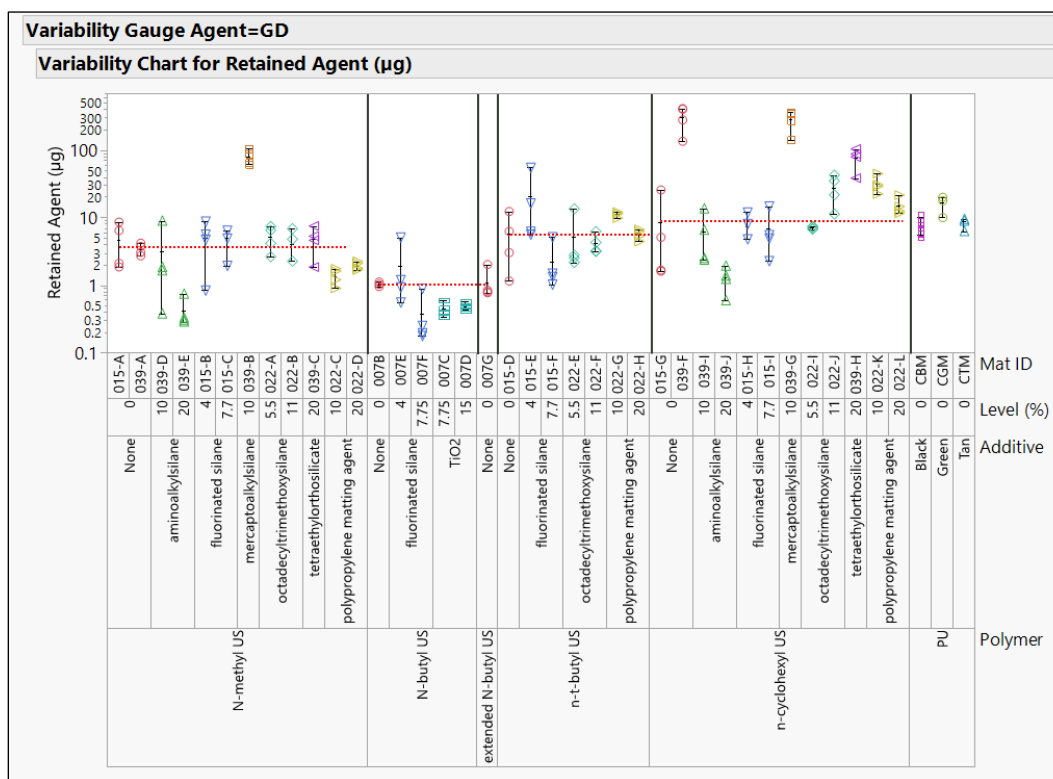
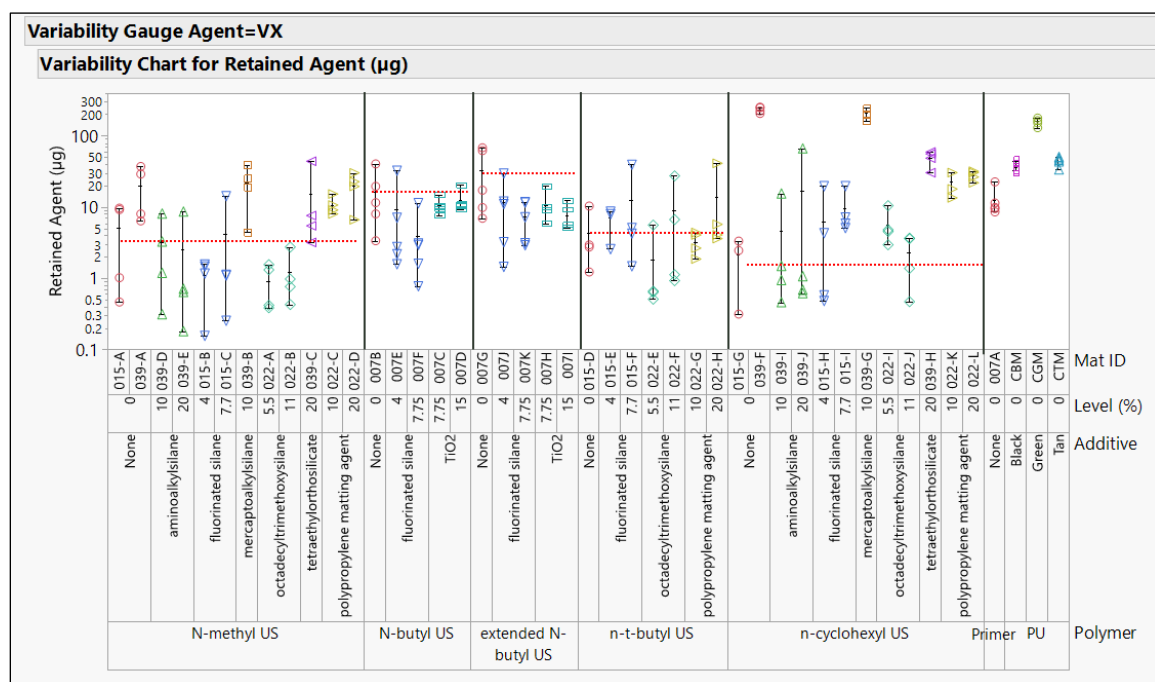
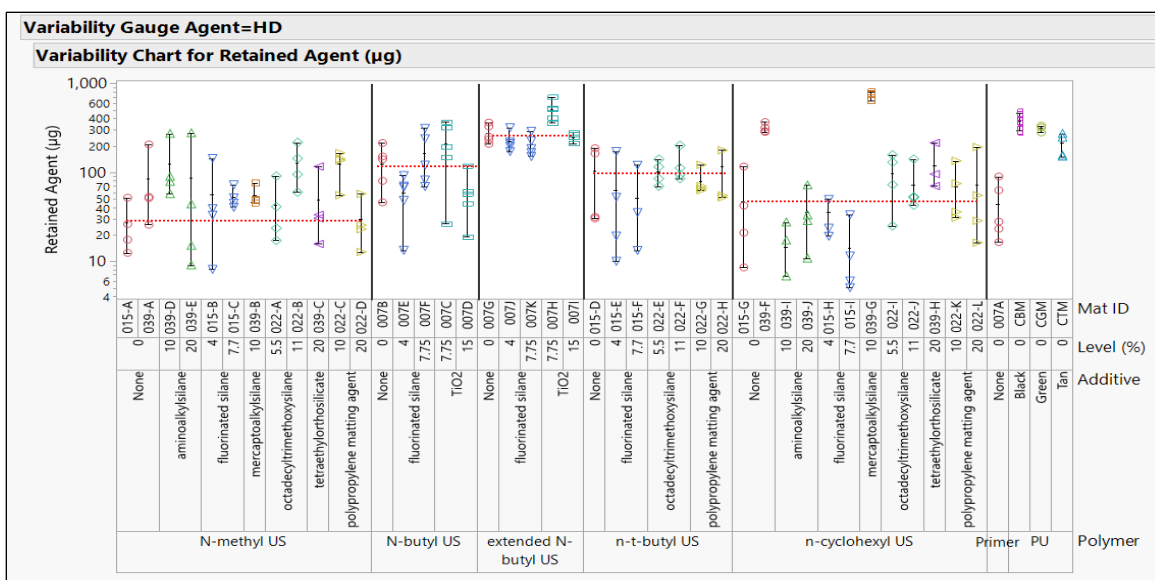


Figure 27. RA results for GD across the polymers and additives tested. Level corresponds to volume loading percentage. See Tables 2, 4, and 5 for sample identifiers; PU polymer corresponds to a polyurethane-based coating with three different pigmentations. US, urea silane.



4.2.6 RA for Films with Higher Loadings of Cross-Linking Additives and Matting Agents and Evaluation of the Impact of Primer

Based on the improved resistance observed in previous results, the APTMS additive was investigated at higher loadings. The effect of a matting agent (solid additive) was also considered. The test used liquid exposure for polymers with varying additives and included both absorbed chemical mass and the possibility of RA signal from surface-adhered bulk liquid. Results from previous work have indicated that agent may permeate through topcoats and down to primer layers.¹ If this occurs and the agent is retained into the primer layer, it could produce bias in the retention measurement for topcoat materials applied to primer as compared to the measurement for direct application to bare metal. The primer layer is key in coating system performance, particularly in providing good adhesion to the substrate. However, for the analysis of agent retention in polymers, this layer may not be required. This test included samples with and without a primer layer so that we could determine whether future samples need to include a primer or whether the polymers can be applied to bare metal. Table 6 denotes a sample set that was used to focus on measurements from existing full-formulation paints and specific additives and solids in conjunction with the *N*-butyl urea silane polymer variant. Fully formulated paint references as well as corresponding binders were included. The influence of APTMS as an additive, among other effects, was pursued further.

Table 6. NRL 014 Sample Set Including Fully Formulated Paint References (Along With Associated Polymer Binder References)*

NRL Sample Identifier	Material	Additive or Solids Loading (vol %)	Description
014A	PS-based paint, green	NA	Fully formulated coating, coating reference, <i>N</i> -butyl urea silane polymer binder
014B	PU-based paint, green	NA	Fully formulated coating, coating reference, PU binder
014C	PU	0	PU binder for 014B
014D	<i>N</i> -Butyl urea silane	0	PS binder for 014A, repeat of 007B
014E	<i>N</i> -Butyl urea silane and APTMS	50	Higher loading for high-impact additive, APTMS
014F	<i>N</i> -Butyl urea silane and polypropylene matting agent	50	Higher loading of matting agent, polypropylene matting agent
014G	<i>N</i> -MUS and fluorosilane	4	Repeat of 015B
014H	<i>N</i> -MUS and APTMS	20	Repeat of 039E
014I	Small-molecule silane with <i>N</i> -butyl urea and cycloaliphatic groups	0	Alternate PS binder to investigate chain size effects
014J	Small-molecule silane with <i>N</i> -butyl urea and cycloaliphatic groups	4	014I with fluorosilane additive
014K	<i>N</i> -butyl urea silane and polyurea matting agent	10	Polyurea matting agent, alternative matting agent composition

*This sample set was used to determine the impact of high loadings of specific additives and solids in multiple polymer binder configurations. All materials were prepared on both primed and bare metal mini-panels.

Summarized mini-panel RA data from sample set 014 are shown in Figure 30. A few key observations are listed below:

- Fully formulated PS- and PU-based paints showed similar RA responses, and the RA responses were similar across all agents for both binder types. Furthermore, with respect to RA response, *fully formulated materials were surprisingly similar to their binder counterparts.*
- The inclusion of matting agents did not drastically increase RA relative to PS polymers, which is somewhat contrary to what was hypothesized based on past work.

- The small-molecule cycloaliphatic variant for *N*-butyl urea silane polymer registered higher RA as compared to the other PS polymers.
- *The APTMS cross-linking additive at high loading was very effective at lowering RA in both N-butyl urea silane and N-MUS; fluorinated silane additive was not as impactful.*
- *The RA response for materials was not strongly dependent on underlying substrate (i.e., whether polymer was sprayed on primer or bare metal).*

Two main takeaways from these measurements have a significant impact on the direction of subsequent work. First, the ability to use unprimed or primed metal as a substrate for films sprayed on mini-panels was confirmed. Measurements of panels from the 014 sample set showed that RA did not vary significantly depending on whether a primer layer was included for a material under evaluation. In most cases, use of a primer was not necessary for adhesion of sprayed films to the substrate and introduced additional sample preparation steps. Second, solids such as matting agents were not as influential in RA responses as originally hypothesized and, therefore, are not as critical to consider in these investigations involving PS-based coatings and composites.

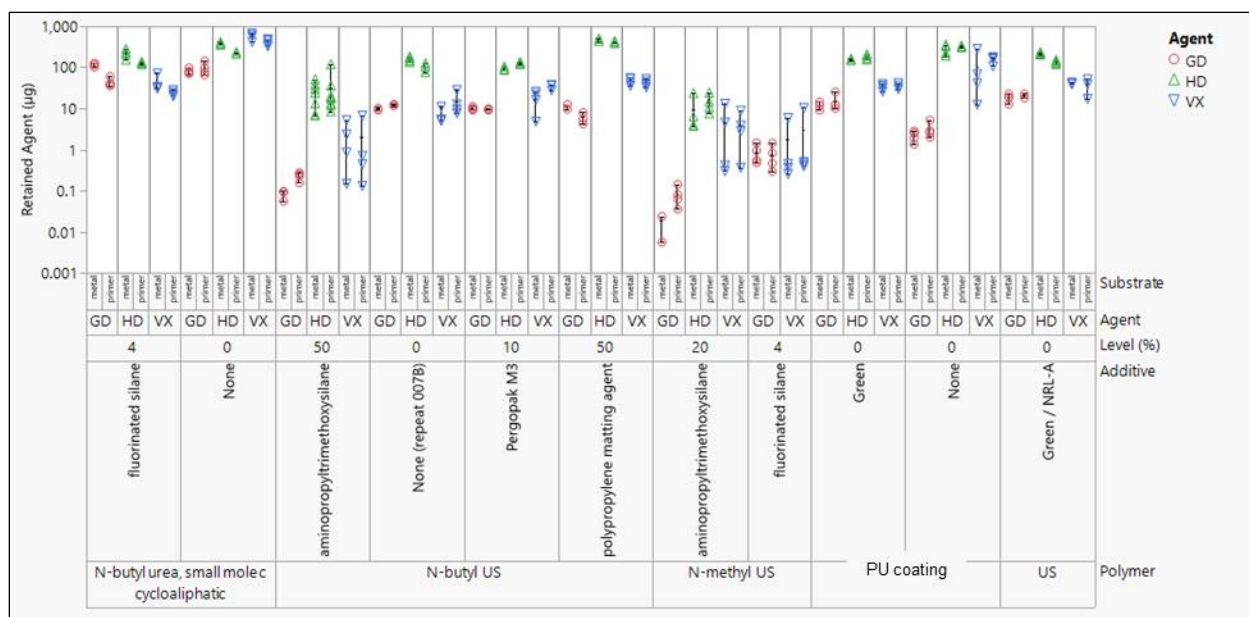


Figure 30. RA data for NRL sample set 014 (see Table 6) that highlights the similarity in RA response for materials with and without primer layers. US, urea silane.

4.2.7 Vapor Exposure Chemical Resistance Measurements

The results in Section 4.2.5 showed that using a CARM-based approach (i.e., liquid-phase contamination and a subsequent water-rinse process) produced very little differentiation in RA for the different permutations considered as a function of primary additives at different loadings to different base PS polymers. Additionally, we observed significant spread

(i.e., variability) in the RA response for replicates within a material type. These results suggest that surface-bound liquid significantly contributes to the RA signal and can potentially mask differences in absorbed mass. This prompted an investigation into the necessary steps to deconvolve the contributions to overall mass uptake.

CARM-based measurements that involve liquid deposition of contaminants and subsequent aqueous post-contamination processing are optimized principally for specific classes of engineered materials, and specifically, with regard to how absorbed mass is captured. As described in Section 3.5, a water-rinse treatment process was used to remove the bulk liquid agent from the coating surface, leaving behind the agent mass retained by the material, including surface-bound and bulk absorbed agent. Through the development of the CARM, a water-rinse process was determined to be appropriate for materials of various types because it was minimally invasive to absorbed mass, but this was established principally for fully formulated coatings. Quantifying RA mass is critical regardless of where in the material the mass is retained because the presence of RA is responsible for potential exposure to unprotected personnel interacting with coated assets and the RA quantity establishes the extent of decontamination that may be required. However, determination of efficacy for removal of bulk liquid contaminant from the surface of any material without employing other types of spectroscopic tools is very challenging. Although critically important, the roles of surface texture or morphology as well as surface chemistry for coatings of interest need to be addressed separately. Ultimately, the CARM is not designed to provide the necessary data for identification and quantification of relative contributions to RA (e.g., whether mass is absorbed or surface bound).

Our initial foray into this method involved HD exclusively because we need to better understand how to promote more HD-resistant materials. Vapor exposure measurements were conducted for three different vapor exposure durations: 90, 300, and 1200 min. We were able to verify that liquid HD does not completely evaporate by 1200 min, so there was no concern that available source vapor would be depleted or that contaminant would be re-emitted from the mini-panel materials. The time-resolved measurements showed that saturation had not been reached for any of the materials surveyed and that silicone and steel served as informative upper and lower bounds, respectively, for mass uptake (i.e., silicone elastomer for an absorbing material for agent and steel for a non-absorbing material). We were able to demonstrate with silicone that the total integrated dose for each well was consistent across all of the wells in the plate and across test sessions, even though we did not have a direct measure of the variable vapor concentration within each well-plate cell. Steel mini-panels exposed to HD adsorbed minimal mass ($<0.25\ \mu\text{g}$), and the recovered mass was not dependent on exposure time for the conditions tested (i.e., total mass uptake was achieved far earlier than the first vapor exposure duration). There was no evidence of bulk liquid condensation. Although finer control over vapor concentration (e.g., introduction of a well-defined activity vapor stream) would be preferable, especially to allow for different types of quantitative analysis, it would require the use of too much contaminant and would also require methods, procedures, and equipment that are not currently in place. We chose to prioritize a measurement that has the potential to serve as a relative screening tool for assessing differences in propensity for mass uptake in the limit of no liquid–solid interaction considerations.

The objective of the vapor exposure measurement was to address mass uptake in the absence of liquid–solid interactions that contribute significantly to the RA measured by

CARM. The various pit defects observed using optical microscopy (Figure 16) could also result in trapped liquids generating a larger magnitude and more variable RA. The vapor exposure process should be unaffected by these pit defects, thereby allowing an unbiased characterization of research-grade samples that present with such defects. The role of bulk liquid entrainment during contamination and the subsequent variable efficacy in removal of surface-bound bulk liquid through a water-rinse treatment process need to be investigated separately. The initial objective of vapor exposure measurement was to provide a more specific discriminator for screening materials based on absorbed mass. To start, we chose a set of materials that had the best opportunity for resolving contrast, at least as indicated by the results from the liquid-phase contamination measurements. Table 7 highlights the materials with liquid exposure RA measurements that prompted the materials selection.

Table 7. Materials Used to Evaluate the Vapor Exposure Method of Assessing Chemical Resistance

NRL Sample Identifier	Material	Description
014B	PU-based paint, green	Highly loaded polymer composite coating
014C	PU	PU reference; different polymer
014D	<i>N</i> -butyl urea silane	Pure PS polymer reference
014E	<i>N</i> -Butyl urea silane + APTMS	Low RA for liquid exposure, includes APTMS
014F	<i>N</i> -Butyl urea silane + matting agent	Example of high absorber, matting agent solids inclusion
039F	<i>N</i> -Cyclohexyl urea silane	Pure polymer, with possible degradation
015G	<i>N</i> -Cyclohexyl urea silane	Pure polymer matching 039F stock solution, possibly not degraded
007J	Extended <i>N</i> -butyl urea silane + fluorinated alkoxysilane additive	Extended polymer structure with low loading of fluorinated alkoxysilane additive, similar response to case with no additive

Results for RA from HD vapor exposure measurements are shown in Figures 31 and 32. Figure 31 shows the variation in RA as a function of vapor exposure time for each material, including silicone and steel reference conditions. The cases where the RA was very low as compared to other materials are immediately apparent from the results, namely, for samples 014E and 015G and at early vapor exposure times, comparable to the results for steel. The case of 015G may be revisited in the future, but reproducibility of response is complicated by increased instability for *N*-cyclohexyl urea silane; therefore, more focus was placed on *N*-MUS and *N*-butyl urea silane structures. This is also shown in Figure 32, where the RA data for Figure 31 were captured with a continuous rather than categorical time axis. The overall profiles for these materials are similar in shape, but it is unclear what this indicates about the transport process. The fits provided in Figure 32 are log–log fits for a power law, RA mass versus time (t), in which ideal Fickian diffusion would track as $n = 0.5$. The fit values are closer to 1 and higher,

which may indicate the presence of a sharp swelling front for penetration into the material, suggestive of Case II diffusion. This is still under investigation as we refine the details of this method and seek to understand the dose conditions, especially regarding what processes are rate limiting in absorption (air-phase diffusivity of agent in contrast to diffusivity in the material).

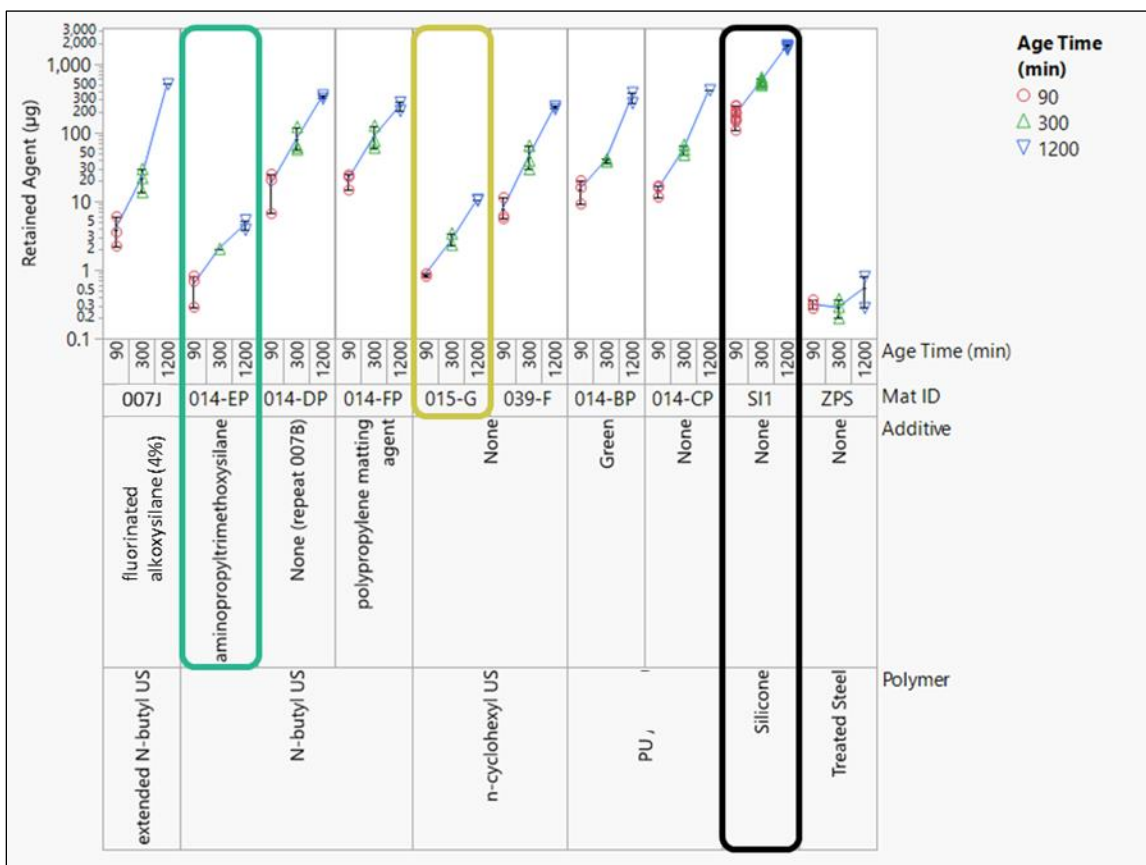


Figure 31. RA data from HD vapor exposure test for select NRL materials and reference materials, including silicone and stainless steel. The black box highlights data corresponding to silicone, and the other colored boxes highlight the materials with very different, low absorption trends, namely, 015G and 014EP. Colors are defined in Figure 32 legend. US, urea silane.

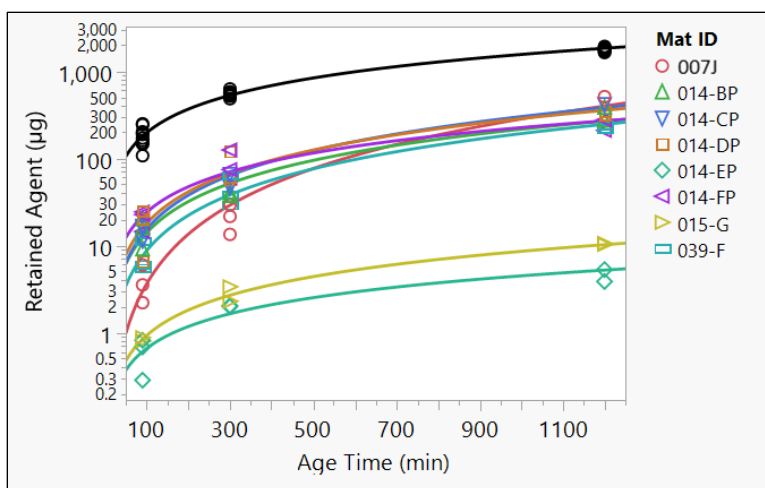


Figure 32. RA data from HD vapor exposure test (see Figure 31) for select NRL materials and reference materials along with log–log fits of RA to time plotted with a continuous (as opposed to categorical) time axis. The black data points correspond to HD absorption in silicone. Profiles are similar for all materials except 015G and 014EP, which had noticeably different responses.

There was also an increase in dynamic range magnitude or signal-to-noise ratio (shown in Figures 33 and 34) that was not nearly as apparent from the liquid exposure data. These results indicate the following:

- The combination of RA data from both measurements indicates that the RA for pure polymers (both PU and PS) was very similar to that for fully formulated paint. Therefore, it is critical that the polymer structure, mechanical properties, and binder chemical environment be tuned to make headway in enhancing resistance for formulated coatings.
- Small differences measured by liquid exposure for specific additives were amplified in many cases when measured by vapor exposure.
- Differences in RA between liquid and vapor exposure were not uniform across all cases, indicating that certain materials configurations are more or less sensitive to certain pathways to mass uptake and retention.
- Additives (e.g., cross-linkers) and solids alter the base polymer in fundamentally different ways, but both impact bulk mechanical behavior and material morphology (surface, interfacial, and bulk). The lack of RA response to variation in solid loadings for these measurements does not preclude the impact of solid inclusion on the overall chemical retention, especially for liquid exposure with an associated post-contamination material treatment.

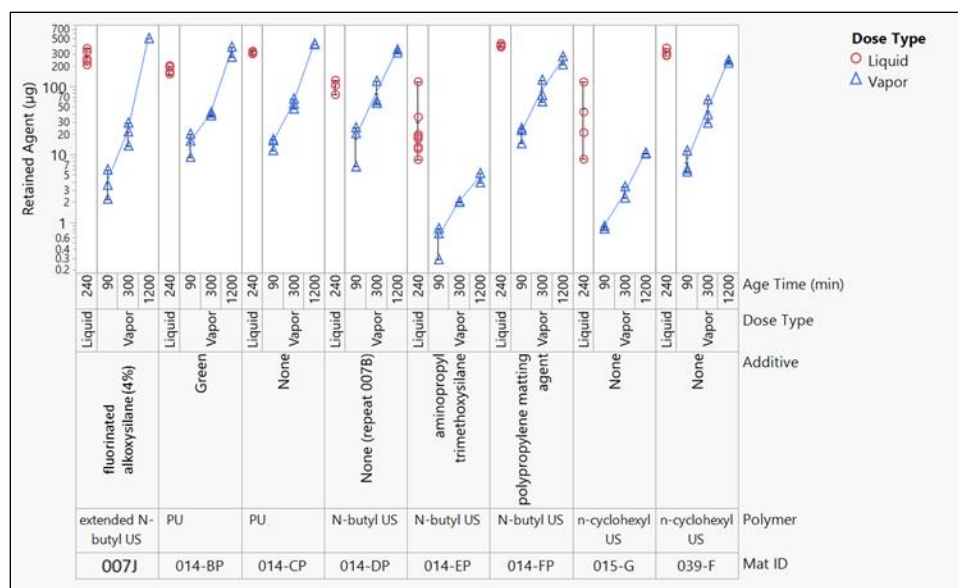


Figure 33. Comparison between HD RA measurements for liquid exposure (red circles) at a single contamination time (240 min) and vapor exposure (blue triangles) at multiple exposure times. US, urea silane.

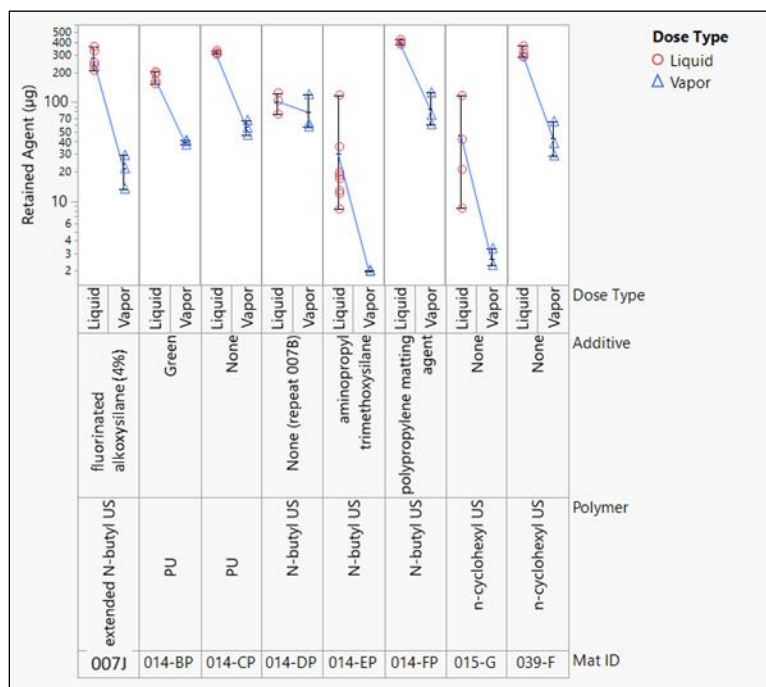


Figure 34. Comparison between RA measurements for liquid (red circles) and vapor (blue triangles) exposure for HD, specifically for similar contamination duration times (240 min for liquid and 300 min for vapor). US, urea silane.

A follow-up vapor exposure test was performed to specifically address previously tested materials with variable additives where there was limited differentiation in RA response. Figure 35 shows a compilation of the RA data for HD recorded for liquid and vapor exposure for most of the NRL materials that have been tested to date. This includes a selection of the base polymers with additives such as fluorinated silane, ODTMS, and aminoalkylsilane as well as another case of inclusion of high loadings of propylene matting agent solids. There are some readily apparent trends to highlight, including the following:

- Variance in RA from vapor exposure can have a larger dynamic range across additives as compared to RA measured from liquid exposure (see the case highlighted for *N*-MUS [purple box in Figure 35]).
- Inclusion of the additive ODTMS does not result in a decrease in RA relative to the baseline for most of the polymer systems (red boxes in the figure).
- Additives with amino functionalities like APTMS and fluorinated silane show promise for decreasing RA for many polymer bases (green boxes in the figure).

These observations are not as clearly identifiable without the benefit of the data texture from RA collected from both liquid and vapor exposure. Not included in this dataset are some aberrant data points for vapor exposure, where we think the high signal for certain replicates was due to the presence of adhesive residue or actual adhesive that had absorbed agent vapor.

We also conducted an initial measurement with a single time point (300 min) exposure to silicone to verify the viability of future GD and VX measurements. Results indicated that it is possible to measure both GD and VX mass uptake from vapor exposure in this fashion. There are trends that need to be verified with respect to possible variances in integrated dose as a function of well position in the well plate array.

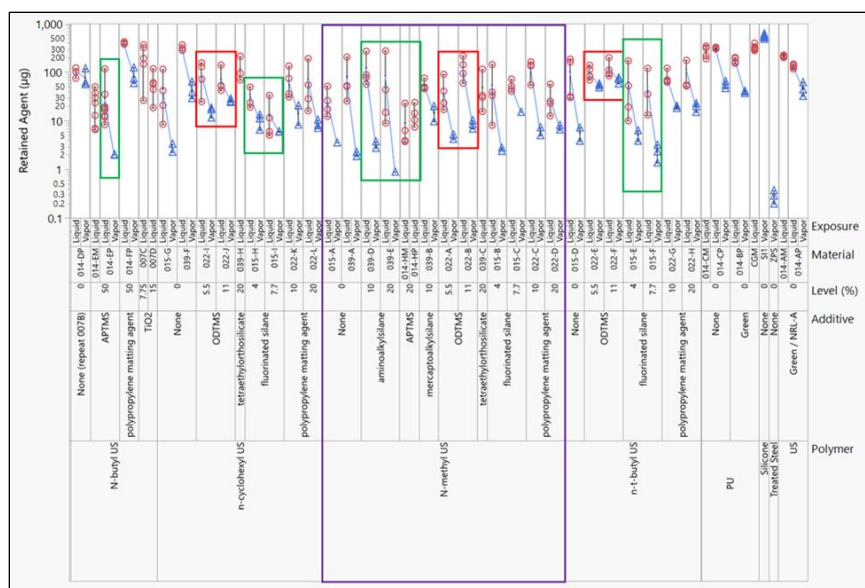


Figure 35. Comparison between RA measurements for HD liquid and vapor exposures, specifically for similar contamination duration times (240 min for liquid and 300 min for vapor), for a broad range of materials. See bulleted text for explanation of highlighted data sections. US, urea silane.

Additional data to highlight the information gathered from liquid and vapor exposure measurements for the specific case of *N*-butyl urea silane as the base polymer compared to *N*-butyl urea silane-based paint as well as compared to PU and a PU-based paint is shown in Figure 36. Two key items should be noted regarding RA as a function of exposure type and RA as a function of additive or solid loading for a given polymer. First, the only case where there was a small difference between liquid and vapor exposure was for *N*-butyl urea silane without any additives. Otherwise, the exposure type seemed to reveal different mechanisms of uptake depending on the additive type. Second, there was very little difference between PU and PU-based paint responses, which indicates that the polymer is highly influential in the RA response.

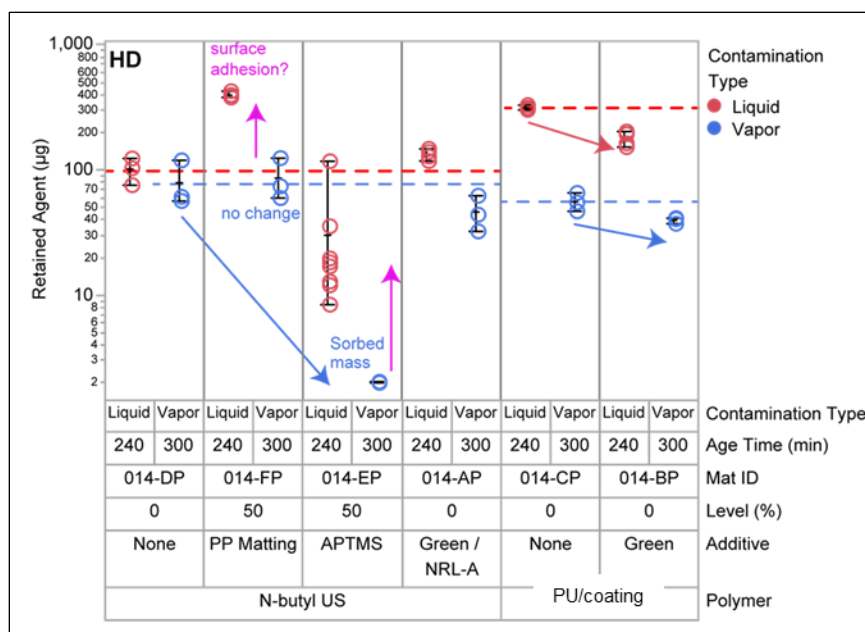


Figure 36. Comparison of liquid and vapor responses for different additives, highlighted for HD. Possible contributions of surface-adhered bulk liquid to RA are identified. US, urea silane.

Ultimately, more work is necessary to determine a more quantitative correlation between liquid and vapor exposure RA responses. Additionally, test hardware can be improved to allow for easier test setup, minimize volume for each cell, and avoid use of any other materials that can act as vapor sinks (e.g., adhesives used to affix mini-panels to the aluminum-lined well plate lid). Figure 37 shows a possible change to the hardware used for executing this type of vapor-exposure test. The current use of available polystyrene multiwell plates does allow for high-throughput processing of vapor exposure to mini-panels; however, the setup burden is significant because the wells need to be lined with metal foil to minimize the opportunity for contaminant liquid or vapor to absorb into materials other than the mini-panel.

We have produced an experimental technique leveraging our current test infrastructure that allows us to isolate surface-bound agent from absorbed agent. This new experimental configuration enables us to better understand how polymer variations influence agent absorption independent of surface interactions that occur with liquid contamination. The vapor-exposure method enables us to deconvolve some of the retention mechanisms so we can develop a strategic path for formulation. Further, these data illustrate that the surface-bound liquid contributions observed with CARM treatment procedures may have been masking the absorbed agent effects that we were seeking to probe with the formulation modifications. This does not, however, indicate any deficiency with use of the CARM to evaluate final formulation coatings.

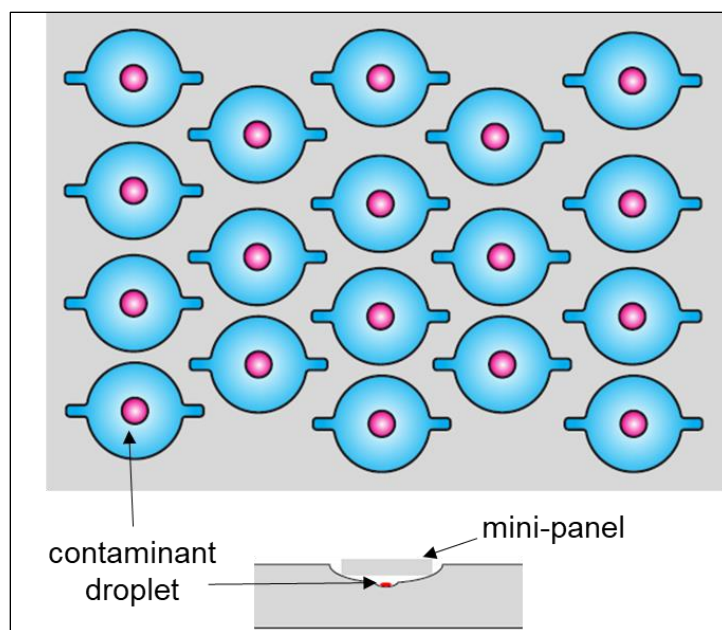


Figure 37. Prototype alternate multiwell plate for vapor exposure measurements. Top: top view of a plate with an array of wells. Each well has a deeper divot in the center where a contaminant droplet would be located. Bottom: side view of single well with a mini-panel resting on the well, directly above the contaminant.

These vapor exposure measurements indicate what might be expected from QCM experiments with probe molecules and future work using DMA for contaminated free films. While we are ultimately interested in solving a challenge for coatings exposed to liquid contaminants, vapor exposure-based measurements, whether for agent or simulant probe molecules used in other techniques, will be very useful for quantifying mass uptake and retention routes that are not driven principally by liquid–solid interactions. By expanding the means of contamination, we anticipate that we will be better able to determine the roles of different coatings properties and constituents in agent solubility, transport, permeation, and adhesion, all of which are responsible for RA mass.

4.2.8 Role of APTMS on HD Retention in Polymer Binder Films

The influence of polymer network structure on agent retention was investigated, with a particular focus on why the cross-linking additive APTMS affects HD resistance for both pure polymer binder films and fully formulated coatings (see Section 4.3). A set of experiments using various loading levels of additives was devised to investigate which properties or factors drive changes in HD retention, including the role of amino functionality and how polymer network structure influences penetrant transport (e.g., correlating changes in RA with changes in cross-link density, molecular weight between cross-links, and system homogeneity). Listed below are the binders, additives, and loading levels considered. It was hypothesized that the inclusion of APTMS has a strong influence on network structure, which yields measurable changes in system mechanical and transport properties.

Binders (two different polymers; see Figure 38 for molecular structures):

- Extended urea silane polymer, 75:25 silane–diamine ratio (resembles commercial configuration); and
- Non-extended urea silane polymer (*N*-butyl), the structure used in most of the experiments described previously.

Additives (varying amine quantity and functionality; 0, 1, 5, 10, and 20% loading levels; see Figure 39):

- APTMS;
- *N*-propyl trimethoxysilane (TMS) (NPTMS);
- 3-(*N,N*-dimethyl-aminopropyl) TMS (diMeAmino TMS); and
- *N*-(2-aminoethyl)-3-aminopropyl TMS (AminoEt-AminoPr TMS).

Lower loading levels were specified to provide dynamic range for the evaluation of additive influence on cross-link density trends. Some trends were anticipated at the 5% volume loading level, and the 1% loading level was also assessed to confirm this. For DMA measurements, the 40% loading films were difficult to handle for sampling; they tended to shatter or break and fall into the instrument. Previous 40% APTMS loaded films did show agent retention signal, but this configuration may push too hard on the resulting material properties.

Vapor exposure chemical resistance measurements with GD and HD were performed for variable additive loadings in two different base polymers. Additionally, simulant exposure measurements were performed for one set of materials to establish probe molecule correlations with the agent retention. The results at high volume percentage loadings of APTMS prompted an investigation into the role of the amino functionality in chemical retention through its influence on the polymer structure or direct chemical interaction with the penetrants. The variable loading, especially to low loading levels, is postulated to show how the base polymer and its response to penetrant exposure are influenced (see Table 8).

Table 8. NRL 055 and 059 Sample Sets Focused on Evaluation of Variable Loading of Additives with Amino Functional Groups of Variable Number and Position in the Additive Molecular Structure

NRL Sample Identifier	Base Polymer	Additive	Additive Loading (vol %)
055-A	Extended chain (25 mol % diamine extender, 75 mol % <i>N</i> -butyl aminosilane)	None	0
055-B/C/D/E		APTMS	1, 5, 10, 20
055-F/G/H/I		NPTMS	
055-J/K/L/M		diMeAmino TMS	
055-N/O/P/Q		AminoEt-AminoPr TMS	
059-A	Non-extended chain (<i>N</i> -butyl urea silane)	None	0
059-B/C/D/E		APTMS	1, 5, 10, 20
059-F/G/H/I		NPTMS	
059-J/K/L/M		diMeAmino TMS	
059-N/O/P/Q		AminoEt-AminoPr TMS	

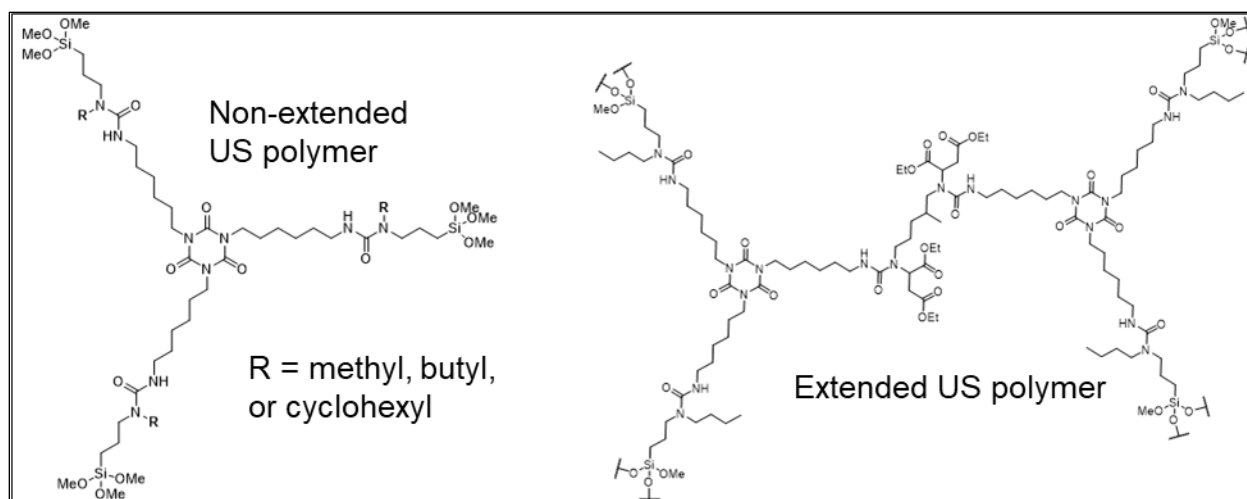


Figure 38. Examples of molecular structures of non-extended urea silane (left) and extended urea silane (right) polymers under investigation. US, urea silane.

Notes on the additives chosen are listed below. Molecular structure descriptions are referenced with respect to APTMS. Molecular structures are shown in Figure 39.

- APTMS: Most responsive additive for influencing RA; involves a single primary amine at one end of an NPTMS chain.
- NPTMS: Amino functionality is removed from APTMS, but the remainder of the molecular structure is retained; no amine functional groups.
- diMeAmino TMS: Steric hindrance or access to amino group on APTMS is increased by replacing hydrogens on amino group of APTMS with methyl groups, resulting in a tertiary amine.
- AminoEt-AminoPr TMS: An aminoethyl chain is added to APTMS, which results in the presence of both a primary and a secondary amine.

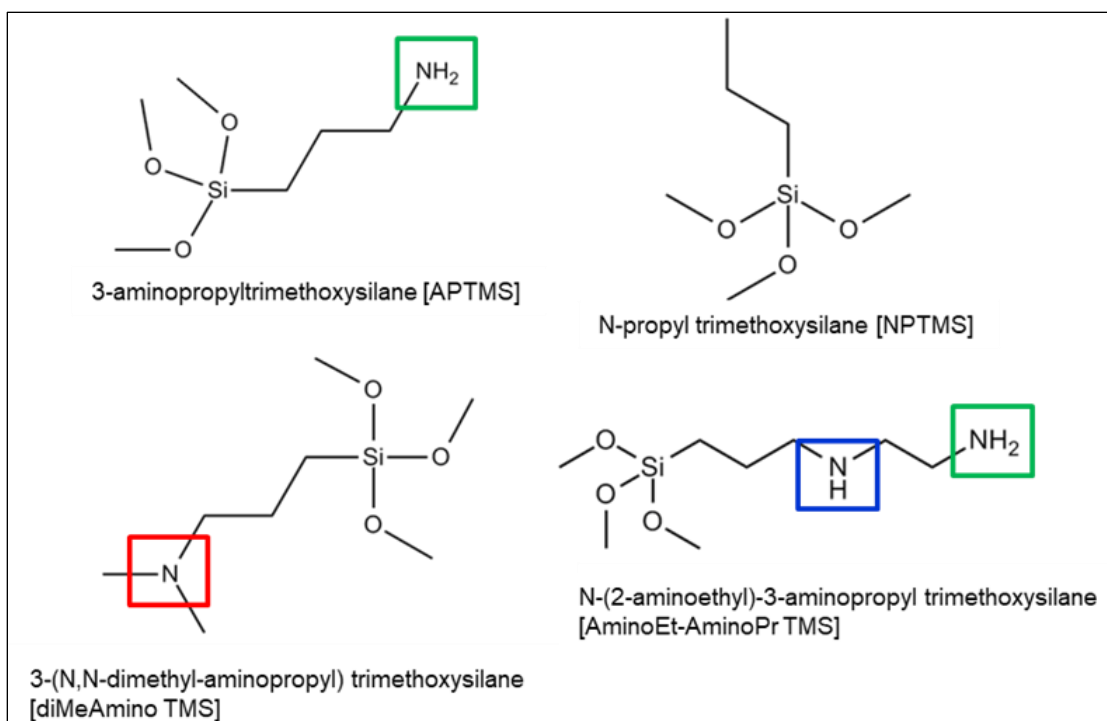


Figure 39. Molecular structures of additives used in NRL 055 and 059 sample sets. The degree of substitution on the amine groups (primary, secondary, or tertiary) is highlighted in green, blue, and red, respectively.

Figures 40 and 41 show the results for GD and HD RA, respectively, as measured by vapor exposure. The variability gauge charts show RA as a function of additive loading levels by volume percentage in each of the two polymers for the additives shown in Figure 39. In agreement with past results, the extended polymer structure absorbed more agent than an analogous non-extended polymer structure. In the case of the extended structure, APTMS continued to have the most impact with regard to chemical resistance. None of the other additives promoted a significant decrease in RA with respect to the baselines, and the variation in RA response with respect to loading level was relatively minor. The optimal loading level for APTMS seems to be close to 10% by volume. This is somewhat different from past measurements that showed RA would continue to decrease with an increased APTMS loading level. A non-monotonic decrease in RA may reflect different regimes of APTMS influence on the overall polymer structure, where lower loading levels may be associated with enhanced cross-linking, but higher loading levels, especially at concentrations that are not amenable for inclusion in full formulations, may suggest the appearance of other structures and phases. In the case of the non-extended structure, the impact of additives and loading levels for both GD and HD was different than in the extended polymer structure case. Higher loading levels of APTMS resulted in lower RA, and there was relatively minimal texture in the RA responses for the other additives as a function of loading level. To understand these trends in RA response as a function of polymer structure class, additive and loading, and agent, complementary mechanical property measurements for the polymer films were obtained.

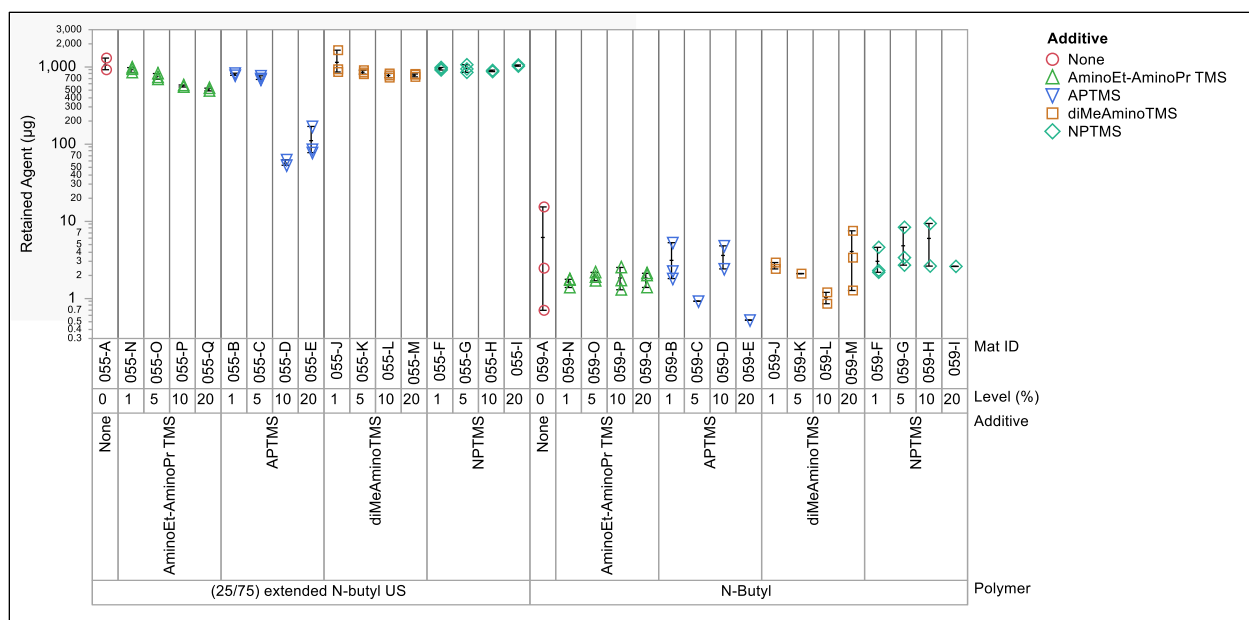


Figure 40. GD vapor exposure RA measurements for NRL 055 ([25/75] extended urea silane [US]) and 059 (N-butyl) materials.

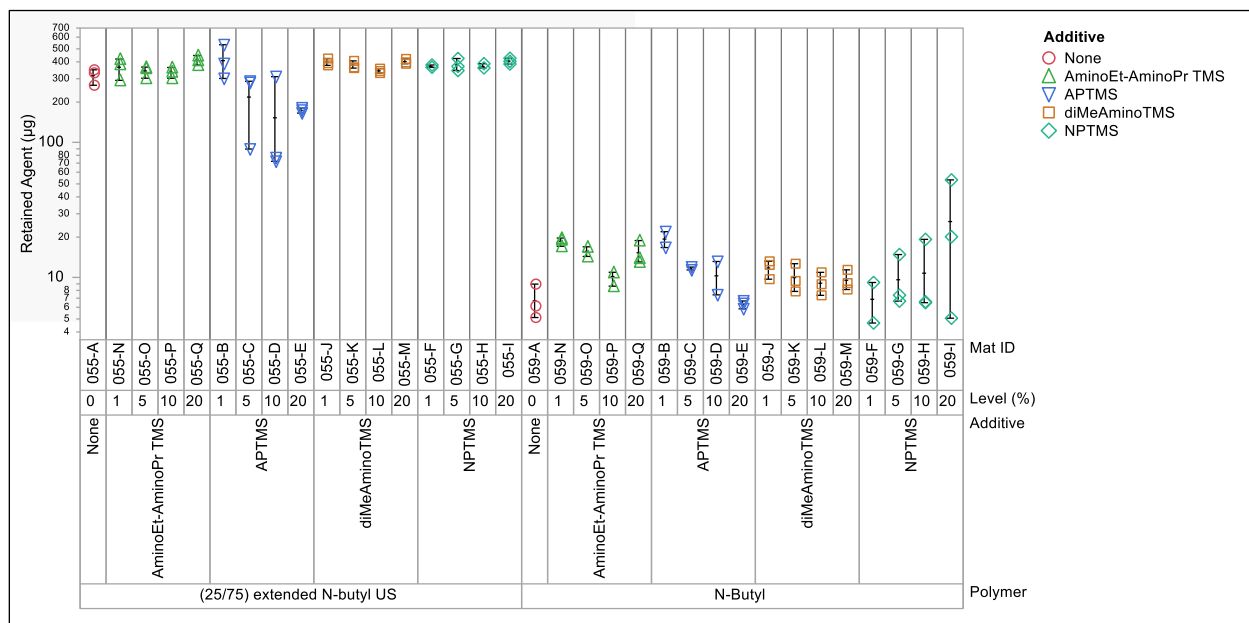


Figure 41. HD vapor exposure RA measurements for NRL 055 ([25/75] extended urea silane [US]) and 059 (N-butyl) materials.

To determine what penetrant and polymer properties, with and without additives, are most influential in determining mass transport and retention, further vapor exposure measurements were made with a set of probe molecules. These species were specifically chosen to address how factors like molecular weight, shape, and size; polarizability; and the presence of specific functional groups correlate to RA and whether these correlations are sensitive to the

polymer structure environment variations determined by variable additive types and loading levels.

DMA and FTIR revealed a great deal of information about polymer structure, particularly regarding stark changes in cross-link density and system homogeneity with the inclusion of APTMS. DMA studies were split into two parts: (1) observing changes across the system at 10% loading of the four additives (APTMS, NPTMS, diMeAmino TMS, and AminoEt-AminoPr TMS) and (2) observing changes in the system as APTMS content was increased up to 20%. In particular, we focused on the tangent ($\tan$) of δ , which describes energy dissipation in the system, and the storage modulus (E'), which describes energy stored in the system. E' can be used to calculate key polymer properties, including global cross-link density. The peak of $\tan \delta$ is a commonly accepted way to determine system T_g , and the full width at half-maximum (fwhm) of the $\tan \delta$ curve indicates system inhomogeneity (the broader the $\tan \delta$ peak, the more heterogeneous the system).

System homogeneity and cross-link density tend to strongly affect transport through polymer networks. We hypothesized that the addition of increasing amounts of APTMS would yield increased cross-link density and system heterogeneity given the strongly reactive nature of the primary amine. The different reactions are illustrated in Figure 42.

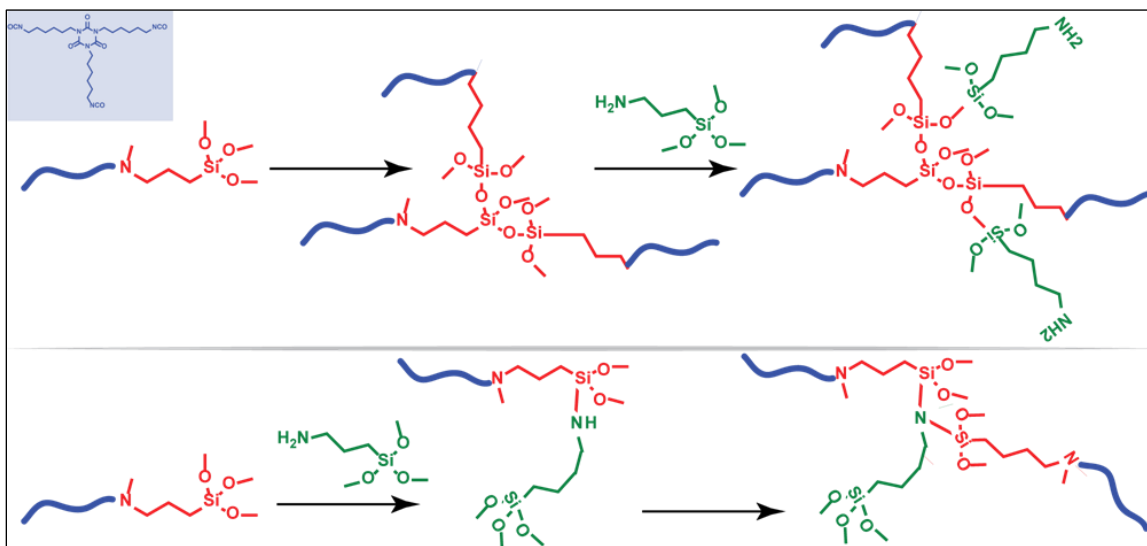


Figure 42. Possible reactions of the polymer binder with the APTMS cross-linker leading to altered network structure and increased system heterogeneity.

Other additives we studied lack this strongly reactive primary amine. Figure 43 shows a comparison of $\tan \delta$ and E' across the four additives at 10% loading collected from DMA. The shift in T_g and increase in fwhm of the $\tan \delta$ track with the reactivity of the amine species present in the different additives. APTMS exhibited the greatest fwhm, the highest T_g , and the greatest cross-link density, indicating a network that is highly heterogeneous and significantly cross-linked. Networks are often illustrated as an idealized, uniform mesh. It is far more likely that the

networks we observed in these materials more closely resemble the system on the right in Figure 44 with variable polymer network relaxations and different associated time constants (Figure 45).

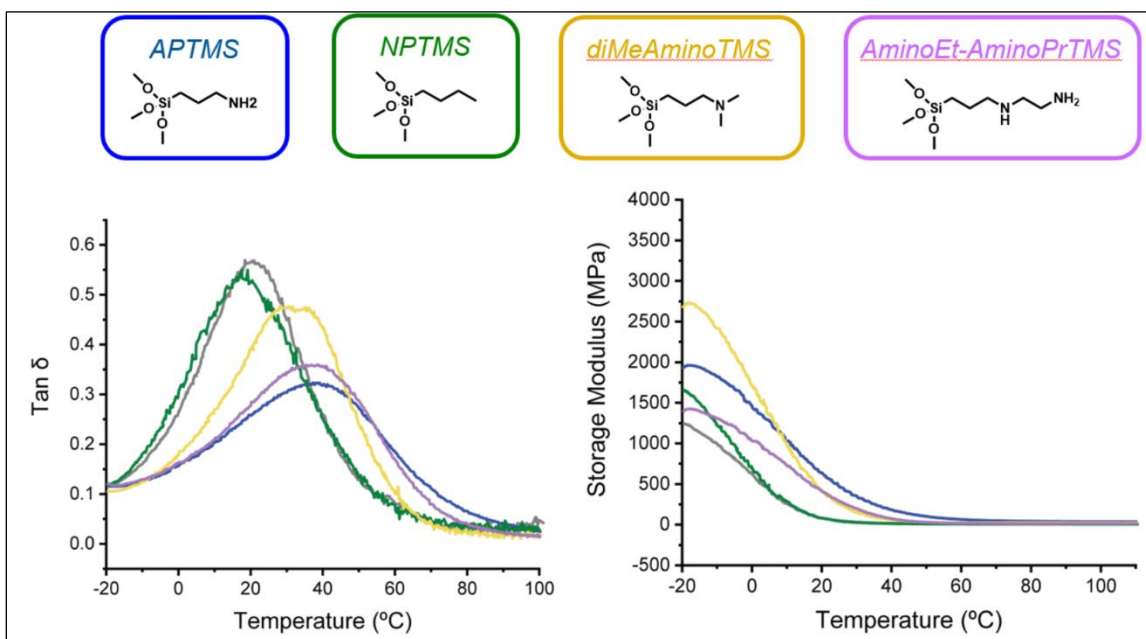


Figure 43. Tan δ and E' of the NRL 055 systems with four different additives at 10% loading. The gray line represents a base system with no additives.

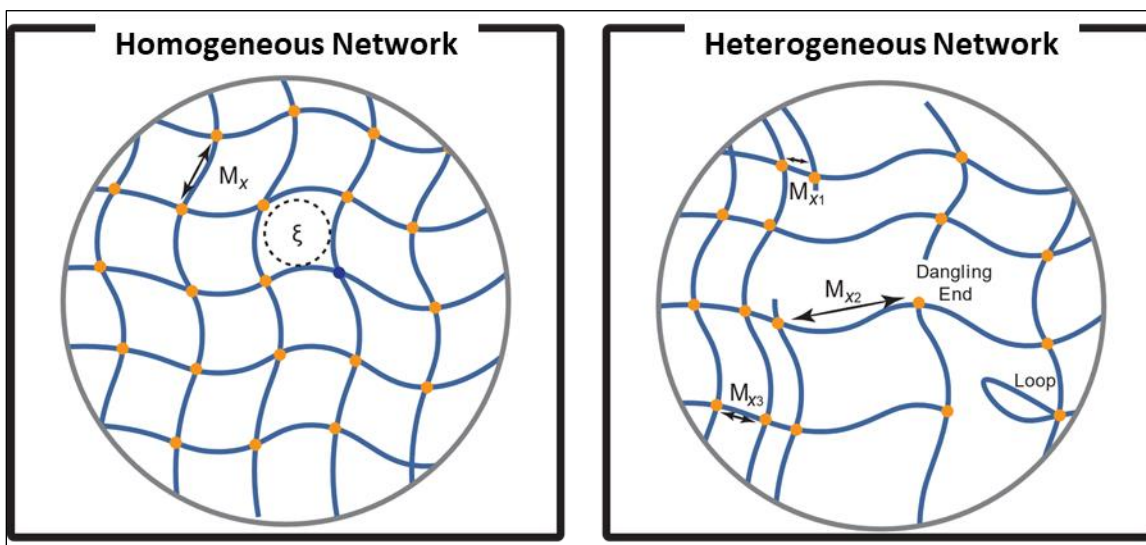


Figure 44. Schematic of an idealized polymer network (left) compared with a more real-world representative network (right). Networks with highly reactive species are susceptible to defects such as dangling chain ends, loops, or the emergence of dendritic structures (not pictured). These networks exhibit varied local molecular weight between cross-links, illustrated by the M_{xx} notation.

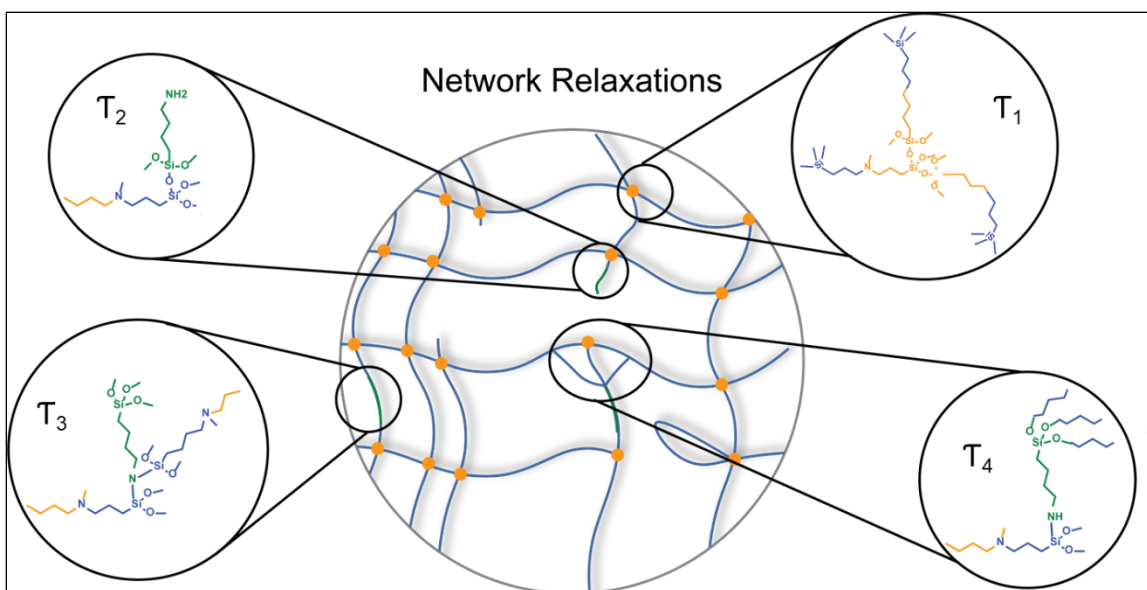


Figure 45. Variable polymer network relaxation time constants as a function of different additive interactions.

The data collected from DMA of the four additives is shown in Figure 46. Again, APTMS exhibited the starkest change in system architecture. AminoEt-AminoPr TMS also exhibited a marked increase in T_g and inhomogeneity.

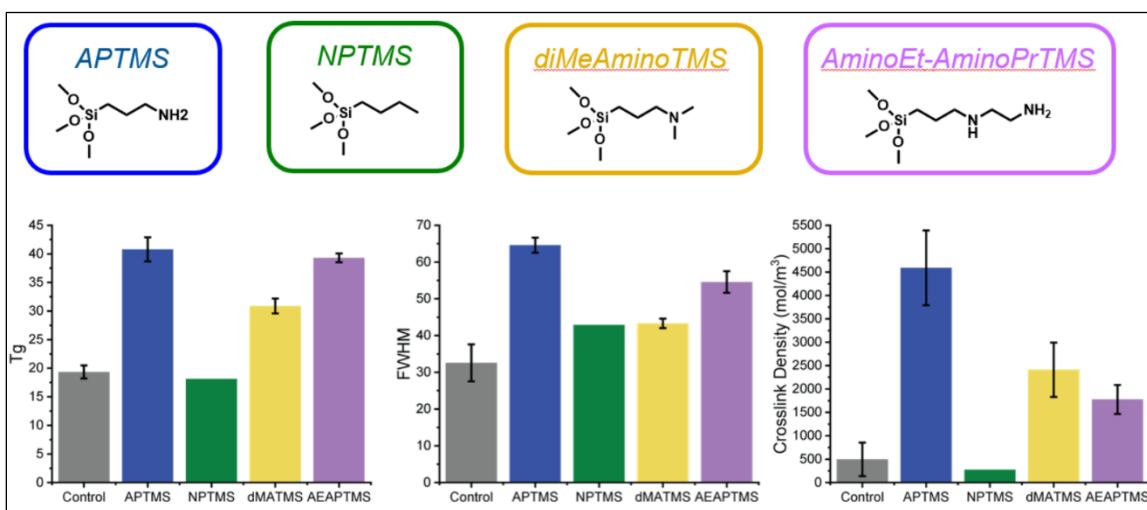


Figure 46. Summary of the T_g , fwhm, and cross-link density of the base NRL 055 system and the four additives at 10% loading.

Next, we studied the change in network structure with the addition of increasing amounts of APTMS. The addition of as little as 1% APTMS strongly affected overall network architecture; there was an immediate increase in cross-link density and system inhomogeneity and a resultant 10 °C increase in system T_g . The general trend seemed to be a steady increase in cross-link density until 10% APTMS loading was reached. At 20% APTMS loading, the cross-link density dropped, and the gradual increase in heterogeneity slowed. At greater than 10% APTMS loading, we think APTMS predominantly added to the system in a manner similar to the mechanism originally proposed by NRL, where the primary mode of addition resulted in a dangling chain end. This yields a lower degree of cross-linking, thereby explaining the reduction in RA. We would like to explore this trend further because understanding this correlation may make it possible to specifically tailor network structure. The findings of this section of the study are summarized in Figures 47 and 48 for NRL 055 and 059 materials, respectively, with variable APTMS loading.

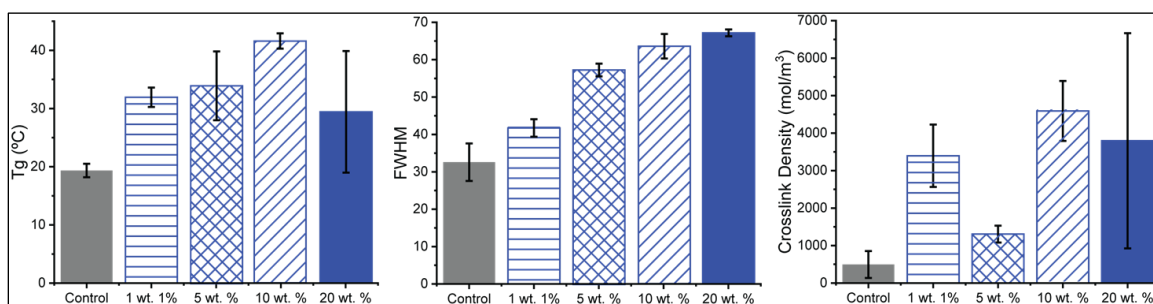


Figure 47. Summary of the T_g , fwhm, and cross-link density of the NRL 055 extended urea silane polymer system with increasing amount of APTMS.

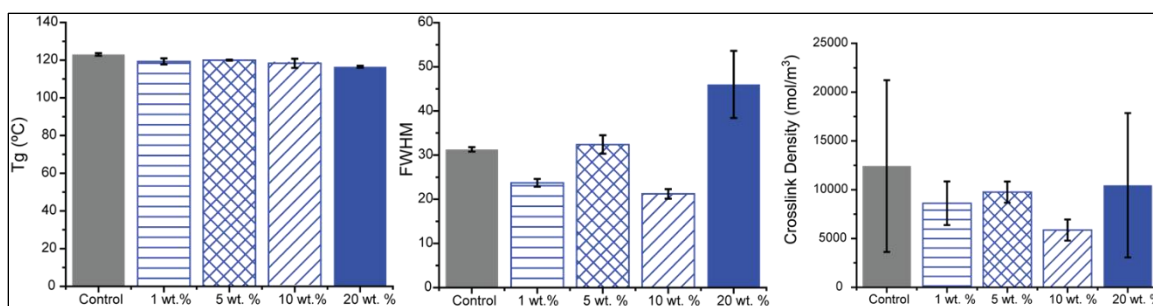


Figure 48. Summary of the T_g , fwhm, and cross-link density of the NRL 059 non-extended urea silane polymer system with increasing amount of APTMS.

From these data, we concluded that we now have a template for modifying network structure that will allow us to exercise some degree of control over system transport. Network structure is clearly one of the primary influences over agent retention. At lower loadings, the introduction of additive with an unencumbered primary amine yields an inhomogeneous, highly cross-linked structure. In the specific case explored in this study, there appears to be a saddle point at 10% APTMS loading that yields a desirable network structure against RA. As loading of that highly reactive additive reaches 10%, the network likely

experiences premature vitrification. Essentially, the network is locked in place, leading to an increase in uncured dangling ends and potential phase separation (see the diagram in Figure 44). With this in mind, we intend to spend the first part of the new fiscal year exploring these findings, expanding the study into the NRL 059 samples to evaluate similarities across the extended and non-extended systems, and probing other methods by which network structure, particularly cross-link density, can be modified.

AFM was performed on free films of (25/75) extended *N*-butyl urea silane with 10% (NRL 055D) and 20% (NRL 055E) APTMS to determine whether features observed via optical microscopy were domains of different material properties or simply variations in surface topography. Figure 49 shows an optical microscopy image of the surface of a 055D mini-panel and the regions imaged using AFM.

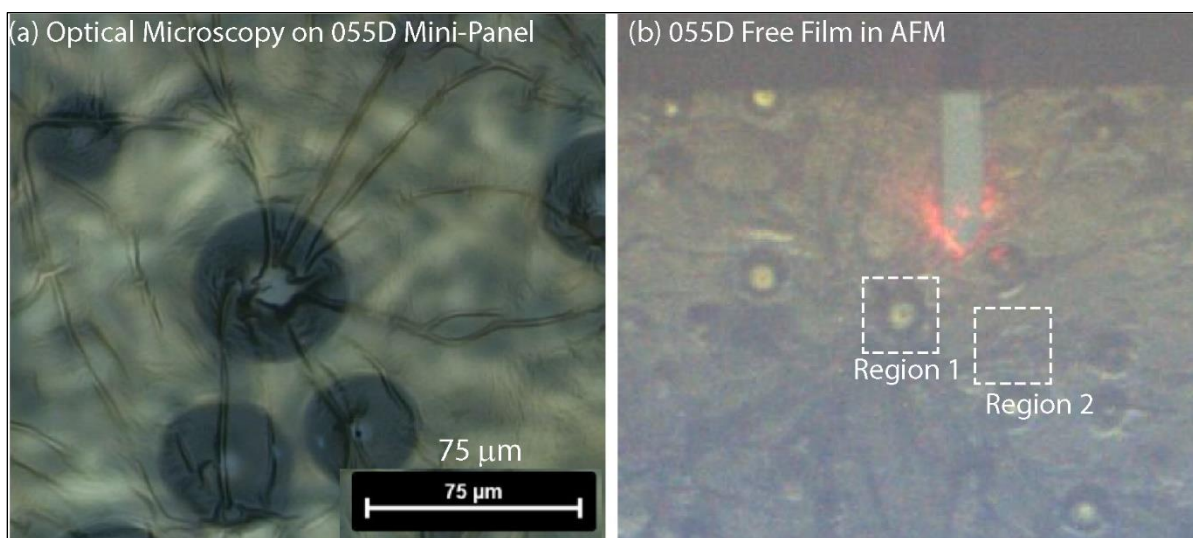


Figure 49. (a) Optical microscopy of 055D mini-panel and (b) 055D free film in AFM setup indicating regions imaged.

The optical microscopy shows circular regions $\sim 20\text{--}50\text{ }\mu\text{m}$ in diameter and long, thin striations. The AFM topography images in Figure 50 show that these features correspond to surface texture on the order of $\sim 1\text{ }\mu\text{m}$, whereas the phase-contrast images (not shown) do not reveal any differences in material properties associated with these features.

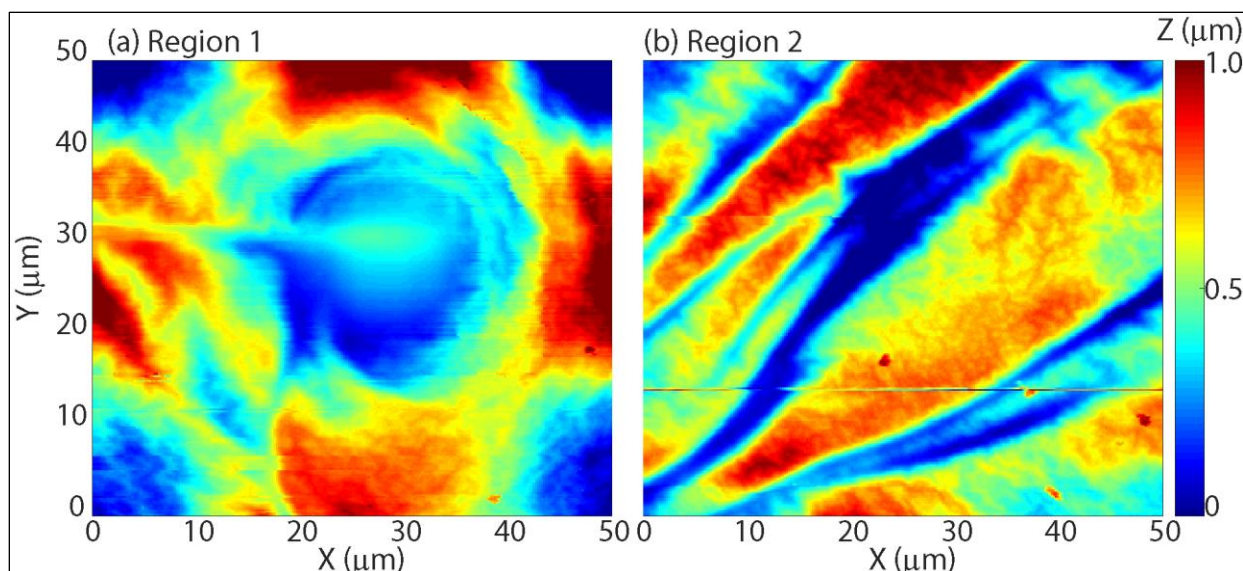


Figure 50. AFM topography images of (a) circular feature (Region 1) and (b) striation pattern (Region 2) on surface of 055D free film sample.

Features on the surface of the 20% APTMS samples (055E) were more difficult to detect with optical microscopy. The AFM images revealed that the 20% APTMS samples had much smaller features ($\sim 1\text{--}5\ \mu\text{m}$ lateral extent) with more uniform topography ($\sim 0.2\ \mu\text{m}$). The phase-contrast image in Figure 51 shows that these features may have different properties from the surrounding continuous matrix, but more careful sample preparation to eliminate the possibility of surface contamination is needed to confirm this.

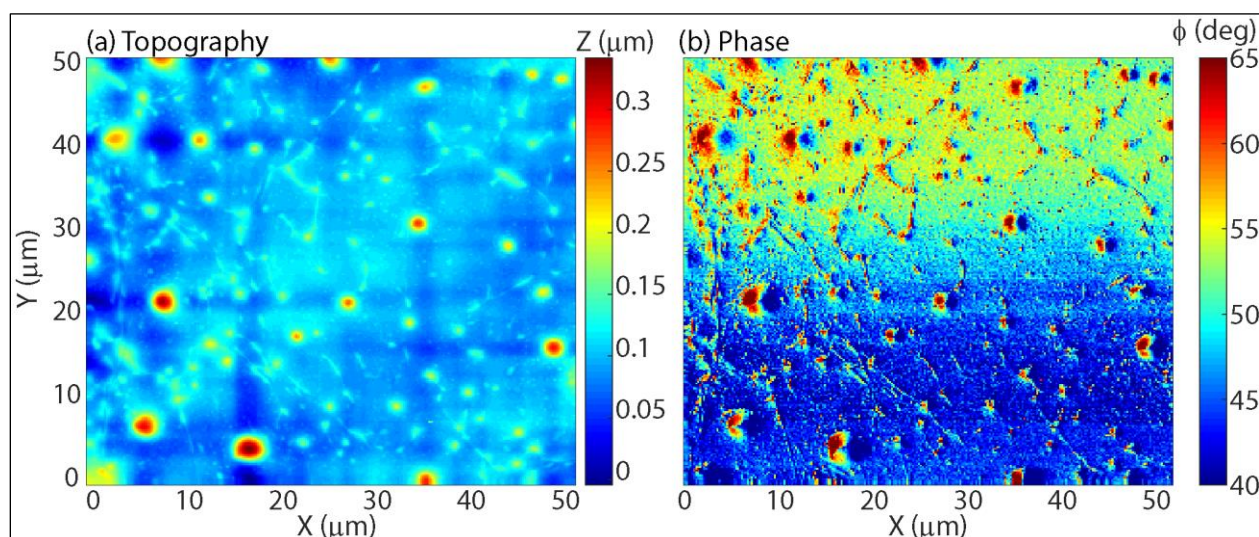


Figure 51. AFM images of 055E free film surface: (a) topography and (b) phase contrast.

4.2.9 Spin Casting PS Polymers for QCM and Initial Probe Molecule Mass Uptake Evaluations

For QCM mass uptake experiments, thinner films are preferred (between 60 and 200 nm, generally). For measurement of viscoelastic properties, the film thickness must be tuned and optimized to ensure the film is thick enough that changes in mechanical behavior can be observed, yet thin enough to ensure that the shear wave that propagates through the film when the crystal is driven into oscillation is not overdamped. Accordingly, it is important that film thickness be measured before testing. We used a white light interferometer to evaluate the thickness of the polymer films cast on the QCM crystals prior to measurement. This technique was used to refine the spin casting techniques to generate films of ideal thickness.

NRL provided two custom urea silanes, *N*-MUS and *tert*-butyl urea silane (*t*-BUS), for QCM evaluation. Our team used these polymers to develop the necessary sample preparation specifications (e.g., spin casting recipes) required to achieve films of the desired thicknesses. We initially started evaluations on *t*-BUS; however, concurrent agent-resistance evaluations indicated that *N*-MUS may provide better agent resistance and should be the focus of further work. Sample handling and method development were readily translatable between the two polymer systems, facilitating the transition. The NRL-developed spin casting methods were used as a starting point, so minimal time was required to optimize casting. Unfortunately, these polymers require an exceptionally long cure time (approximately 10 days). Two images of the same crystal coated with a 0.5 μm *N*-MUS film are shown in Figure 52. For reference, the quartz crystal is 14 mm in diameter and approximately 0.3 mm thick. The images were captured from two angles to show two features. The image on the left shows that the film appears uniform, as confirmed via white light interferometry (e.g., the film is approximately 0.5 μm thick at the center and at the edges). The image on the right shows that the film appears to be textured, although it is yet unknown whether said heterogeneity exists within the film (e.g., voids or inclusions) or at the surface of the film (as in film roughness). The patterning, however, is similar to patterning that has been observed in mini-panels coated with paint films using the same *N*-MUS polymer backbone.

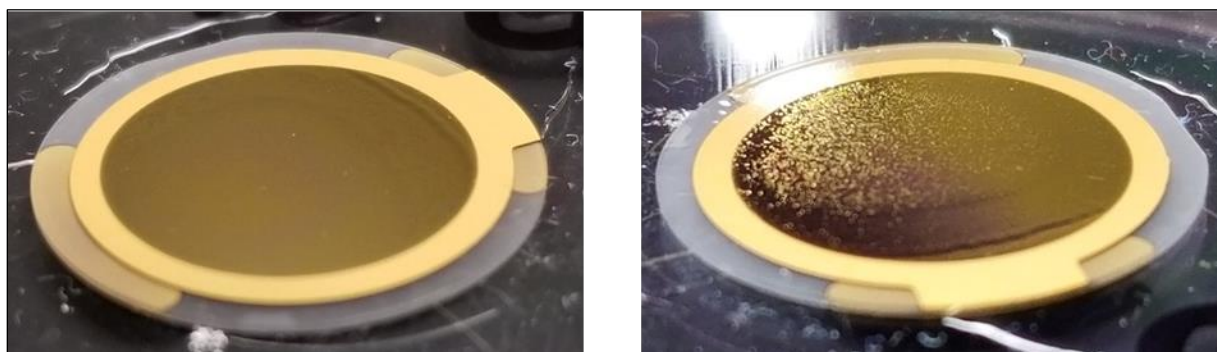


Figure 52. QCM crystal coated with 0.5 μm *N*-MUS film. Left: lighting shows relative uniformity of surface. Right: lighting highlights inhomogeneity inherent to the film type.

These films were created from a parent stock containing 33% *N*-MUS in butyl acetate. This parent stock was further diluted to 2% *N*-MUS in butyl acetate. On the surface of the QCM crystal, 15 μL of this 2% *N*-MUS solution was deposited, and the crystal was spun at 200 rpm for 35 s before it was ramped up to 400 rpm for 10 s. The crystal was then cured at room temperature with relative humidity maintained between 40 and 60% (as required for the polymer to sufficiently cross-link and cure) for approximately 10 days until all of the solvent evaporated and the film was stable. The same methodology was used on further iterations of films. To achieve different thicknesses, the dilution factor was changed, but all other parameters remained the same.

To further achieve measurement reproducibility and reliability, a cleaning process was instituted for the crystals based on guidance from QCM manufacturers. Crystals are removed from their packaging and rinsed in an organic solvent mixture (50/50 acetone–MeOH). The crystals are then dried with nitrogen gas, sonicated in ethanol for 1 min, and then dried again with nitrogen gas. A further option for surface cleaning is to use a UV-ozone treatment for 15 min, followed by rinsing with DI water and drying with clean nitrogen. A sonicator (Fisherbrand CPXH series heated ultrasonic cleaning bath; Thermo Fisher Scientific; Waltham, MA) and UV-ozone cleaner (Nano ProCleaner–UV Ozone Cleaner; BioForce; Ghent, NY) were used for the cleaning process.

Prior studies highlighted in Section 3.10.2 involved the mass uptake of penetrants such as IPA into glassy PU. These evaluations helped to identify target parameters for evaluation of the *N*-MUS films and provided a framework for working with the QCM under conditions similar to those used for this evaluation. In accordance with manufacturer recommendations for the Gamry/MicroVacuum QCM, these evaluations were performed using thinner films (target, $<0.5\ \mu\text{m}$) to optimize data acquisition conditions for mass uptake. Similar to previous studies, these first-pass evaluations were intended to gauge how much time was required to observe penetrant vapor uptake and penetrant chemical desorption.

This work started with hexane penetration into *N*-MUS. Figure 53 shows an example of the collected data and analysis for a $0.4\ \mu\text{m}$ thick *N*-MUS film exposed to a hexane vapor activity of 1 in a single step. The Sauerbrey mass uptake is shown as measured from the fundamental frequency shift, and calculations were performed for $d\rho$, ρG_n^* , and ϕ_n as a function of exposure to hexane vapor. QCM data were analyzed using RheoQCM, a Python-based code developed by the Shull research group to evaluate the film's viscoelastic properties. Very little hexane actually absorbed into the *N*-MUS ($0.7\ \mu\text{g}/\text{cm}^2$), and there was no appreciable swelling ($\Delta d\rho$ was low). With those quantities, a low volume fraction was calculated (0.027) based on the hexane molar volume ($130.7\ \text{cm}^3/\text{mol}$) and molar mass ($86.18\ \text{g}/\text{mol}$). This was approximately $10\times$ lower than the hexane penetration into PU that was measured under similar conditions.⁴⁸ This results in a Flory–Huggins interaction parameter of 2.8, which reflects a lack of absorption into the polymer.

In discussion with personnel from the Shull Group, we determined that the RheoQCM calculations need to be firmly outside of the Sauerbrey limit to be viable. The materials under consideration present a technical challenge because there are cases where transitions from rigid to viscoelastic film limits occur as a function of mass uptake; therefore, we have to reevaluate when this type of computational approach should be used. Of particular note

in this case, the shear modulus calculated by RheoQCM is too low ($\sim 4 \times 10^7$ Pa; however, compared to the PS films evaluated in this study, it should be in the gigapascal range). The viscoelastic property information in Figure 53 shows a shear modulus value that is too low for this material despite resolving a very low viscoelastic phase angle; this means that the film behaves as a rigid thin film. The near-term principal objectives for this work do not necessarily require resolution of viscoelastic effects, and this is an area for future work.

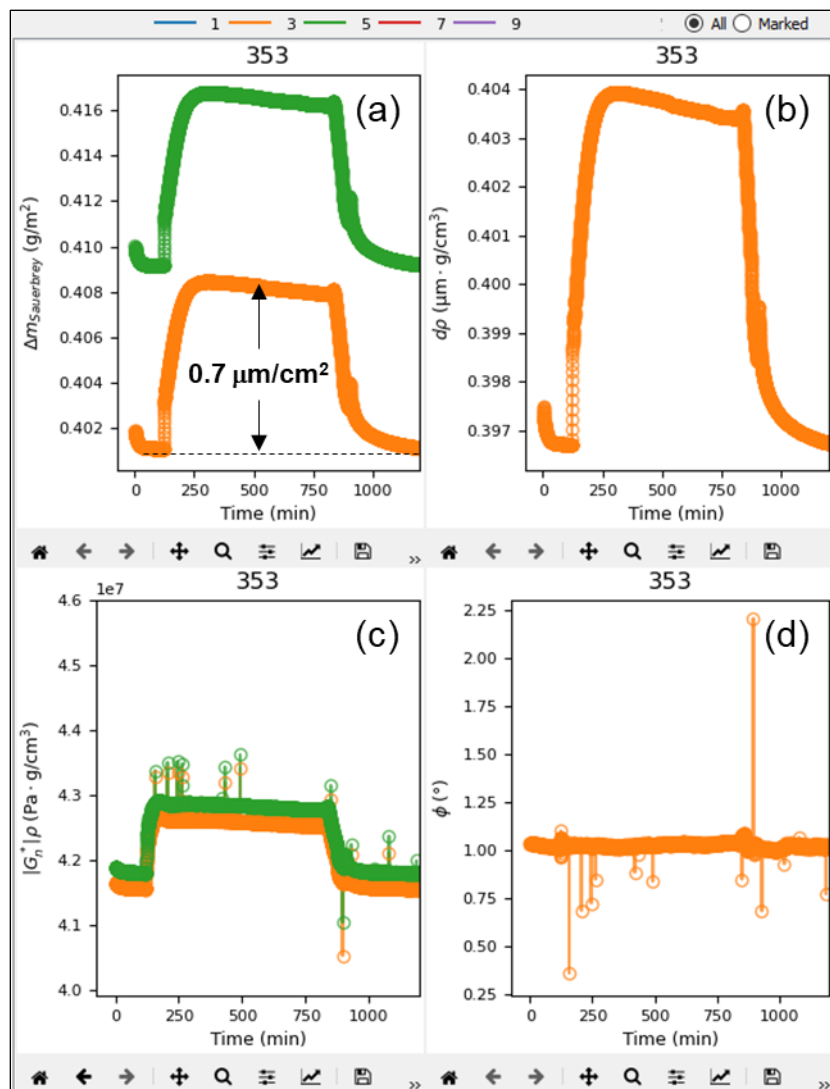


Figure 53. QCM analysis for hexane absorption (vapor activity of 1, discrete step) into a 0.4 μm thick *N*-MUS polymer film. (a) Change in Sauerbrey mass, (b) $d\rho$, (c) ρG_n^* , (d) ϕ_n . Calculations were performed using the third (orange) and fifth (green) modes of the excitation.

We have moved forward on optimizing the conditions for evaluating penetrants beyond hexane. The temperature starting point for these measurements was 20 $^{\circ}\text{C}$ (based on the volatility of hexane; same temperature maintained at saturator cell for vapor generation as the QCM measurement cell), and we used a set of relatively thin *N*-MUS films to screen the initial responses for many of the penetrant molecules selected. As an example, the mass uptake of

2-chloroethyl ethyl sulfide (CEES) into *N*-MUS (37 nm thick) is shown for an activity of 1 in Figure 54. For the first 3 h, the system was equilibrated under pure nitrogen gas. At the 3 h point, CEES was introduced and allowed to flow for 9 h, after which the gas flow through the system returned to nitrogen only. The system was then allowed to equilibrate for another 7–12 h (as needed). This particular example was for a very thin *N*-MUS film, so the measured frequency shift (−33 Hz) was relatively low and indicative of less absolute mass uptake but was still above the baseline of CEES adsorption on an uncoated crystal run concurrently (−15 Hz). In contrast to this, hexane exposed to an *N*-MUS film of similar thickness registered a frequency shift that was indistinguishable from the response of a bare crystal exposed to the same hexane vapor flow. We have also taken initial measurements on hexanol and chlorohexane in addition to hexane and CEES.

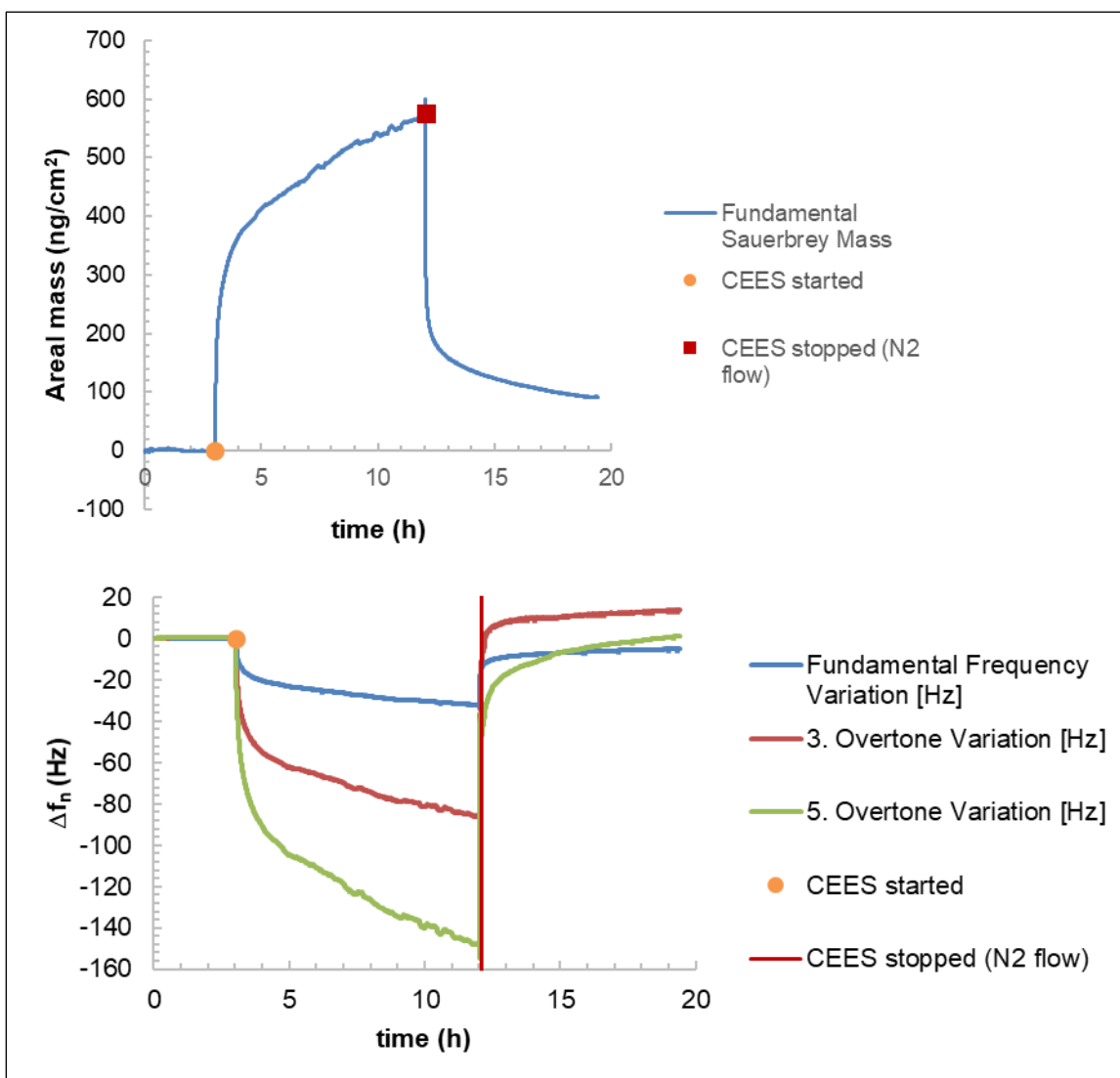


Figure 54. QCM results for CEES penetration into *N*-MUS at an activity of 1. Top: mass uptake by the film. Bottom: frequency shifts as recorded by the QCM.

Based on these screening results, the decision was made to increase the system temperature for all solvents (except hexane, which is limited by its vapor pressure) and the thickness of the polymer film. As noted, the films evaluated in the initial molecule probing study were all quite thin (<75 nm). Future work will finalize crystal cleaning procedures, which can affect hydrophilicity and surface energy of the QCM crystals and in turn impact how spin cast solutions spread. Work is ongoing to remedy this challenge, so the next set of films should be closer to the target range for mass uptake evaluated via QCM (~100–200 nm). This should significantly increase the frequency shifts to ensure all data are easily distinguishable from system noise. Additionally, the temperature will be increased from 20 to 30 °C. The temperature increase will dramatically increase the concentration of penetrant molecule flowing through the system. Such an increase will enable the film to absorb mass and reach equilibrium more quickly. These two facets of the experiment should enable better data quality in a shorter period of time.

4.3 Development of Model Polymer Composites for Determining Chemical Retention Mechanisms of Coatings

This work investigated how changing binder characteristics and the solid content, particle size, surface modification, and other characteristics changed the transport properties of the overall composite to inform future coatings formulation efforts (i.e., how to create model systems that involve the inclusion of solids as a function of type, core and shell composition, size, and weight percentage). The purpose of this effort was to understand how polymer macroscopic mechanical characteristics were affected by the integration of solids (e.g., T_g , molecular weight between cross-links, tensile strength, polymer dynamics, etc.).

4.3.1 Evaluation of Select Additives in PS-Based Coatings Using Vapor and Liquid-Phase Exposure Measurements

Based on vapor-exposure RA measurements for the APTMS additive in sample set 014 (see Figure 36), the impact of APTMS additive on fully formulated coatings was tested in sample set 027 (see Table 9). Liquid and vapor exposure measurements for RA were performed for all materials listed. This was the first evaluation of the impact and benefit of a specific additive type on chemical resistance behavior for fully formulated materials.

Table 9. NRL 027 Sample Set Focused on Determination of APTMS and ODTMS Impact on RA for Both PS-Based Paint and an Extended Polymer Structure

NRL Sample Identifier	Material	Description	Additive Loading (vol %)	Data Use
027A	PS-based paint, green	Standard PS-based paint	0	Coating reference, <i>N</i> -butyl urea silane polymer binder
027B	PU-based paint, green with APTMS	027A with APTMS, mid-level abundance	20	Inclusion of APTMS in paint at mid-level to evaluate effect on additive on RA
027C	PU-based paint, green with APTMS	027A with APTMS, high-level abundance	40	Inclusion of APTMS in paint at a high level to evaluate effect on additive on RA
027D	Extended chain structure (50 mol % diamine extender, 50 mol % <i>N</i> -butyl aminosilane) polymer	027A with ODTMS	20	Inclusion of alternate additive to confirm viability and serve as a contrast to APTMS
027E	Extended chain structure (50 mol % diamine extender, 50 mol % <i>N</i> -butyl aminosilane) polymer	Base extended polymer blend	0	Extended polymer blend reference
027F	Extended chain structure (50 mol % diamine extender, 50 mol % <i>N</i> -butyl aminosilane) polymer	Extended polymer blend with APTMS, mid-level abundance	20	Inclusion of APTMS in extended polymer material at a mid-level to evaluate effect on additive on RA
027G	Extended chain structure (50 mol % diamine extender, 50 mol % <i>N</i> -butyl aminosilane) polymer	Extended polymer blend with APTMS, high-level abundance	40	Inclusion of APTMS in extended polymer material at a high level to evaluate effect on additive on RA

RA results for the fully formulated materials with and without APTMS or ODTMS are shown in Figures 55 and 56; results show the effect of APTMS on an extended polymer structure. For the fully formulated paints, the inclusion of ODTMS was confirmed to either be non-impactful or detrimental to RA for all three contaminants, depending on exposure type. In contrast, the benefit of inclusion of APTMS seems to have translated to the fully formulated materials. The effect of APTMS on GD and VX was present, but interestingly, the magnitude of the RA decrease relative to the baseline material was dependent on the type of exposure. This was due to several effects; GD and VX liquid or vapor uptake occurs differently in these materials, and the effect of the treatment process for the liquid-exposure measurements may be more impactful for GD than VX. The inclusion of APTMS had a significant impact on

HD RA, regardless of exposure type. Based on optical microscopy measurements, it is possible that enrichment of pure polymer at the surface may be partially responsible for the decrease in RA for these materials. The additives also modified most mechanical and thermal properties of these full formulations, as hypothesized. However, to evaluate the correlation between specific mechanical characteristics and chemical retention, dedicated DMA measurements on variations to baseline polymer structures for a range of additive loadings need to be performed. The next phase of work will focus on more directly coupling chemical-uptake behavior with changes in mechanical properties of coatings and key constituents (e.g., polymer binder).

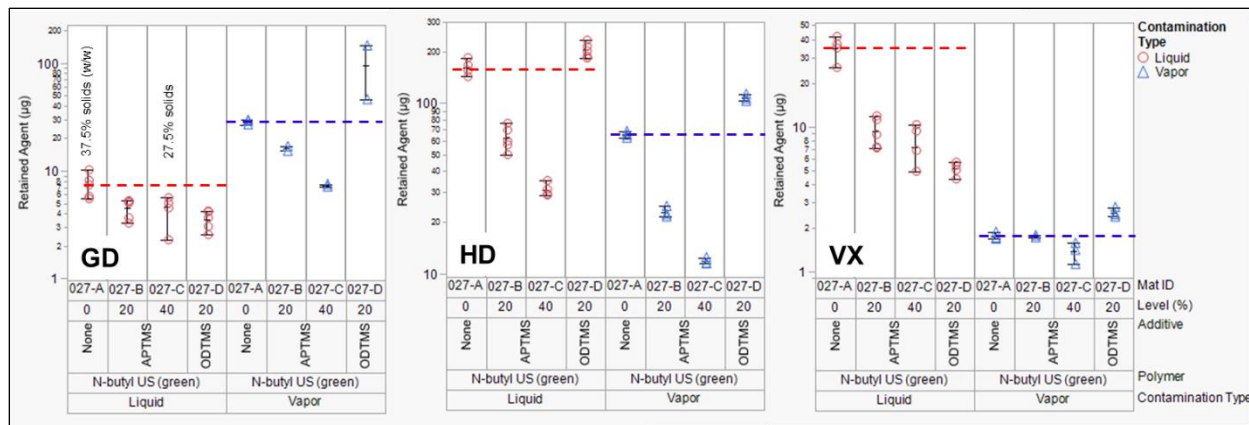


Figure 55. RA data for HD, GD, and VX for liquid and vapor exposure for fully formulated paints based on a non-extended, *N*-butyl urea silane (US) polymer binder.

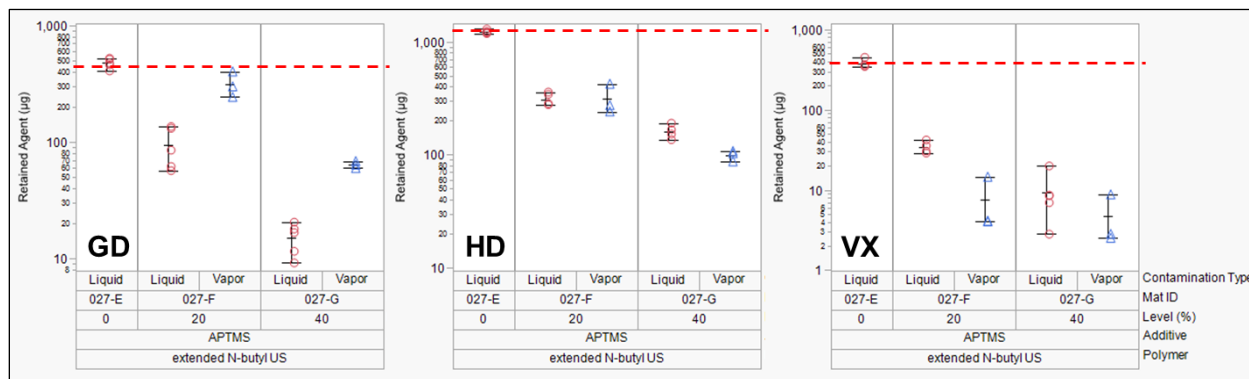


Figure 56. RA data for HD, GD, and VX for liquid and vapor exposure for an extended polymer structure and the inclusion of APTMS. US, urea silane.

DMA data collection on NRL 027 topcoat samples (Figure 57) demonstrated some marked differences as the *N*-butyl urea systems were loaded with increasing amounts of the APTMS (20 and 40% loading) and ODTMS (20% loading) silane additives. The APTMS sample $\tan \delta$ curves showed significant broadening compared with the base, silane-free sample. This indicated a notable increase in system heterogeneity, which was unsurprising because there is a fairly large proportion of silane additive to overall polymer content, encouraging system-phase

separation of excess silane. APTMS samples also exhibited a significantly increased T_g as compared with the base system. For the ODTMS samples, the $\tan \delta$ peak showed a shoulder between 50 and 60 °C and a peak at roughly 75 °C. This was likely due to the large proportion of ODTMS as compared with the polymer binder in the system, leading to phase separation and development of two distinct system T_g values, but it could also indicate crystallization events contributing to a second T_g . Understanding the genesis of these features will be a primary focus of future work. Further investigation of the changes in the system and analysis of the $\tan \delta$ curves will help provide context for the behavior of these systems when exposed to penetrant vapor and will allow for correlations between system structure and penetrant diffusion.

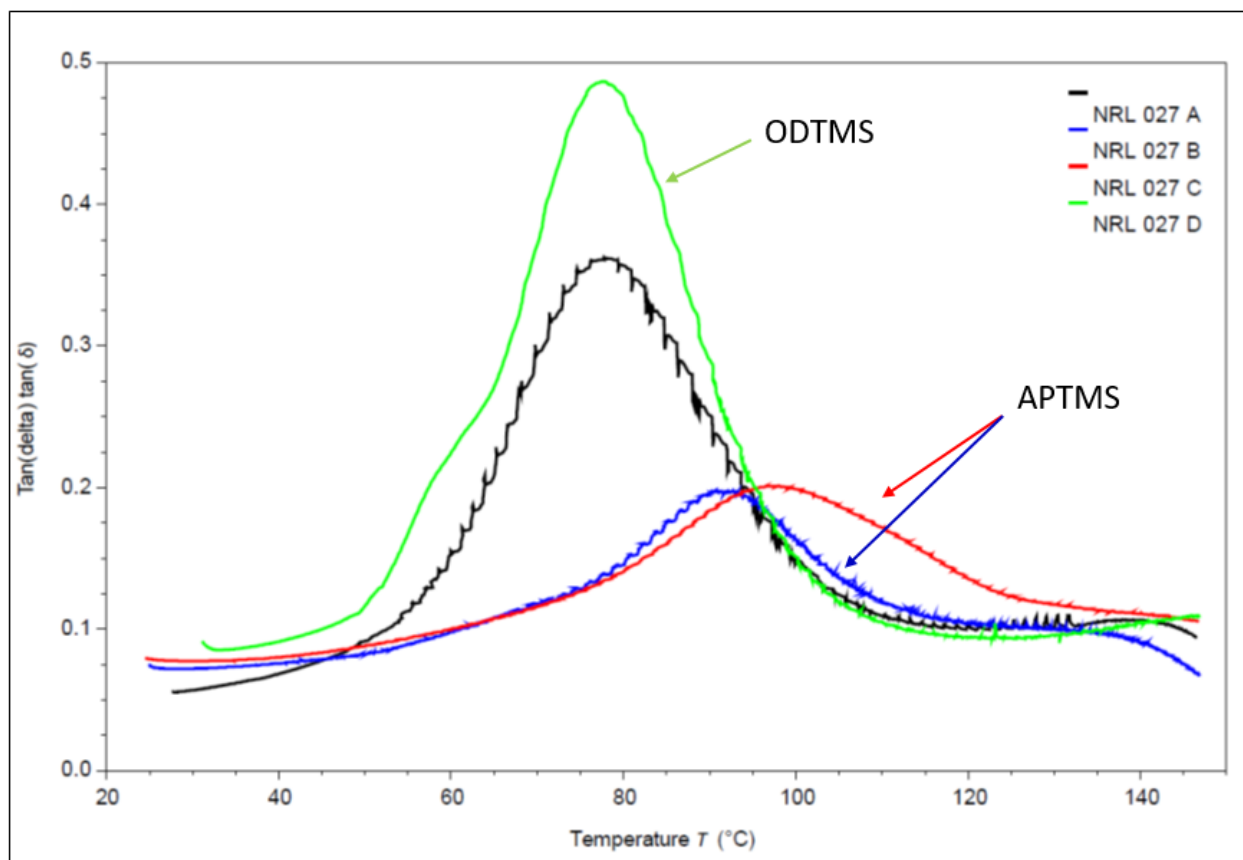


Figure 57. Comparison of $\tan \delta$ curves for NRL 027 topcoat samples. There is a marked broadening in the peak for the APTMS-loaded samples as compared with the base sample. The ODTMS-loaded sample shows a shoulder in its $\tan \delta$ peak.

4.3.2 Interrogating Polymer–Solid Interfaces in Model Polymer Composites Using Neutron Scattering and Inverse GC

In collaboration with the NIST Functional Polymers Group, preliminary measurements (principally for sensitivity) that involved the use of neutron reflectometry were performed to evaluate chemical concentration gradients in the vicinity of PU–TiO₂ interfaces following exposure to chemicals such as acetonitrile and MeOH. TiO₂ particles are used

extensively in coatings formulations as part of pigment packages to provide opacity,⁴⁹ and the chemicals were chosen due to our understanding of how acetonitrile and MeOH transport through PU. The neutron reflectometry measurement relies on the creation of an idealized system consisting of a planar arrangement of a thin (<100 nm) polymer layer on a smooth solid surface to represent the polymer–solid interface in the material of interest. This type of model system allows the details of the interface to be directly probed in the absence of the complicating factors in the actual composite material. As a first attempt, NIST personnel deposited a 35 nm thick layer of PU onto a 75 nm thick layer of TiO₂; Figure 58 shows a schematic of the material preparation. Neutron reflectometry measurements (forward elastic scattering geometry) were performed as this layered system was exposed to solvent vapor, to capture a composite neutron reflectivity profile (Figure 59) with scattering contributions that are specific to the type of scatterer (e.g., hydrogen versus deuterium) as a function of depth in the layer material.

Figure 59 illustrates the material processing steps for removing all of the solvent in every vacuum drying step. There was no strong evidence of a solvent layer at the PU–TiO₂ interface based on modeling of the variation in scattering length density (SLD), as shown in Figure 60. Both solvents appeared to uniformly swell the PU layer; this was evaluated using deuterated MeOH and deuterated acetonitrile to differentiate from the polymer scattering signal. It is possible that any chemical aggregation at the TiO₂–PU interface was lost in the instrument resolution, interfacial smearing, or correlated fit parameters. We are in discussions with NIST personnel regarding optimal sample preparation, layer thickness, and chemical exposure steps to increase the opportunities to resolve localized chemical concentration rather than uniform distribution throughout the polymer layer.

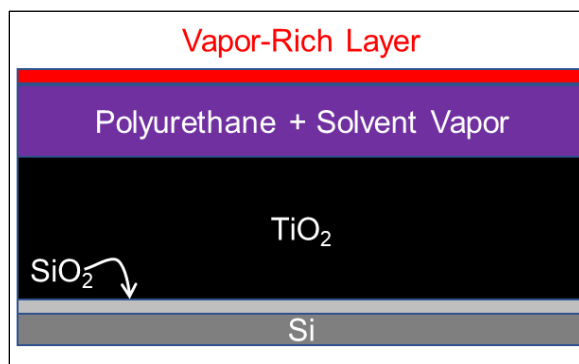


Figure 58. Materials setup schematic for proving solvent aggregation at PU–TiO₂ interfaces. The PU layer was spin cast to 35 nm thickness while the TiO₂ was sputter deposited onto SiO₂ to 75 nm thickness.

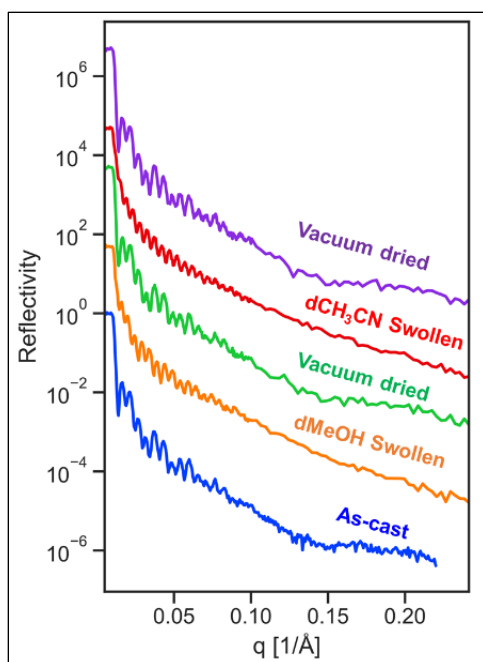


Figure 59. Neutron reflectivity (elastic scattering; intensity as a function of scattering wavelength q , which is a component of scattering vector and momentum transfer normal to the surface) measurements as a function of processing steps.

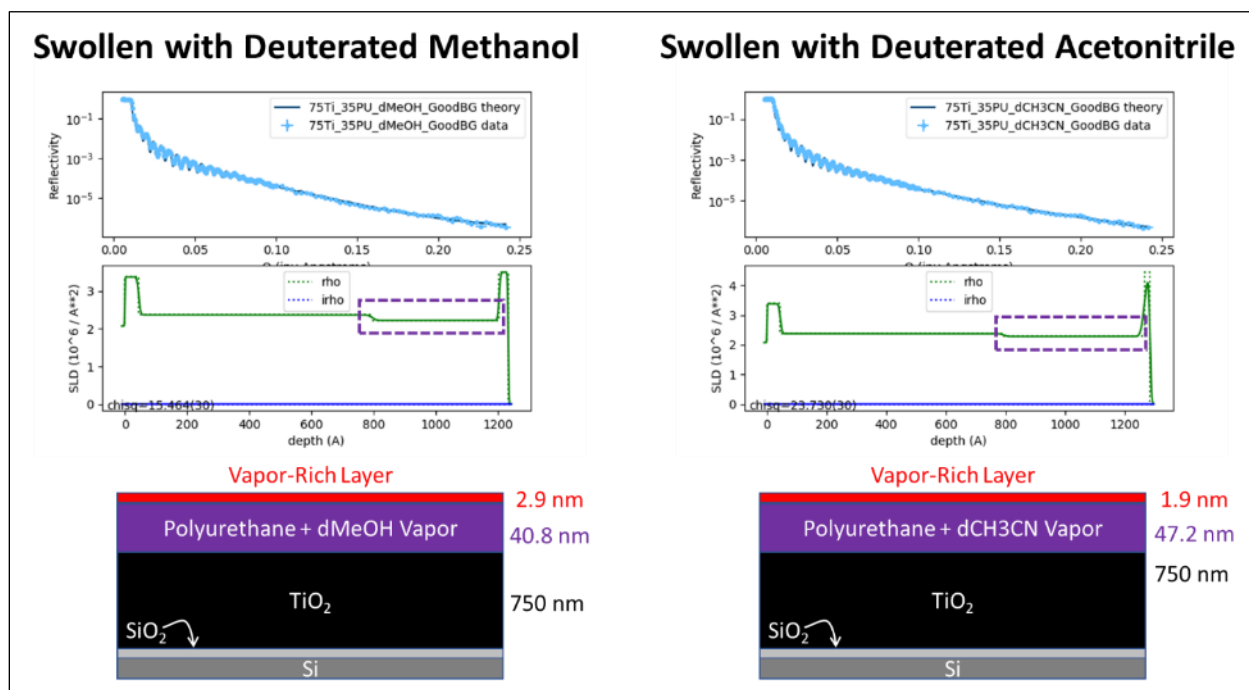


Figure 60. Modeling results for reflectivity profiles (top panels, blue traces) to determine SLD (middle panels, green traces) as a function of depth. The thickness of each layer as determined by reflectivity is shown in the cross-section schematics (bottom panels). The SLDs associated with the deuterated MeOH and acetonitrile are highlighted in the purple dashed boxes; these were uniform across the thickness of the swollen PU.⁵⁰

This work area will move forward because of the material selections that precipitate from evaluation of NRL materials. The emphasis should be on thin polymer films that are as close as possible to those used in existing formulations currently under study. Discussions occurred with NIST personnel on charting work that would be pursued when laboratory facilities are available, especially with increased coordination with NRL on materials. Two types of model systems will be studied initially: one with a “good” polymer–solid interface and one with a “poor” interface. These will be prepared by depositing the same PS polymer on a solid that interacts strongly with the functional groups of the polymer and on a solid that interacts weakly with the polymer. The exact solid surfaces have not yet been chosen, but possible choices include silica for the strongly interacting solid and polystyrene for the weakly interacting solid. This will provide two points of reference on opposite ends of the spectrum, improving confidence that the measurement will be able to reliably distinguish chemical concentrations near these two types of interfaces. Once this initial study is complete, focus will shift toward solids of interest in coatings formulations to help determine which solid additives are most responsible for enhanced transport mechanisms in coatings materials. This information can then be used to identify alternative solid materials to fulfill the same functionality or appropriately modify the surfaces of solids currently in use to enhance the incorporation in the polymer matrix.

After discussion with NIST and NRL, we decided to create model good and poor interfaces using silane-functionalized silica as the solid component interacting with the PS. Example silanes from each category are shown in Figure 61. The methoxy or ethoxy groups of the silanes react with the native hydroxyl groups on the silica surface and also cross-link to form a surface network. We anticipated that the amine- and hydroxyl-based silanes would interact with the urea linkage of the PS via hydrogen bonding, whereas the nonpolar silanes would not hydrogen bond and would form a weaker solid–polymer interface. Additionally, the degree of surface interaction can be tuned with the number of hydrogen bonding groups and the distance of the hydrogen bonding groups from the surface (see amine functional silanes in Figure 61).

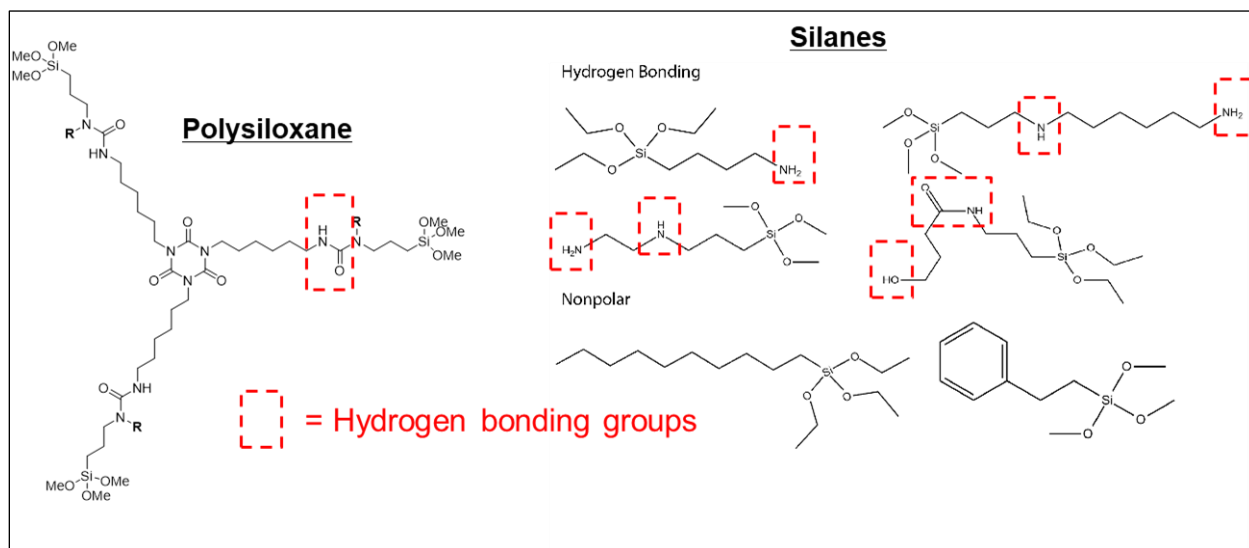


Figure 61. Example silanes that will be used to study the influence of the solid–polymer interface on chemical transport in composites. Shown are hydrogen bonding groups present on specific silanes as well as on the base PS polymer structure.

To better understand the neutron reflectometry results, future work will focus on determining the various two-way interactions between the components. Specifically, penetrant–polymer interactions will be determined by contact angle of the liquid penetrant on silane-treated silicon, polymer–solid interactions will be determined by colloidal probe AFM in which silane-treated silica particles are attached to an AFM cantilever and brought into contact with the polymer surface to measure adhesion force, and penetrant–polymer interactions will be determined by equilibrium mass uptake in QCM. This approach aims to determine whether the degree of chemical compatibility and adhesion between a polymer matrix and an embedded solid dictates or drives penetrant mass transport behavior.

We will be using a baseline PS polymer from NRL deposited on silane-treated silicon surfaces for neutron reflectometry experiments or silica particles integrated into the polymer matrix for breakthrough and mass uptake measurements. The specific silane functionality will be chosen to either promote chemical linkages to specific functional groups on the PS backbone or have weaker chemical interactions with the polymer. Probe molecules will include a series of hexane- or octane-based liquids that are currently part of QCM measurements aimed at quantifying interaction parameters for chemicals absorbed in PS films (i.e., to model specific aspects of HD functionality as well as molecular shape and size). We anticipate that this work will result in the identification of materials and chemicals that will be highly pertinent to resolving transport in coatings composites and that can be measured appropriately with neutron reflectometry in future efforts. Candidate materials have been received to pursue this work.

The intention of the work with NIST was to explore other means of quantifying strength and type of chemical–material interactions for coatings materials that would be informative in describing contaminant retention. Quantifying absorption thermodynamics, including solubility coefficients, for penetrant species is an important consideration in overall chemical resistance for polymer composites. DEVCOM CBC and NIST personnel discussed prospective inverse gas chromatography (IGC) measurements for free films of full paint formulations produced by NRL, and materials were sent to NIST for initial evaluation of viability. By measuring polymer material retention times of different probe molecule vapors, it is possible to infer solubility parameters and estimate sorption equilibrium of any chemical with known solubility parameters in the polymer.⁵¹ This type of measurement is a complement to in-progress QCM evaluations of chemical interaction parameters for polymer films, but in this case, the full material system is under measurement, which accounts for the effects of solids dispersed in a polymer composite.

NIST performed IGC measurements on the full paint formulations prepared with the diamine extended chain polymer blend (50 mol % diamine extender, 50 mol % *N*-butyl aminosilane; NRL 027E) as the binder and the same formulation with 20% (NRL 027F) and 40% (NRL 027G) volume loading of APTMS. It should be noted that these were tested as free films mounted in a flow cell as opposed to the traditional packed column configuration. This results in less available material surface area and thus a lower measurement signal. The probe molecules used in these experiments were the linear aliphatics from C₇ to C₁₁ and the polar molecules acetone, acetonitrile, ethyl acetate, ethanol, water, and methylene chloride. The retention volume (V_{gi}) for each probe molecule is used to compute the dispersive (γ_p^D) and specific (γ_p^S) components of the surface energy of the polymer, respectively.⁵² Likewise, the retention volumes

can be used to estimate the interaction parameter (χ_{ip}) of the polymer with each probe molecule. In the limit of infinite dilution of the probe molecules, the interaction parameter (χ_{ip}^∞) can be related to V_{gi} through the following:⁵¹

$$\chi_{ip}^\infty = \ln \left(\frac{RT}{V_{gi} p_i^0 M_i} \right) - \frac{p_i^0}{RT} (B_{ii} - V_i) \quad (2)$$

where p_i^0 , M_i , V_i , and B_{ii} are the saturated vapor pressure, molar mass, molar volume, and second virial coefficient of probe i , respectively, at temperature T (R is the universal gas constant). With knowledge of the Hildebrand (δ_i) or Hansen (δ_i^D , δ_i^P , δ_i^H) solubility parameters of the probes, the following expressions can be used to plot χ_{ip}^∞ against the solubility parameters of all the probe molecules and find a best-fit value for the corresponding polymer solubility parameters:

$$\chi_{ip}^\infty = \frac{V_i}{RT} (\delta_i - \delta_p)^2 \quad (3)$$

$$\chi_{ip}^\infty = \frac{V_i}{RT} [(\delta_i^D - \delta_p^D)^2 + (\delta_i^P - \delta_p^P)^2 + (\delta_i^H - \delta_p^H)^2] \quad (4)$$

The resulting surface free energy and Hildebrand solubility parameter values are provided in Table 10. Because these materials are fully formulated coatings tested in a thin film configuration, extreme care should be taken in using the absolute values (e.g., for comparison with data published in the literature), but the relative values can be used for comparison within this dataset. This suggests that APTMS loading at levels above 20% results in a significant reduction in the Hildebrand solubility parameter and thus, the cohesive energy density of the coating. However, the DMA results show a significant increase in the T_g of the coating with APTMS addition, which could cause a reduction in the absorption rate of the probe molecules. The above analysis does not account for the fact that the polymer is cross-linked, which will influence the value of χ_{ip}^∞ . In this case, the chemical potential in the polymer must account for the elastic free energy resulting from deformation of the cross-linked network upon absorption of the probe molecule. For example, the Flory–Rehner theory can be used to account for this in terms of the cross-link density, which can be determined from mechanical measurements such as DMA. It is also important to execute the experiments above the T_g of the polymer to avoid these effects and ensure that the probe molecules have equal access to the polymer bulk across all samples.

The possibility of obtaining Hansen solubility parameters for the polymer or coating was considered; however, upon reviewing the currently available experimental data, there is insufficient information to perform this calculation. Additional experiments would have to be performed using additional probe molecules spanning ranges of polar (δ_i^P) and hydrogen bonding (δ_i^H) solubility parameters.

Table 10. Surface Energy and Solubility Parameters for NRL 027 Series (Fully Formulated PS Paint) With Extended Chain Binder System, With and Without APTMS Additive

NRL Sample Identifier	Binder Type	APTMS Loading (vol %)	γ_p^D (mJ/m ²)	γ_p^S (mJ/m ²)	δ_p (MPa) ^{0.5}
027E	Extended chain structure (50 mol % diamine extender, 50 mol % <i>N</i> -butyl aminosilane) polymer	0	30.1	10.3	11.0
027F		20	46.3	13.1	6.4
027G		40	42.2	10.4	6.9

5. CONCLUSIONS

The main research objective of this work was to elucidate physicochemical mechanisms responsible for the chemical resistance behavior of current coatings systems to inform formulation efforts. It was anticipated that a complementary tool set capable of determining materials' mechanisms for chemical retention could be used to advance coatings development and decontamination technology. We hope that the identification of contaminant aggregation and transport as functions of coatings composition will make it possible to tune material properties.

This report illustrates the process of deconstructing an engineered material to understand the critical factors that govern agent resistance. To arrive at a rudimentary understanding of the dominant mechanisms for uptake and retention, it is not viable to only work with end-state material (i.e., measure agent retention solely for fully formulated coatings). Too many competing effects are introduced as functions of coatings constituents and processing steps to allow for a controllable and clear association of factors that dominate mass transport. It was known at the inception of this work that disassembly of a paint material is not trivial and requires control of synthesis and sample preparation, specifically to allow for very different types of measurements to occur. The collaboration between DEVCOM CBC and NRL was established to partner capabilities in assessment of agent resistance for materials with coatings formulation development expertise.

The principal outputs of this work include the following:

- The combination of RA data from both measurements reveals that the RA for pure polymers (both PU and PS) is very similar to that for fully formulated paint. This indicates that tuning the polymer structure, mechanical properties, and binder chemical environment is critical in enhancing resistance for formulated coatings (i.e., the presence of solid additives was not very influential in altering RA and, therefore, may not be a primary factor in controlling agent resistance for the polymers studied).
- Liquid- and vapor-phase exposures of agent species to materials in different configurations and form factors can be used to capture different influences on chemical agent absorption. In particular, the use of liquid agent droplets on relatively smooth polymer surfaces (relative to rougher, more corrugated

paints) results in difficulties with unique association of absorbed chemical mass due to inefficient removal of surface-bound agent liquid. This finding does not point out a deficiency with CARM as much as it underscores the need to use different experiment configurations to appropriately capture critical influences on mass transport. Ultimately, CARM is to be used for evaluation of end-state materials, but the routes for chemical ingress are *not* uniquely determined through liquid-phase exposure.

- Differences in RA between liquid and vapor exposure were not uniform across all cases, indicating that certain material configurations are more or less sensitive to certain pathways to mass uptake and retention. Small differences measured by liquid exposure for specific additives were amplified for many cases when measured by vapor exposure.
- Additives (e.g., cross-linkers) and solids alter the base polymer in fundamentally different ways, but both impact bulk mechanical behavior and material morphology (surface, interfacial, and bulk). The lack of RA response to variation in solid loadings for these measurements does not preclude the impact of solid inclusion on the overall chemical retention, especially for liquid exposure with an associated post-contamination material treatment.
- Inclusion of solids in PS-based materials had less impact than in PU-based coatings.
- Cross-linking additives can be used to control polymer network attributes to enhance chemical resistance in a coating system. This finding is more than identification of a specific cross-linking additive that is relevant to a particular polymer chemistry class; instead, it suggests that the polymer binder mechanical characteristics are crucial for end-formulation development.

Future work in this area is required to develop next-generation coatings capable of providing enhanced chemical resistance while still complying with a full set of technology requirements. For significant progress to be made in this area, a foundation of formulation optimization rules to produce resistive coatings needs to be built. Lessons learned regarding chemical mass transport and retention pathways must be leveraged from other permselective material development, including membranes, fuel cells, and other coatings technologies. Ultimately, with this in place, it would be possible to optimize laboratory-scale formulation parameters for enhanced chemical agent resistance with sufficient phase space to allow for tuning of the performance attributes of other coatings (e.g., gloss, signature management, and corrosion resistance). The work can focus principally on chemical agent resistance with the goal of understanding what is needed to achieve enhanced resistance while allowing for sufficient formulation optimization to address requirements of end-state technology.

LITERATURE CITED

1. Cooley, K.A.; Pearl, T.P.; Varady, M.J.; Mantooth, B.A.; Willis, M.P. Direct Measurement of Chemical Distributions in Heterogeneous Coatings. *ACS Appl. Mater. Interfaces* **2014**, 6 (18), 16289–16296.
2. Willis, M.P.; Stevenson, S.M.; Pearl, T.P.; Mantooth, B.A. An Inverse Analysis Approach to the Characterization of Chemical Transport in Paints. *J. Vis. Exp.* **2014**, 90, e51825.
3. Boyne, D.A.; Varady, M.J.; Lambeth, R.H.; Eikenberg, J.H.; Bringuier, S.A.; Pearl, T.P.; Mantooth, B.A. Solvent-Assisted Desorption of 2,5-Lutidine from Polyurethane Films. *J. Phys. Chem. B* **2018**, 122 (7), 2155–2164.
4. Varady, M.J.; Boyne, D.A.; Pearl, T.P.; Lambeth, R.H.; Mantooth, B.A. Composition-Dependent Multicomponent Diffusivity of 2,5-Lutidine with Acetonitrile in Polyurethane. *Polymer* **2019**, 180, 121697.
5. Varady, M.J.; Knox, C.K.; Cabalo, J.B.; Bringuier, S.A.; Pearl, T.P.; Lambeth, R.H.; Mantooth, B.A. Molecular Dynamics Study of Competing Hydrogen Bonding Interactions in Multicomponent Diffusion in Polyurethanes. *Polymer* **2018**, 140, 140–149.
6. Varady, M.J.; Mantooth, B.A. Unsaturated Hemiwick Dynamics on Surfaces with Irregular Roughness. *J. Colloid Interface Sci.* **2021**, 604, 104–112.
7. Varady, M.J.; Pearl, T.P.; Bringuier, S.A.; Myers, J.P.; Mantooth, B.A. Agent-to-Simulant Relationships for Vapor Emission from Absorbing Materials. *Ind. Eng. Chem. Res.* **2017**, 56 (38), 10911–10919.
8. Alleborn, N.; Raszillier, H. Spreading and Sorption of a Droplet on a Porous Substrate. *Chem. Eng. Sci.* **2004**, 59 (10), 2071–2088.
9. Alleborn, N.; Raszillier, H. Dynamics of Films and Droplets Spreading on Porous Substrates. *Tappi J.* **2007**, 6 (3), 16–23.
10. D’Onofrio, T.G.; Navaz, H.K.; Markicevic, B.; Mantooth, B.A.; Sumpter, K.B. Experimental and Numerical Study of Spread and Sorption of VX Sessile Droplets into Medium Grain-Size Sand. *Langmuir* **2009**, 26 (5), 3317–3322.
11. Markicevic, B.; Hoff, K.; Li, H.; Zand, A.R.; Navaz, H.K. Capillary Force Driven Primary and Secondary Unidirectional Flow of Wetting Liquid into Porous Medium. *Int. J. Multiphase Flow* **2012**, 39, 193–204.

12. Markicevic, B.; Li, H.; Sikorski, Y.; Zand, A.; Sanders, M.; Navaz, H.K. Infiltration Time and Imprint Shape of a Sessile Droplet Imbibing Porous Medium. *J. Colloid Interface Sci.* **2009**, *336* (2), 698–706.
13. Markicevic, B.; Navaz, H.K. The Influence of Capillary Flow on the Fate of Evaporating Wetted Imprint of the Sessile Droplet in Porous Medium. *Phys. Fluids* **2010**, *22* (12), 122103.
14. Schwöpe, A.D.; Klein, J.M.; Sidman, K.R.; Reid, R.C. Sorption-Desorption Phenomena of Chemicals from Polymer (Paint) Films. *J. Hazard. Mater.* **1986**, *13* (3), 353–367.
15. Schwöpe, A.D.; Goydan, R.; Little, A.D.; Reid, R.C. *Methodology for Estimating the Migration of Additives and Impurities from Polymeric Materials*; EPA 560/5-85-015; U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances: Washington, DC, 1990.
16. Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press USA: New York, NY, 1980.
17. Wang, T.; Zhang, Y.L.; Shi, X.P.; Wu, L.G.; Zhang, X.Y.; Zhang, S.Q. Polyurethane Hybrid Membranes with Confined Mass Transfer Channels: The Effect of Functionalized Multi-Walled Carbon Nanotubes on Permeation Properties. *Chem. Eng. Sci.* **2019**, *201*, 191–200.
18. Shelekhin, A.B.; Dixon, A.G.; Ma, Y.H. Adsorption, Diffusion and Permeation of Gases in Microporous Membranes. III. Application of Percolation Theory to Interpretation of Porosity, Tortuosity, and Surface Area in Microporous Glass Membranes. *J. Membr. Sci.* **1993**, *83* (2), 181–198.
19. Ferrari, M.C.; Galizia, M.; De Angelis, M.G.; Sarti, G.C. Gas and Vapor Transport in Mixed Matrix Membranes Based on Amorphous Teflon AF1600 and AF2400 and Fumed Silica. *Ind. Eng. Chem. Res.* **2010**, *49* (23), 11920–11935.
20. Maghami, S.; Sadeghi, M.; Mehrabani-Zeinabad, A.; Zarabadi, M.; Ghalei, B. The Role of Interfacial Morphology in the Gas Transport Behavior of Nanocomposite Membranes: A Mathematical Modeling Approach. *Ind. Eng. Chem. Res.* **2019**, *58* (25), 11022–11037.
21. Minelli, M.; De Angelis, M.G.; Sarti, G.C. Predictive Calculations of Gas Solubility and Permeability in Glassy Polymeric Membranes: An Overview. *Front. Chem. Sci. Eng.* **2017**, *11* (3), 405–413.
22. Monsalve-Bravo, G.M.; Bhatia, S.K. Modeling Permeation through Mixed-Matrix Membranes: A Review. *Processes* **2018**, *6* (9), 172.
23. Pal, R. Permeation Models for Mixed Matrix Membranes. *J. Colloid Interface Sci.* **2008**, *317* (1), 191–198.

24. Park, G.S. Transport Principles—Solution, Diffusion and Permeation in Polymer Membranes. In *Synthetic Membranes: Science, Engineering and Applications*; Bungay, P.M., Ed.; D. Reidel Publishing Company: Dordrecht, Holland, 1986; pp 57–107.
25. Kanehashi, S.; Chen, G.Q.; Scholes, C.A.; Ozcelik, B.; Hua, C.; Ciddor, L.; Southon, P.D.; D'Alessandro, D.M.; Kentish, S.E. Enhancing Gas Permeability in Mixed Matrix Membranes Through Tuning the Nanoparticle Properties. *J. Membr. Sci.* **2015**, *482*, 49–55.
26. Sun, X.; Turnage, S.; Iezzi, E.B.; Yang, Y.; Chang, B.; Muthgowda, N.C.; Balijepalli, S.K.; Dhuyvetter, N.; Wang, L.P.; Solanki, K.N.; Rykaczewski, K. Water Permeation and Corrosion Resistance of Single- and Two-Component Hydrophobic Polysiloxane Barrier Coatings. *J. Coat. Technol. Res.* **2017**, *14* (6), 1247–1258.
27. Pearl, T.P.; Mantooth, B.A.; Eikenberg, J.H.; Reust, P.; Fritsche, M.G.; White, M.A. High-Throughput Chemical Agent Resistance Method as a Screening Tool for Coatings Development. *J. DoD Res. Eng.* **2021**, *4* (2), 2–10.
28. Shukla, P.; Jagdhari, T.; Fugaro, A.P.; Boreyko, J.B. Characterizing Hygroscopic Materials via Droplet Evaporation. *Langmuir* **2020**, *36*, 1871–1877.
29. Shue, M.; Lalain, T.; Mantooth, B.; Humphreys, P.; Hall, M.; Smith, P.; Sheahy, M. *Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations*; ECBC-TR-883; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2011; UNCLASSIFIED Report (ADA546021).
30. Elabd, Y.A.; Sloan, J.M.; Barbari, T.A. Diffusion of Acetonitrile in Conformational Isomers of an H₁₂MDI Polyurethane. *Polymer* **2000**, *41* (6), 2203–2212.
31. Elabd, Y.A.; Sloan, J.M.; Tan, N.B.; Barbari, T.A. Effect of Penetrant–Polymer Interactions on Molecular Diffusion in Conformational Isomers of a Heterogeneous Polymer. *Macromolecules* **2001**, *34* (18), 6268–6273.
32. Varady, M.J.; Pearl, T.P.; Stevenson, S.M.; Mantooth, B.A. Decontamination of VX from Silicone: Characterization of Multicomponent Diffusion Effects. *Ind. Eng. Chem. Res.* **2016**, *55* (11), 3139–3149.
33. Wolf, C.; Angellier-Coussy, H.; Gontard, N.; Doghieri, F.; Guillard, V. How the Shape of Fillers Affects the Barrier Properties of Polymer/Non-Porous Particles Nanocomposites: A Review. *J. Membr. Sci.* **2018**, *556*, 393–418.
34. Evans, K.M.; Hardy, J.K. Predicting Solubility and Permeation Properties of Organic Solvents in Viton Glove Material Using Hansen's Solubility Parameters. *J. Appl. Polym. Sci.* **2004**, *93* (6), 2688–2698.

35. Ma, J.; Zhou, L.L. A New Procedure for Calculating Hansen Solubility Parameters of Carbon Nanotube/Polymer Composites. *Polym. Bull.* **2012**, *68* (4), 1053–1063.
36. Liu, G.Y.; Hoch, M.; Wrana, C.; Kulbaba, K.; Qiu, G.X. A New Way to Determine the Three-Dimensional Solubility Parameters of Hydrogenated Nitrile Rubber and the Predictive Power. *Polym. Test.* **2013**, *32* (6), 1128–1134.
37. Narses, S.; Sadaka, F.; Brachais, C.H.; Couvercelle, J.P. Polymer Stain Resistance: Prediction versus Experiment. *J. Appl. Polym. Sci.* **2013**, *129* (5), 2891–2904.
38. Dorey, S.; Pahl, I.; Uettwiller, I.; Priebe, P.; Hauk, A. Theoretical and Practical Considerations When Selecting Solvents for Use in Extractables Studies of Polymeric Contact Materials in Single-Use Systems Applied in the Production of Biopharmaceuticals. *Ind. Eng. Chem. Res.* **2018**, *57* (21), 7077–7089.
39. Villmow, T.; John, A.; Potschke, P.; Heinrich, G. Polymer/Carbon Nanotube Composites for Liquid Sensing: Selectivity Against Different Solvents. *Polymer* **2012**, *53* (14), 2908–2918.
40. Delgado, D.E.; Sturdy, L.F.; Burkhart, C.W.; Shull, K.R. Validation of Quartz Crystal Rheometry in the Megahertz Frequency Regime. *J. Polym. Sci., Part B: Polym. Phys.* **2019**, *57* (18), 1246–1254.
41. DeNolf, G.C.; Sturdy, L.F.; Shull, K.R. High-Frequency Rheological Characterization of Homogeneous Polymer Films with the Quartz Crystal Microbalance. *Langmuir* **2014**, *30* (32), 9731–9740.
42. DeNolf, G.C.; Haack, L.; Holubka, J.; Straccia, A.; Blohowiak, K.; Broadbent, C.; Shull, K.R. High Frequency Rheometry of Viscoelastic Coatings with the Quartz Crystal Microbalance. *Langmuir* **2011**, *27* (16), 9873–9879.
43. Sturdy, L.F.; Wright, M.S.; Yee, A.; Casadio, F.; Faber, K.T.; Shull, K.R. Effects of Zinc Oxide Filler on the Curing and Mechanical Response of Alkyd Coatings. *Polymer* **2020**, *191*, 122222.
44. Shull, K.R.; Taghon, M.; Wang, Q.F. Investigations of the High-Frequency Dynamic Properties of Polymeric Systems with Quartz Crystal Resonators. *Biointerphases* **2020**, *15* (2), 021012.
45. dePolo, G.E.; Schafer, E.; Sadman, K.; Rivnay, J.; Shull, K.R. Sample Preparation in Quartz Crystal Microbalance Measurements of Protein Adsorption and Polymer Mechanics. *J. Vis. Exp.* **2020**, *155*, e60584.
46. Sadman, K.; Wiener, C.G.; Weiss, R.A.; White, C.C.; Shull, K.R.; Bogt, V.D. Quantitative Rheometry of Thin Soft Materials Using the Quartz Crystal Microbalance with Dissipation. *Anal. Chem.* **2018**, *90* (6), 4079–4088.

47. Sturdy, L.F.; Yee, A.; Casadio, F.; Shull, K.R. Quantitative Characterization of Alkyd Cure Kinetics with the Quartz Crystal Microbalance. *Polymer* **2016**, *103*, 387–396.
48. Grissom, T.G.; Sirrine, J.M.; Long, T.E.; Esker, A.R.; Morris, J.R. Interaction Parameters for the Uptake of Sulfur Mustard Mimics Into Polyurethane Films. *Prog. Org. Coat.* **2017**, *107*, 14–17.
49. SpecialChem. *Titanium Dioxide Pigment for Paints & Coatings - Complete Guide*; <https://coatings.specialchem.com/selection-guide/complete-guide-on-titanium-dioxide> (accessed 29 August 2022).
50. NIST NCNR. *Neutron Reflectometry*; https://www.ncnr.nist.gov/programs/reflect/NR_article/index.html (accessed 29 August 2022).
51. Yampolskii, Y.; Belov, N. Investigation of Polymers by Inverse Gas Chromatography. *Macromolecules* **2015**, *48* (19), 6751–6767.
52. Voelkel, A.; Strzemiescka, B.; Adamska, K.; Milczewska, K. Inverse Gas Chromatography as a Source of Physicochemical Data. *J. Chromatogr. A.* **2009**, *1216*, 1551–1566.

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ACRONYMS AND ABBREVIATIONS

$ G_n^* $	shear modulus
Γ_n	half-width at half maximum
Δf_n	change in frequency of n th overtone
δ_i	Hildebrand solubility parameter
$\delta_i^D, \delta_i^P, \delta_i^H$	Hansen solubility parameters
μ_q	quartz shear modulus
ρ	film density
ρG_n^*	hardness
ρ_q	quartz density
$\phi_{c,m}$	volume fraction
ϕ_n	viscoelasticity
AFM	atomic force microscopy
AminoEt-AminoPr TMS	<i>N</i> -(2-aminoethyl)-3-aminopropyl trimethoxysilane
APTMS	3-aminopropyl-trimethoxysilane
ARL	U.S. Army Research Laboratory
ATR	attenuated total reflectance
B_{ii}	second virial coefficient of probe i
CARM	chemical agent resistance method
CEES	2-chloroethyl ethyl sulfide
CONOPS	concept of operations
d	film thickness
$d\rho$	swelling
d_{polymer}	polymer film thickness
DEVCOM CBC	U.S. Army Combat Capabilities Command Chemical Biological Center
DI	deionized
diMeAmino TMS	3-(<i>N,N</i> -dimethyl-aminopropyl) trimethoxysilane
DMA	dynamic mechanical analysis
DSB	Decontamination Sciences Branch
E'	storage modulus
FTIR	Fourier transform infrared
fwhm	full width at half-maximum
GC	gas chromatography
GD	soman; pinacolyl methyl phosphonofluoridate (nerve agent)
HD	distilled mustard; bis(2-chloroethyl)sulfide (blister agent)
HDI	1,6-hexamethylene diamine
IGC	inverse gas chromatography
IPA	isopropanol
LC	liquid chromatography
LD	log difference
MeOH	methanol
M_i	molar mass of probe i
MMM	mixed-matrix membrane

MPTMS	3-mercaptopropyl-trimethoxysilane
MS	mass spectrometry
NCO	isocyanate
NH	amino
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
<i>N</i> -MUS	<i>N</i> -methyl urea silane
NPTMS	<i>N</i> -propyl trimethoxysilane
NRL	U.S. Naval Research Laboratory
ODTMS	octadecyltrimethoxysilane
PDMS	polydimethylsiloxane
p_i^0	saturated vapor pressure of probe <i>i</i>
PMMA	poly(methyl methacrylate)
PS	polysiloxane
PU	polyurethane
PVC	pigment-to-volume concentration
QCM	quartz crystal microbalance
QCM-D	quartz crystal microbalance with dissipation
<i>R</i>	universal gas constant
RA	remaining agent
rpm	revolutions per minute
SEM–EDS	scanning electron microscopy–energy-dispersive X-ray spectroscopy
SLD	scattering length density
<i>T</i>	temperature
<i>t</i> -BUS	<i>tert</i> -butyl urea silane
TEOS	tetraethyl orthosilicate
T_g	glass transition temperature
TMS	trimethoxysilane
US	urea silane
V_{gi}	retention volume
V_i	molar volume of probe <i>i</i>
VX	[2-(diisopropylamino)ethyl]- <i>O</i> -ethyl methylphosphonothioate (nerve agent)
χ_{ip}	interaction parameter of the polymer
γ_p^D	dispersive component of surface energy
γ_p^S	specific component of surface energy

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Command Chemical Biological Center
(DEVCOM CBC)
FCDD-CBR-PD
ATTN: Pearl, T.
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Morrissey, K.

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