Surface Evaluations of Two-Component Hybrid Organosilane Coatings with Polar and
Non-Polar Liquids

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by

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DEDICATION

This is dedicated to my husband Dustin, for his continuous love and support throughout this journey.

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

>92% distilled bis(2-chloroethyl) sulfide ....HD
2-chloroethyl phenyl sulfide 2-CEPS
Amino-functional polysiloxane/silanes ....AFPS
Attenuated Total Reflectance...ATR
Carbon Dioxide...CO_2
Chemical Agent Resistant Coating..CARC
Chemical Warfare Agent ....CWA
Chemical Warfare Agent Simulant...CWAS
Epoxy-functional polysiloxane ....EFPS
Fourier Transform Infrared ....FTIR
Military Detail Specification...MIL-DTL
Military Defense Specification ....MIL-SPEC
Near-Infrared...NIR
O-Ethyl *S*-(2-diisopropylaminoethyl) methylphosphonothioate....................................VX
Particle Size Distribution ....PSD
Rate constant..*k*
Safety Data Sheet...SDS
Scanning Electron Microscope ....SEM
Single-Component 1K
Surface Free Energy...SFE
Substitution, Nucleophile, Bimolecular..S_N^2
Titanium Dioxide ....TiO_2
Two-Component 2K
Ultra-High Purity ....UHP
Ultra Violet ....UV
Visible...VIS
Volatile Organic Content ....VOC
Weight Percent...wt%
World War I ....WW I

ABSTRACT

SURFACE EVALUATIONS OF TWO-COMPONENT HYBRID ORGANOSILANE
COATINGS WITH POLAR AND NON-POLAR LIQUIDS

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Polymers and oligomers are often used in thermosetting (thermoset) coatings because
they can provide a cross-linked solid material that cannot be melted. Properties,
including exterior durability, corrosion resistance, and solvent resistance, are appealing in
the coatings industry because they can be applied to a substrate as a layer of protection.
When a substrate is not protected, it is exposed to thermal, ultra-violet, biological, and
chemical degradation. Once the substrate begins to corrode it can become defective,
dangerous, and expensive to repair. For years, coatings have been applied to vehicles to
prevent corrosion of the substrate. This concern is critical for all military ground vehicles
that are exposed to harsh environmental conditions, such as sea water, as well as potential
attack from chemical warfare agents. This study focuses on the performance of two
component hybrid organosilane coatings based on epoxy- and amine- functional materials
versus a commercially available polyurethane coating currently used on military ground

vehicles. Different ratios of epoxy to amines and a blend of different additives were prepared to formulate a chemical resistant coating. Coatings were exposed to water and non-polar liquids (e.g., chemical warfare agent simulants (CWAS)) and analyzed using multiple analytical techniques. This study identified formulations that provided better chemical repellency than the polyurethane chemical agent resistant coating (CARC) used by the military.

1. BACKGROUND

1.1 Coatings

Nearly 35,000 years ago, paint was created using natural materials such as clay, chalk, animal fat, and albumen. In the earlier years of discovery, paint was made in small quantities and was mainly used for art. Techniques for altering the color and consistency of the paint were later discovered, allowing the uses for paint to be broadened. In the eighteenth century, paint was being manufactured in factories, which allowed for consumer use due to affordability. Large scale production of paint resulted in people coating the interior and exterior of their homes and businesses. However, it took two more centuries before the function of paint was understood.[1]

Coatings are composed of pigments, a binder, solvents, and various additives, depending on the manufacturer. The pigment, a coloring agent, is mixed with a binder, or "vehicle", that is later dissolved in a solvent. This mixture creates an even consistency allowing the product to be applied uniformly to the substrate. Once the application is complete, the solvent will evaporate and leave a coated substrate that contains a hard polymer layer.[1-2]

Polymers may be formed through polymerization of monomers, condensation or addition reaction materials. Acrylic polymers are formed when there is repetitive chemical bonding of monomers through free radicals, cationic and anionic species.[1-4] However, most polymers used in coatings are formed through condensation or addition reactions. Condensation polymerization is an endothermic process, which means heat

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from an outside source is needed to initiate the reaction. Through condensation a polymer is formed plus a simple byproduct, such as water, alcohol, or an acid. On the other hand, the addition polymerization route does not form any byproducts and is an exothermic process.[5-6]

Introducing different functional groups into the backbone of the polymer can alter the mechanical and chemical properties. Whether it is adding elasticity in our jeans or providing a tough protective layer for our military structures against chemical warfare agents (CWA), choosing the right polymer is important, especially when needing that polymer to carry out a specific job. One of the most important uses for polymers is in the coatings industry. The proper type of polymer and crosslinks can prevent CWA from absorbing and adsorbing, thereby providing the substrate with protection from degradation. Cross-linking is the process of linking one polymer with another through covalent and ionic bonding.[4] The cross-linking density increases if the number of available functional groups increase. It is important to establish a high crosslink density because it enhances the properties of the linear polymer chain system by increasing resistance against wear and chemical attack.[7]

The military is often exposed to harsh environments and the exterior of their vehicles need to remain in operational condition. Applying the proper coating system can protect the substrate from weathering or chemicals that could potentially reduce the performance of the vehicle and/or affect the warfighter. If a coating can be developed that provides resistance to heat, ultra-violet (UV) light, and chemicals, then it could potentially increase the life of the coating as well as extend the life of the vehicle.

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Repairing and replacing coatings are extremely expensive and further problems can lead to replacing entire military vehicles. Therefore, it is extremely important to protect the substrate and use a proper topcoat that can withstand the harsh conditions and have an extended service life.

1.2 Epoxy Polysiloxane Hybrid

In the mid-1990's, a new weather-resistant coating known as organosilanes (also known as polysiloxanes) was introduced as a replacement for polyurethane coatings. Polysiloxanes can be characterized as an organic-inorganic hybrid coating that contains a silicon-oxygen (Si-O) backbone. It is popular in industrial settings due to its resistance to increased temperatures, photo-oxidation, and certain acids and solvents.[8-9] Si-O has a stronger bond strength of 451.87 kJ·mol^{-1} compared to the carbon-carbon (C-C) and carbon-hydrogen (C-H) bond strengths of 351.46 kJ·mol^{-1} and 414.22 kJ·mol^{-1}, respectively.[9-10] An increase in bond strength increases the coatings durability and resistance to thermal degradation (up to 1400°F or 760°C).[9]

In this study, an epoxy resin is reacted with amino-functional polysiloxanes and alkoxysilanes. Structures of the epoxy and amine resin are found in Figure 1.1 and Figure 1.2, respectively. The end product result in the amine group opening the epoxy ring to form a covalent bond, thereby creating an epoxy polysiloxane thermoset.[11-12] A copolymer is formed by reacting one monomer with a different monomer during polymerization. The continuous cross-linking of the epoxy fragments with the linear

polysiloxane forms a network that is difficult for chemical agents to penetrate and reduces surface tension.[8, 13-14]

The benefits of using an epoxy polysiloxane hybrid coating is the physical increase in corrosion resistance by providing a strong barrier against water, chlorides, sulfate ions, and other chemicals and solvents.[13] Epoxy hybrid coatings increases the coatings affinity for the hydroxyl groups (OH) present on inorganic surfaces. Most coating systems on military ground vehicles require a zinc-rich primer, an intermediate coat (or tie coat), and the CARC topcoat. Using an organosilane topcoat, with better adhesive properties eliminates the need for the intermediate coat.[8-9, 15]

Organic polymers are prone to UV and thermal degradation. When burned, they excrete toxic fumes. The organosilane is primarily high in solids and low in volatile organic content (VOC). Having a low VOC coating lowers the combustibility of the organosilane coating, thereby making it more environmentally friendly while also maintaining color and gloss. Previous studies of epoxy polysiloxane copolymer show an increase in weatherability, flexibility, compressive strength, and chemical resistance.[13]

Epoxides are known to have limited reactivity and will not cross-link with themselves. Adding the amino-functional polysiloxanes and silanes to the epoxy polysiloxanes, shown in Figure 1.1, promotes crosslinking resulting in increased weatherability and chemical resistance of the coating. The primary amine, shown in Figure 1.2, initiates the reaction by attacking the least substituted carbon on the epoxide ring. Covalent bonds are formed with one or more epoxy functional polysiloxanes, thus leading to an increase in the crosslink density.[13]

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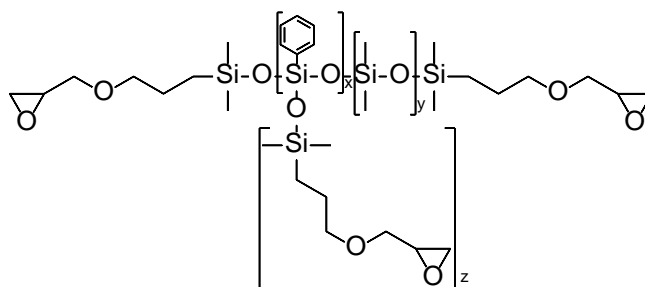
Figure 1.1: An example of an epoxy-functional polysiloxane
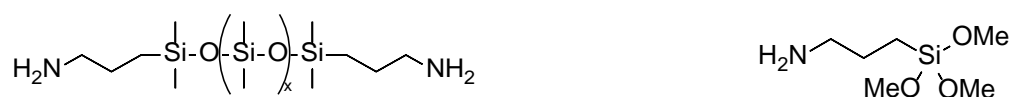
Figure 1.2: An example of an amino-functional polysiloxane (left) and amino-silane (right).

It is extremely important that the military has access to a coating that can protect their structures and soldiers from adverse situations. Epoxy polysiloxane coatings can provide protection from harsh environmental conditions, while at the same time resisting chemical degradation. Preventing corrosion of the substrate and extending the service life of the coating reduces cost, but most importantly protects our military members and allows them to continue to excel in their duties.

1.3 Polyurethanes

Polyurethanes are formed by reacting diisocyanate with compounds containing more than one hydroxyl groups (-OH) through addition reactions.[2] Figure 1.3 represents the reaction between a diisocyanate and a diol to form a polyurethane polymer.

Formation of the polyurethane polymer induces a durable coating that increases

weatherability and chemical resistance, while also maintaining the flexibility needed to

prevent cracking and damage of the substrate.[10, 16] The diisocyanate portion of the

polymer is stiff and rigid while the carbon chain region from the polyol is softer and

rubbery.

$$O{=}C{=}N\diagup\diagdown\diagup N{=}C{=}O \quad + \quad HO\diagup\diagdown\diagup OH \longrightarrow \left[\begin{array}{c} \underset{\parallel}{O}\ H \\ C{-}N\diagup\diagdown\diagup N{-}\underset{\parallel}{\overset{O}{C}}{-}O{-}\underset{H_2}{C}{-}\underset{H_2}{C}{-}\underset{H_2}{C}{-}O \end{array}\right]_n$$
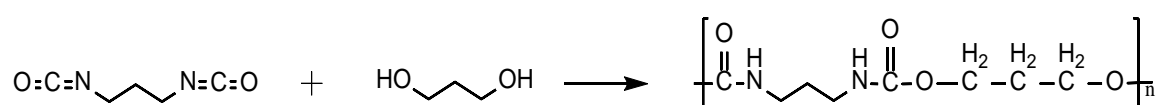
Figure 1.3: Example of diisocyanate reacting with a diol to form a polyurethane polymer.

Chemical Agent Resistant Coating (CARC) polyurethanes became commercially

available within the military back in the 1980s to replace a coating that contained heavy

metals.[17] A single component (1K) CARC polyurethane, which is qualified to MIL-

DTL-53039 requirements, is currently used on military vehicles because it is a moisture

cured coating (low VOC) that provides flexibility and corrosion protection for military

ground vehicles.[10, 17-18] Although it provides protection against CWAs, it is not

completely chemical agent resistant. It is only capable of protecting the substrate by

retarding the absorption of the chemicals. Unfortunately, polyurethanes contain

carbamate (urethane) linkages, which promote hydrogen bonding and are not

hydrophobic. The hydrophobicity feature is necessary for repelling water or chemical

agents.

In addition to the CARC control being hydrophilic, the isocyanates are a huge health concern because they are classified as irritants. When acutely exposed, one may begin to feel irritation on the skin or in the respiratory system. Chronic exposure can result in permanent damage to the brain and nervous system.[10, 19] Safety data sheets (SDS) for polyurethane CARC warn that the product may also contain one or more carcinogens.
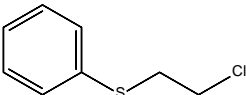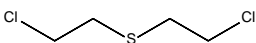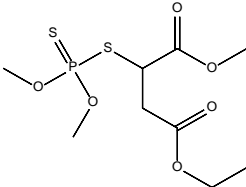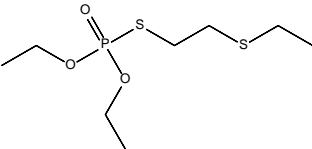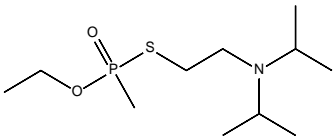
1.4 Chemical Warfare Agent Simulants

Vesicants and nerve agents, known as CWA, are a concern for the military and have been stockpiled since World War I (WW I). CWA are easy to synthesize and highly lethal, making them a huge threat to our military. CWA are derived from pesticides where the compounds are non-polar. Non-polar compounds are not water soluble, which allows them to remain in the environment for extended periods of time. These CWA include sulfur mustard (mustard gas, bis(2-chlorethyl) sulfide, HD) and *O*-ethyl *S*-(2-diisopropylaminoethyl) methylphosphonothioate (VX). To determine the chemical resistance of an organosilane and polyurethane coating, chemical warfare agent simulants (CWAS) were used to mimic actual chemical warfare agents (CWA). The chosen CWAS are structurally similar to live agents but are less toxic to work with.[16] CWAS have both polar and non-polar characteristics and should represent the omniphobicity of the coating. Table 1.1 displays the CWAS and the CWAs they intend to chemically mimic.

2-CEPS is structurally identical to sulfur mustard except one of the chlorines in sulfur mustard is replaced by a phenyl group in 2-CEPS. Presence of the phenyl group

does create a bulkier molecule but is similar because both chlorine and phenyl groups are electron withdrawing. However, removing one of the chlorines makes the molecule less toxic and easier to work with in a lab not set up for analysis of live agents. Malathion and Demeton-S were chosen to mimic VX because of the neighboring phosphonate-like group and sulfur group. Phosphonate groups are commonly used in herbicides and pesticides, but compared to VX, they are safer to work with.

Table 1.1: Chemical warfare agent simulants (CWAS) tested in place of chemical warfare agents (CWAs).

Chemical Warfare Agent Simulant	Chemical Warfare Agent
2-Chloroethyl phenyl sulfide (CEPS)	Sulfur Mustard
Malathion　　　　　　Demeton-S	VX

2. THESIS

2.1 Thesis Statement

For years the military has relied on coatings to provide protection against environmental corrosion, chemical and biological degradation, and camouflage. Protection heavily lies on the need for a polymer system that operates in harsh conditions and the use of pigments and additives that extend the quality of a coating by providing additional corrosion protection as well as infrared reflectance to avoid detection. A qualified 1K polyurethane CARC coating is currently being used. Using polyurethanes are a health concern because of the presence of isocyanates and the fact that they do not repel chemicals but rather retard their absorption.

This fundamental research will compare an epoxy polysiloxane hybrid coating to a currently qualified polyurethane CARC coating known as Green 383. When the epoxy functional polysiloxanes are introduced to a primary amino-functional polysiloxane, the epoxy rings will open and form a covalent bond between the two compounds. Greater cross-linking is achieved through addition reactions forming a durable and corrosion resistant coating. Incorporating a strong bond strength like the Silicon-Oxygen (Si-O) bond into the backbone, increases the coatings resistance to thermal degradation.

Coatings were formulated at a 1.0:1.0, 1.1:1.0, and 1.0:1.1 molar ratio of epoxy to H-amine groups. Ratios were chosen due to excess amine causing blushing, where the coating would form a greasy layer on the surface, and excess epoxy would result in a slow curing coating. The most chemical resistant epoxy:amine ratio was further used in

the succeeding formulations where one-by-one, new formulations introduced pigment, matting agent, and two different additives were added at different weight percent (wt%) to understand if and how the ingredients affected the chemical resistance.

Pigment not only adds color, but can also provide corrosion and environmental protection. Titanium dioxide (TiO_2) is one of the most important pigments used today. Because it has strong opacity and tinting strength, very little is needed in the formulation. When less pigment is used, the coating's elasticity and durability improve. TiO_2 was incorporated in the second round of formulations at a weight percent of 10, 25, and 40%. Percentages were chosen to find the best formulation that would hide the underlying substrate and test how increasing pigment influences the contact angles of each liquid.

Matting agent is needed to reduce gloss and reflect light. It also enhances surface roughness which can affect the wettability of the surface. Matting agent was added in at 10, 15, and 20% weight. Through literature research it was discovered that Ramé-Hart reported in a September 2010 newsletter, increase surface roughness could result in increased wettability for samples that had apparent contact angles lower than 90°. Their study included measurements before and after abrasively sanding surfaces of materials that initially had contact angles both above and below 90°. According to Wenzel's equation, if the apparent contact angle is above 90, roughness will increase the contact angle and if the apparent contact angle is below 90, roughness will decrease the contact angle.[20]

Fluoroalkyl silane was chosen due to the perfluorinated side group and the triethoxy silane. Triethoxy silane has an affinity for the epoxy and amine resin and reacts

into the coatings matrix. Fluorine is extremely electronegative and has low reactivity. The perfluorinated side group that has a low affinity for the coating would extend out of the surface and decrease the SFE of the coating. Also, the presence of the dimethylene, or C2 spacer, between the trimethoxy silane and the fluorinated side group creates a more environmentally friendly alternative to typical perfluorinated additives. Due to the fluorines having low reactivity, they often have long biological half-lives that result in bioaccumulation. Dimethylene will act as the breaking point and transforms or partially environmentally degrades. The dimethylene spacer is lost, and limited de-fluorination of adjacent fluorines are possible. The transformed product would be a per-fluorinated end-point compound.[21-22]

Mercaptosilane has a trimethoxy silane group that would react into the coatings matrix. Instead of a strong electronegative atom sticking out of the surface, this additive introduces a thiol. Thiols (–SH) have a higher affinity for the sulfur-based CWA and will interact at the surface of the coating, minimizing interaction between the coating and live agent.

Contact angle measurements of ultra-high purity (UHP) water, diiodomethane, and hexadecane were used to identify the omniphobicity and calculate the surface free energy (SFE) of the different formulations. SFE values were calculated using the contact angle measurements of UHP water (polar) and diiodomethane (dispersive) according to the Owens-Wendt theory.[23]

Samples showing greater chemical resistance out of the different formulation sets were exposed to CWAS 2-CEPS, Demeton-S, and Malathion for 90 minutes. To see how

the contact angles of CWAS changed over time, contact angles were recorded at 0, 1, 5, 10, 15, 20, 30, 60, and 90 minutes. CWAS were chosen based on their structural similarities to live agents.

3. METHODS

3.1 Coatings

Coating refers to a thin layer spread over a substrate either for decorative, protective, or functional purposes and sometimes all three. Coatings contain more than just the polymer resin; additives and pigments are added in small amounts to make up the final coating system. Although they are added in at such a small-scale, they can affect the mechanical and chemical properties, inhibit corrosion and both chemical and microbial attack.

Catalysts are additives that provide more free radicals to speed up the polymerization process through addition reactions, thereby, resulting in initiation of crosslinking and a coating with a shorter drying time. Dibutyltin bis (2-ethylhexanoate in 50% xylene will act as the Lewis acid catalyst in the 2K epoxy-amine polysiloxane formulations. Tin oxide-based catalyst is a hard acid that holds a high positive charge, Sn^{4+}. The hard acid will react with primary amine, a hard base, on the amino-functional polysiloxane and amino-silane resin.

The need for extended service life and chemical resistant coatings led to the consideration of a 2K epoxy polysiloxane hybrid coating. Using the polyurethane Green 383 CARC coating as a control, surface analysis and chemical resistant tests were performed against a series of 2K epoxy-amine organosilane formulations in hopes of identifying a more chemical resistant coating system.

The starting formulations involved altering the molar ratios by 1.0:1.0, 1.1:1.0, and 1.0:1.1 of epoxy functional polysiloxane to amine functional polysiloxane without the addition of pigment, matting agent, and additives. This clear coating system allowed for a baseline analysis of the ratios to identify the best ratio to move forward with. These specific ratios were chosen because the amine hardener had to be in the range of 0.7-1.2 equivalent weight to 1 equivalent weight of epoxide. When less than 0.7 amine equivalent weight was used, there was marked decrease in the cure time due to excess epoxy. Use of the amine equivalent weight greater than 1.2, resulted in amine blushing at the surface.[13] Each coating was spray applied to a 3-inch x 6-inch aluminum panel with a dry film thickness around 2 mils. Raw materials used in the coatings formulations can be found in Tables 3.1 and Table 3.2.

Formation of the epoxy polysiloxane hybrid coating involved an S_N2 reaction where the aliphatic primary amine (a nucleophile and weak base) attacks the least substituted carbon of the epoxide ring (an electrophile), thereby causing the ring to open and form a covalent bond. The negatively charged oxygen will pick up the acidic proton on the quaternary amine and form a hydroxyl group. The opening of the epoxide ring is a concerted process and is often referred to as a bimolecular substitution reaction or a S_N2 (substitution, nucleophilic, bimolecular) mechanism that exhibits over all second order kinetics, see Equation 1.[1, 11-12] An example of the reaction mechanism for the epoxy-amine organosilane formation is represented in Figure 3.1.
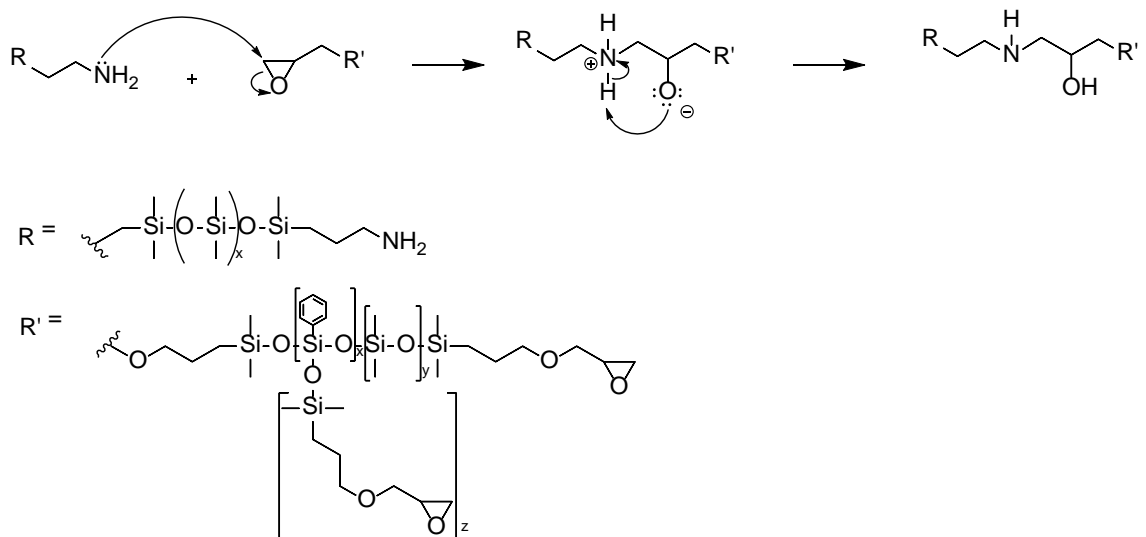
Figure 3.1: Aliphatic amine opening the epoxy ring forming a covalent bond.

$$\text{Rate} = k[\text{EFPS}][\text{AFPS}] \tag{1}$$

k = rate constant

EFPS = epoxy-functional polysiloxane

AFPS = amino-functional polysiloxane/silanes

Raw Material Used in Formulations:

Table 3.1: MIL-DTL-53039 Single Component (1K) Aliphatic Polyurethane CARC.

Raw Material	wt%	Raw Material	wt%
Polyurethane	31	Cobalt titanate spinel	0.4
Dispersant	1	Methyl isoamyl ketone	23.5
Rheology modifier	0.1	VM&P naphtha	3.2
Flow modifier	<0.1	Xylene	1.4
Surfactant	0.1	n-Butyl acetate	1.3
Dibutyl tin dilaurate	0.5	Aromatic 100	1.3
Celite	18.5	Mineral spirits	1.2
Imsil	3.6	Propylene glycol	0.1
TiO_2	9.5	Isobutyl ketone	0.1
Iron oxide hydrate	2.5	n-Butyl acid phosphate	0.1
Carbazole dioxazine violet	<0.1	Bentone	0.5

Table 3.2: High Solids Two-Component (2K) Organosilane Topcoat.

Raw Material
Epoxy-functional polysiloxane
Amino-functional polysiloxane
Lewis acid catalyst
Titanium dioxide
Polyurea matting agent
Perfluorinated additive
Mercaptosilane
Solvents

3.1.1 Two Component Formulation of Varying Epoxy-Amine Ratios

Formulations started with a pigment and additive free coating to outline the baseline hydrophobicity and surface free energy of the 2K coating at different molar ratios. An epoxy to amine polysiloxane ratio of 1.0:1.0, 1.1:1.0, and 1.0:1.1 were chosen

based on known performance issues of coatings when epoxy or amine is added in excess. Excess epoxy could result in a slow curing coating and excess amine could result in amine blushing on the surface and effect its wettability.

Amine blushing is the result of unreacted aliphatic amine present at the coatings surface having an affinity for the carbon dioxide (CO_2) and moisture in the air. This surface phenomenon results in the formation of hydrates and carbamates leaving a greasy discolored film on the coatings surface. The presence of excess epoxy can also result in amine blushing due to the slow curing process that leaves the amine vulnerable for an extended period. Amine blushing can affect adhesion and wettability, and when exposed to moisture the coating is susceptible to blistering.

3.1.2 Two Component Formulation of Varying TiO₂ Percentages

The second round of formulations (002) involved the addition of TiO_2 at 10, 25, and 40 wt% to the most chemical resistant coating prepared in section *3.1.1*. Although the addition of pigment was not expected to have a huge effect on hydrophobicity, it was necessary to test the different percentages to identify which formulation had the desired hiding power and crosslink density. The smaller percentage of TiO_2 will not have sufficient hiding power but will have increased crosslinking to provide a durable coating. Too much TiO_2 will provide the substrate with coverage but negatively affect the coatings ability to have higher crosslinking.

TiO_2 was added into the epoxy side of the formulation where a bulk paste was created prior reducing the TiO_2 percentages to 10, 25, and 40 wt%. Producing the grind

paste in bulk assured minor variation in pigment particle size. By creating a more

homogeneous mixture, changes in hydrophobicity will solely be based on the presence of

TiO_2 at different weight percentages and not the size of the pigment particles. A

homogeneous mixture also provides the resin with uniform pigment dispersion for better

coverage and uniform physical and chemical properties across the substrate.

Poor particle size distribution (PSD) directly affects matting, adhesion, physical

and chemical durability, flow during application, and opacity.[24] An increase in particle

size increases both visible (VIS) and near-infrared (NIR) reflectance by extending further

out of the coatings surface.[25] However, larger particles may negatively affect the

crosslink density and result in an increase in the number of pores present and pore size.

Particle size was measured using a one-path Hegman gage, in accordance with

ASTM D1210-05, a *Standard Test Method for Fineness and Dispersion of Pigment-*

Vehicle Systems by Hegman-Type Gage. As the paste was being mixed, small samples

were taken and measured until a fineness of grind value of 5 Hegman (35 µm) was

achieved. Keeping the particle size at 5 Hegman or slightly larger was necessary to avoid

the formation of smaller particles that would result in a high gloss coating.[26] However, a

particle size too large that could negatively affect cross-link density was also not

desirable.

3.1.3 Two Component Formulation of Varying Matting Agent Percentages

The third round of formulations (003) introduced Pergopak M3, a flattening

compound, to reduce the gloss and reflectance of the coating. It was hypothesized that

adding matting agent would increase surface roughness and decrease the wettability of

the surface. It is important that the substrate is hid without the performance of the

coating being effected as a result of overloading it with solids. Because of the difference

in hiding power and contact angles, both 25 wt% and 40 wt% TiO_2 were used in the 003

formulations, with three different percentages of matting agent at 10, 15, and 20 wt%.

3.1.4 Two Component Formulation of Varying Additives and Percentages

The fourth and fifth round of formulations (004 and 005) included the addition of

the fluoroalkylsilane and mercaptosilane additives, respectively. Fluoroalkyl silane was

added into the 004 formulations at 0.25%, 0.5%, 1.0%, and 2.0 wt%. However, due to

differences in molecular weight, mercaptosilane was added in at a 1 mol equivalence to

the fluoroalkyl silane. The calculated mole percentages for mercaptosilane were 0.096,

0.193, 0.385, and 0.770 mol%. Weight percentages of fluoroalkyl silanes, a large

molecule with the molecular weight of 510.36 $g{\cdot}mol^{-1}$, were calculated based on the

weight percent of all solids. The weight percent and molecular weight of fluoroalkyl

silane was then used to calculate the mol percent of mercaptosilane, with a molecular

weight of 196.34 $g{\cdot}mol^{-1}$, needed for formulations 005.

Fluoroalkyl silane, seen in Figure 3.2, is known as a surface modifier that contains

thirteen fluorine atoms extended on an eight-carbon chain resulting in an extremely

electronegative molecule. The triethoxysilane end of the molecule is more structurally

similar to the epoxy silane and amino silane resins used. Unlike the triethoxysilane

portion, fluorine has a low affinity for the resins causing the perfluorinated side groups to

make their way out of the coating and extend out of the surface. The result is a coating

with increased omniphobicity and decreased SFE. All formulations described in section

3.1.1 through 3.1.4 are listed in Table 3.3.
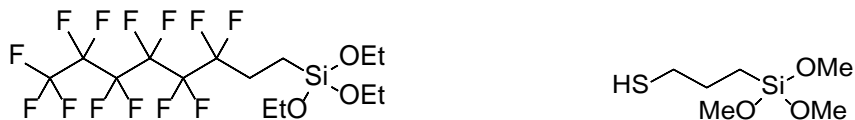
Figure 3.2: Tridecafluoro-1,1, 2,2-tetrahydrooctyl)triethoxysilane (left) and mercaptosilane (right).

Table 3.3: Breakdown of the formulations and weight percent of each ingredient

Sample	Epoxy:Amine	TiO2 (wt%)	Pergopak (wt%)	Fluoroalkyl Silane (wt%)	Mercaptosilane (mol %)
001-A	1:1	-	-	-	-
001-B	1.1:1	-	-	-	-
001-C	1:1.1	-	-	-	-
002-A	1.1:1	10.0	-	-	-
002-B	1.1:1	25.0	-	-	-
002-C	1.1:1	40.0	-	-	-
003-A	1.1:1	40.0	10.0	-	-
003-B	1.1:1	40.0	15.0	-	-
003-C	1.1:1	40.0	20.0	-	-
003-D	1.1:1	25.0	10.0	-	-
003-E	1.1:1	25.0	15.0	-	-
003-F	1.1:1	25.0	20.0	-	-
004-A	1.1:1	25.0	15.0	0.25	-
004-B	1.1:1	25.0	15.0	0.5	-
004-C	1.1:1	25.0	15.0	1.0	-
004-D	1.1:1	25.0	15.0	2.0	-
005-A	1.1:1	25.0	15.0	-	0.096
005-B	1.1:1	25.0	15.0	-	0.193
005-C	1.1:1	25.0	15.0	-	0.385
005-D	1.1:1	25.0	15.0	-	0.770

3.2 Sample Exposure

After each set of formulations, the samples were spray applied to 3-inch x 6-inch aluminum, chromium, and tin Q-Panels. Prior to the coatings application a M12 Form Leneta Spray Monitoring sticker was placed on aluminum Q-Panels like the example seen in Figure 3.3. Leneta Spray Monitoring stickers were chosen because they have a solvent resistant surface with a strong, permanent adhesion that represents a coatings opacity.[27] The stickers have four black and white alternating blocks which are used to test the hiding power of a coating that could not be seen directly on a substrate.

Figure 3.3: Uncoated M12 Leneta Spray Monitoring sticker on aluminum Q-Panel

Using a goniometer, contact angle measurements of UHP water, hexadecane, and diiodomethane were taken to determine the hydrophobicity, oleophobicity, and SFE of each formulation. Select formulations with greater resistance to UHP water, diiodomethane, and hexadecane were exposed to CWAS 2-CEPS, Malathion, and Demeton-*S*. Static contact angles were measured for each CWAS at 0 minutes.

Simulants were exposed to the coatings for a total of 90 minutes while contact angle measurements were taken at 0, 1, 5, 10, 15, 20, 30, 60, and 90 minutes.

3.3 Microscopy

3.3.1 Scanning Electron Microscopy – Energy Dispersive X-Ray (SEM-EDX)

Micrographs were obtained using a dual-beam scanning electron microscope (FEI Helios Nanolab) with a secondary electron detector. Prior to SEM analysis, samples on Q-Panels were trimmed to a size of 1 in^2 to fit on the stage. Images were taken from the center of the sample to avoid areas that were deformed during trimming. Accelerating voltage was set between 3 and 5 *kV*. Images to identify porosity were taken at 1000x and 2500x magnification. Images at 150x magnification were taken to view the surface roughness of each sample to identify any correlation between surface roughness and contact angles.

3.4 Goniometry

3.4.1 Contact Angle

Contact angle and surface free energy measurements were obtained using an automated Ramé-hart Model 590, F4 series goniometer with a 150w Fiber Optic Illumination attachment. Using the sessile drop technique, 10 µL of a liquid was manually released onto the surface of the substrate. DROPimage Advanced v2.5 software captured images of the drops and measured the angle of contact (θ) and is also

referred to as the Young's Angle (θ_Y).[28] Below are the two ASTM used as a guide during contact angle analysis.

- ASTM D7334-08(2013): Standard Practice for Surface Wettability of
  Coatings, Substrates and Pigments by Advancing Contact Angle Measurement
- ASTM D7940-13: Standard Test Method for Measurement of the Surface
  Tension of Solid Coatings, Substrates and Pigments Using Contact Angle
  Measurements

Static contact angle measurements and images were captured immediately at zero minutes for all liquids. CWAS were exposed to samples for a total of 90 minutes while contact angle measurements were taken at 0, 1, 5, 10, 15, 20, 30, 60, and 90 minutes. A watch glass was placed over the liquid and substrate to retard evaporation.

Three categories of static contact angle measurements were considered during this investigation: not omniphobic (static contact angle measurements less than 90°), omniphobic (static contact angle measurements greater than 90°), and super omniphobic (static contact angle measurements greater than 150°).[29] Static contact angles are captured when the three phase boundary, solid, liquid, and gas, reach equilibrium.[30] This phenomenon is calculated using young's equation and can be seen in Figure 3.4.
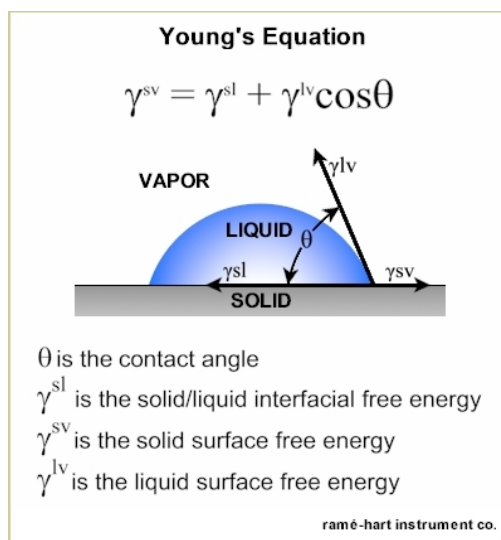
Figure 3.4: Three-phase equilibrium contribution to the Young's Equation[30]

3.4.2 Surface Free Energy (SFE)

The surface free energy (discussed later in section 4.1) was determined using the Owens-Wendt theory with water and diiodomethane. Owens-Wendt theory assumes that the surface free energy ($\gamma_{S,L}$) is equal to the sum of the surface free energy related to dispersion interactions ($\gamma_{S,L}^{d}$) and polar acid-base interactions ($\gamma_{S,L}^{p}$) where S and L are the subscripts for the solid phase and wetting liquid, respectively. [23, 31-32] Owens-Wendt Theory SFE is calculated using equations 2-4 with known solvent parameter values found in Table 3.4.

$$\gamma_{S,L}^{d} = \left(\frac{(1+\cos\theta_d)\gamma_L^{d}}{2\sqrt{\gamma_{L,d}^{LW}}} \right)^{2} \tag{2}$$

$$\gamma_{S,L}^{p} = \left(\frac{(1+\cos\theta_d)\gamma_L^{p} - 2\left(\sqrt{\gamma_{S,L}^{d}} \cdot \sqrt{\gamma_{L,p}^{LW}}\right)}{2\sqrt{\gamma_{L,p}^{AB}}} \right)^{2} \tag{3}$$

$$\gamma_{S,L} = \gamma_{S,L}^{d} + \gamma_{S,L}^{p} \tag{4}$$

Table 3.4**:** Surface Properties of Liquids.

Liquid	Solvent Parameters (mJ/m²)		
	γL	γ - polar/AB	γ - dispersive/LW
Water	72.8	51	21.8
Diidomethane	50.8	0	50.8

γL	Liquid Surface Energy
AB	Acid/Base Interactions
LW	Lifshitz-Van der Waals

4. RESULTS AND DISCUSSION

4.1 Polyurethane Coating

Spray applied Green 383, the current qualified product, was used as the control and tested against various formulations of 2K epoxy-amine organosilane. The control resulted in very low contact angles for UHP water and diiodomethane and no contact angles were recorded for hexadecane, Demeton-*S*, Malathion, and 2-CEPS due to the high wettability of the coatings surface. A 10-µL droplet of the four liquids either immediately absorbed into the coating, or greatly wetted the surface and extended beyond the cameras frame resulting in a recorded contact angle of 0.0°. The contact angles for UHP water and diiodomethane were 24.8 ± 2.0° and 36.4 ± 1.9°, respectively. Contact angles and drop images are reported in Table 4.1. Surface free energy values using the Owen-Wendt Theory were calculated from the contact angles of water (polar) and diiodomethane (dispersive) for each sample using Equations 2-4 using the solvent parameters from Table 3.4.

4.2 Organosilane Coatings

Upon manipulating the formulation of the 2K epoxy-amine polysiloxane hybrid coating, there were noticeable changes in the wettability of the surfaces. The epoxy:amine ratio of 1.1:1 (sample 001-B) had the highest contact angles for hexadecane and diiodomethane and the lowest surface free energy out of the 001 formulations. The 1.1:1 ratio was chosen to be used in the remaining formulations due to the low surface
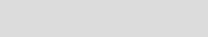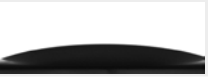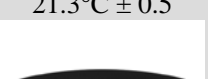
free energy value of 27.93 mJ•m^{-2} versus the reported 39.32 mJ•m^{-2} and 39.83 mJ•m^{-2} values for the 1:1 and 1:1.1 ratios, respectively.

Testing of formulations with 10%, 25%, and 40% TiO$_2$ concluded that the amount of TiO$_2$ and the water contact angle were inversely proportional. Very little variation in diiodomethane contact angles were noted and a slight increase in hexadecane contact angles for 002-A and 002-C. Although sample 002-A with 10% TiO$_2$ had the better contact angle of 100.0 ± 1.3, it did not have sufficient hiding power and was not used in the succeeding formulations. Both 002-B and 002-C were used in the next series (003) formulations for two different reasons. 002-B had the slightly better water contact angle and 002-C had the better diiodomethane and hexadecane contact angles, and the greatest hiding power.

With the exception of 005-B and 005-C, all of the epoxy-amine organosilane coating formulations were hydrophobic with UHP water contact angles greater than 90°. Diiodomethane contact angles averaged in the lower 60° range for all formulations except formulation 004 where the average contact angle was approximately 30° higher than all other samples. Contact angles for UHP water, diiodomethane, and hexadecane increased and the SFE decreased drastically for all formulations containing the fluoroalkylsilane additive in formulation 004. The presence of the extremely electronegative fluorine atoms residing at the surface decreases the surface free energy and wettability of the coating, resulting in higher chemical resistance due to the limited reactivity of the fluorine atoms. All UHP water, diiodomethane, and hexadecane contact angle

measurements and images are listed in Table 4.1 and Figure 4.1 (a-c). Results of the

surface free energy calculations are found in Table 4.2 and Figure 4.2.

Table 4.1: Static contact angles of UHP water, diiodomethane, and hexadecane.

Sample	UHP Water	Diiodomethane	Hexadecane
1k 383 Green	24.8°C ± 2.0	36.4°C ± 1.9	Wetted Out
001-A	95.5°C ± 0.4	61.0°C ± 0.8	15.4°C ± 0.5
001-B	97.4°C ± 0.8	63.1°C ± 0.8	16.1°C ± 0.6
001-C	94.5°C ± 0.5	60.4°C ± 0.5	17.3°C ± 0.4
002-A	100.0°C ± 0.3	61.0°C ± 0.6	19.6°C ± 1.1
002-B	96.3°C ± 1.0	60.6°C ± 0.3	17.8°C ± 1.0
002-C	94.9°C ± 0.7	61.6°C ± 0.5	19.7°C ± 0.7
003-A	95.3°C ± 0.4	61.3°C ± 0.6	20.8°C ± 0.4
003-B	94.4°C ± 0.4	61.5°C ± 0.8	18.2°C ± 0.6
003-C	93.6°C ± 0.6	62.4°C ± 0.8	20.9°C ± 0.5
003-D	95.0°C ± 0.5	60.2°C ± 1.1	22.6°C ± 0.4
003-E	95.2°C ± 0.2	62.7°C ± 0.4	20.9°C ± 0.5
003-F	92.3°C ± 0.9	63.9°C ± 0.8	21.3°C ± 0.5

Sample	UHP Water	Diiodomethane	Hexadecane
004-A	106.7°C ± 1.4	97.7°C ± 0.6	58.4°C ± 0.8
004-B	107.4°C ± 0.4	96.6°C ± 0.8	59.1°C ± 0.7
004-C	107.5°C ± 1.0	102.0°C ± 0.4	59.9°C ± 0.7
004-D	108.4°C ± 0.6	97.3°C ± 0.4	61.8°C ± 0.3
005-A	91.1°C ± 0.5	63.1°C ± 0.5	26.9°C ± 0.8
005-B	87.6°C ± 0.5	63.7°C ± 0.5	25.5°C ± 1.3
005-C	87.6°C ± 0.8	64.0°C ± 0.2	29.2°C ± 0.3
005-D	92.6°C ± 0.5	64.4°C ± 0.5	26.2°C ± 0.6

(a)

(b)

(c)
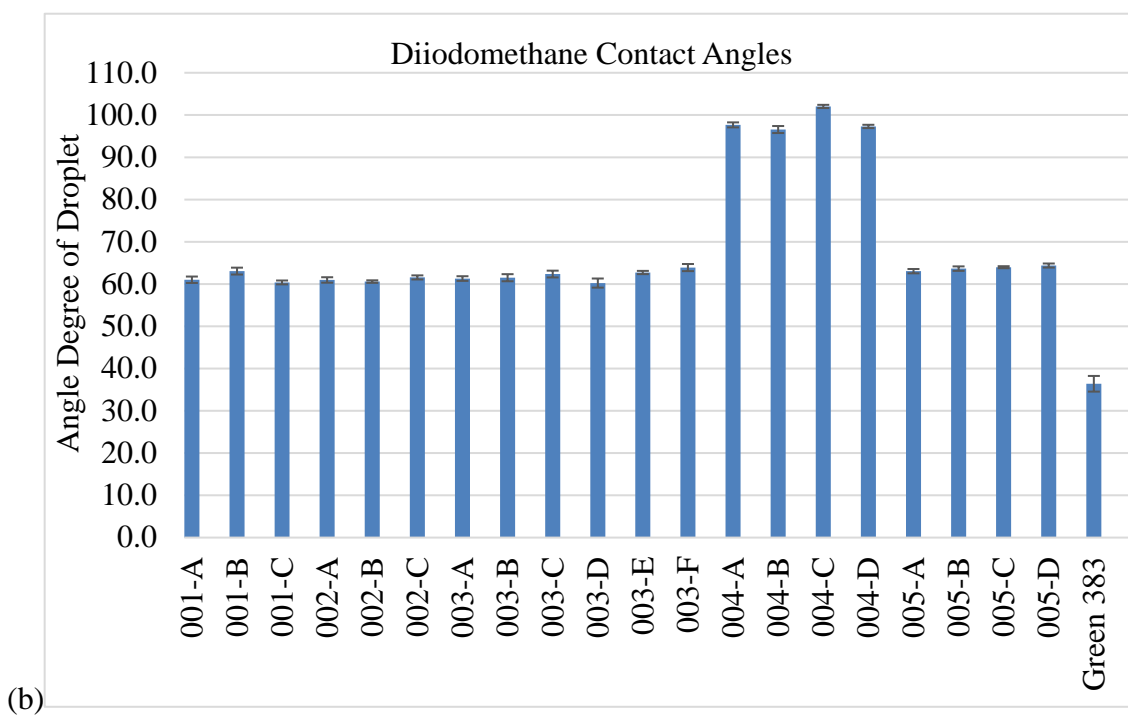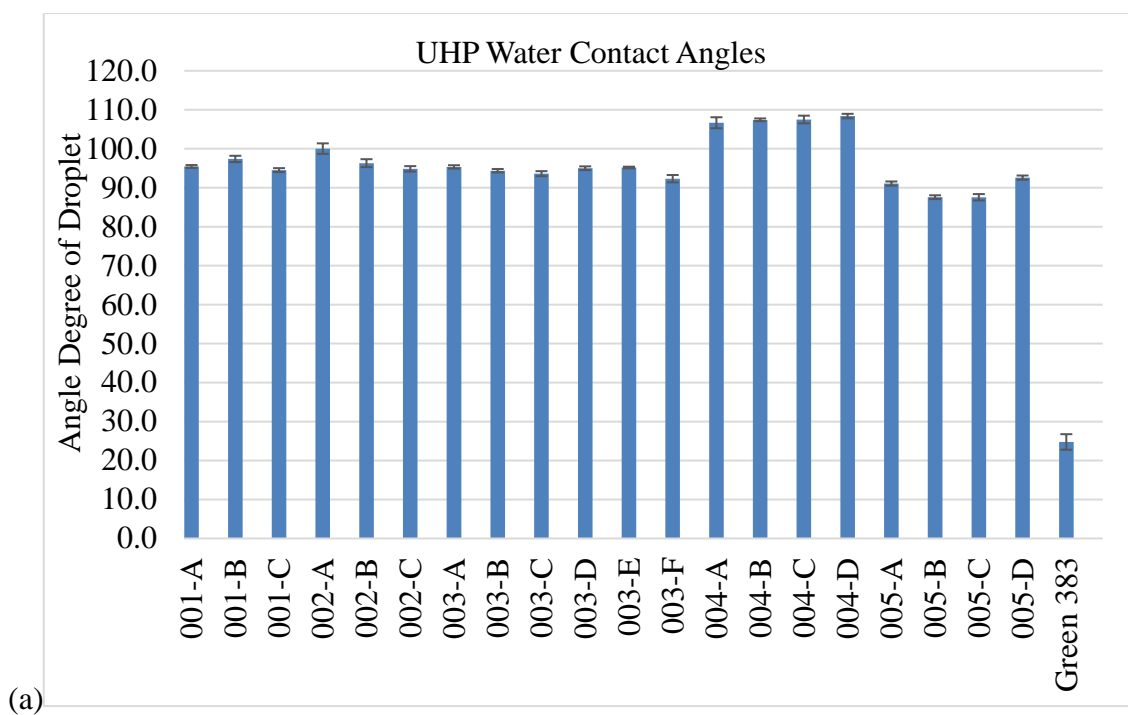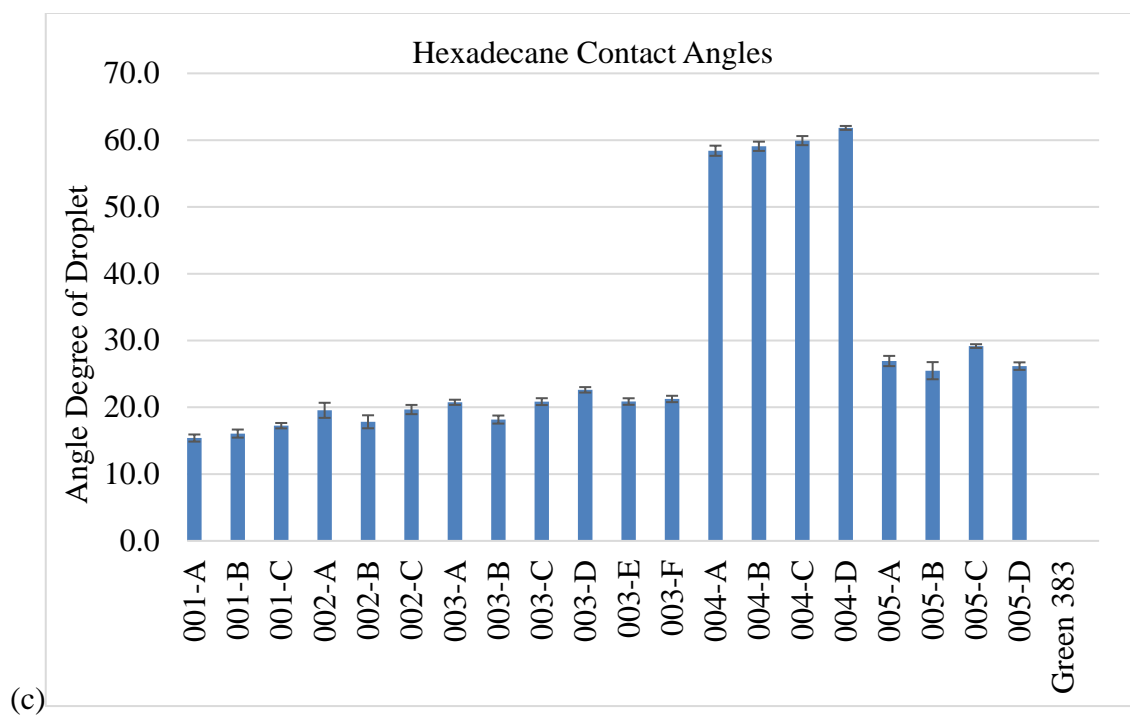
Figure 4.1: Contact Angles (a) UHP Water (b) Diiodomethane (c) Hexadecane

Table 4.2: Surface free energy calculation using the Owens-Wendt Theory.

Surface	γ-Dispersive (mJ/m²)	γ-Polar (mJ/m²)	γ-Surface (mJ/m²)
Green 383	36.20	5.66	41.86
001-A	27.99	1.33	29.32
001-B	26.81	1.12	27.93
001-C	28.35	1.47	29.83
002-A	28.02	0.56	28.58
002-B	28.24	1.13	29.37
002-C	27.67	1.50	29.18
003-A	27.83	1.38	29.21
003-B	27.71	1.61	29.32
003-C	27.21	1.87	29.08
003-D	28.44	1.36	29.80
003-E	27.00	1.54	28.54
003-F	26.33	2.36	28.69
004-A	9.54	2.61	12.15
004-B	9.96	2.27	12.24
004-C	7.96	2.96	10.92
004-D	9.68	2.12	11.80
005-A	26.82	2.61	29.43
005-B	26.48	3.80	30.28
005-C	26.28	3.85	30.14
005-D	26.06	2.34	28.40
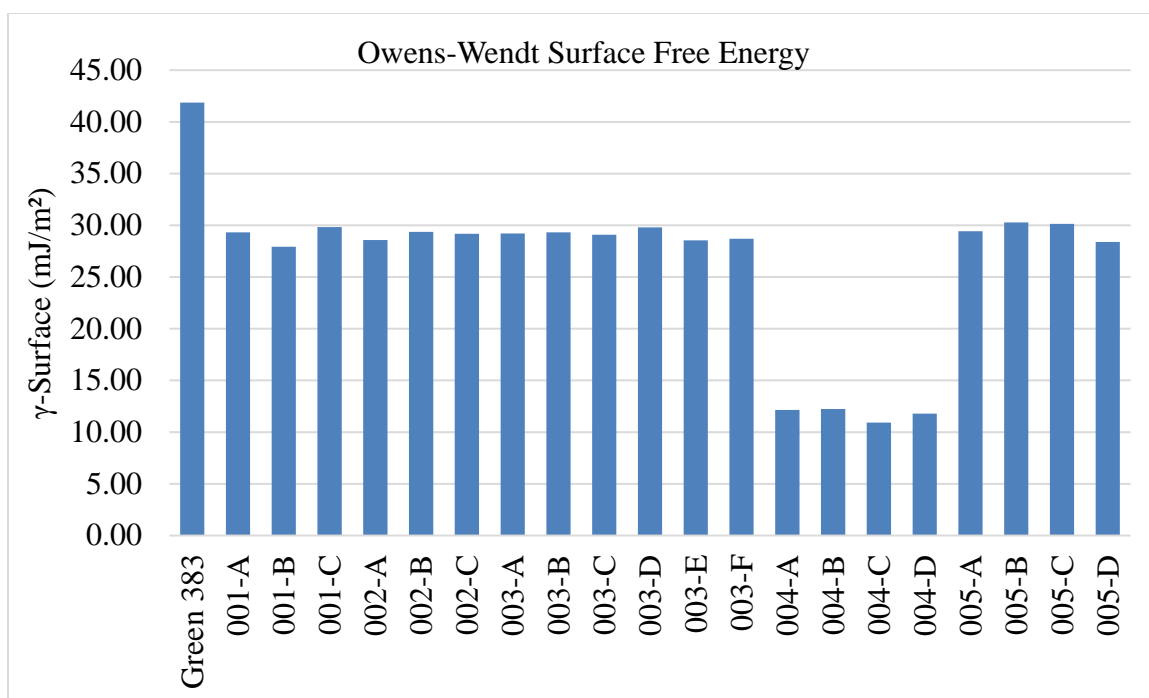
Figure 4.2: Owens-Wendt Surface Free Energy Values

4.3 Chemical Warfare Agent Simulant Exposure (CWAS)

CWAS were applied to the samples recording the highest UHP water contact angles and lowest SFE values for formulation sets 003, 004, and 005, and let stand for a total of 90 minutes. The exception was made for 003-A that did not have the lowest SFE value from samples 003-A, 003-B, or 003-C, but did have the slightly higher UHP water contact angle. As with the previous polar and nonpolar liquid contact angles, CARC Green 383 was used as the control.

CWAS and CWAS are fairly non-polar, hexadecane was used to understand how oleophobic each formulation was. The CARC control was extremely oleophilic, no hexadecane angles were recorded due to the non-polar liquid absorbing into the surface

immediately. The oleophilic CARC control also could not resist the non-polar CWAS. All three CWAS were also immediately absorbed into the coating, resulting in a contact angle of zero degrees.

Formulation 004-D had the highest CWAS contact angles. Formulations 003-A, 003-E, and 005-D were exposed to 2-CEPS and had corresponding contact angles from 0 – 90 minutes. Sample 005-D did have slightly higher Malathion and Demeton-S contact angles during the entire exposure period. All 2K epoxy-amine organosilane samples had a greater rate of absorption within the first twenty minutes of exposure and began to plateau between twenty and ninety minutes. Absorption monitoring results are found in Tables 4.3 – 4.5. Exposure results of the CWAS for 90 minutes can be found in Figure 4.3 (a-c).

Table 4.3: One-hour exposure of 2-CEPS. Contact angle measurements at 0, 15, 30, and 60 minutes.
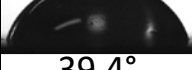
		Minute(s)			
		0	15	30	60
2-CEPS	CARC GREEN 383	0.0°C No Image	0.0°C No Image	0.0°C No Image	0.0°C No Image
	003-A	45.2°	38.7°	35.7°	34.5°
	003-E	43.9°	37.9°	35.1°	35.1°
	004-D	80.0°	73.4°	72.4°	70.9°
	005-D	45.8°	39.4°	36.5°	36.0°

Table 4.4: One-hour exposure of Malathion. Contact angle measurements at 0, 15, 30, and 60 minutes.

		Minute(s)			
		0	**15**	**30**	**60**
Malathion	**CARC GREEN 383**	0.0°C No Image	0.0°C No Image	0.0°C No Image	0.0°C No Image
	003-A	42.8°	37.3°	36.5°	35.1°
	003-E	37.8°	34.8°	33.0°	32.8°
	004-D	80.0°	77.1°	75.4°	74.0°
	005-D	46.7°	40.3°	37.8°	36.8°

Table 4.5: One-hour exposure of Demeton-S. Contact angle measurements at 0, 15, 30, and 60 minutes.

	Minute(s)			
	0	**15**	**30**	**60**
CARC GREEN 383	0.0°C No Image	0.0°C No Image	0.0°C No Image	0.0°C No Image
003-A	28.8°	25.3°	24.1°	22.6°
003-E	26.6°	21.6°	21.2°	21.0°
004-D	73.1°	65.9°	64.8°	64.2°
005-D	33.2°	25.9°	25.7°	25.7°

(a)

(b)

(c)
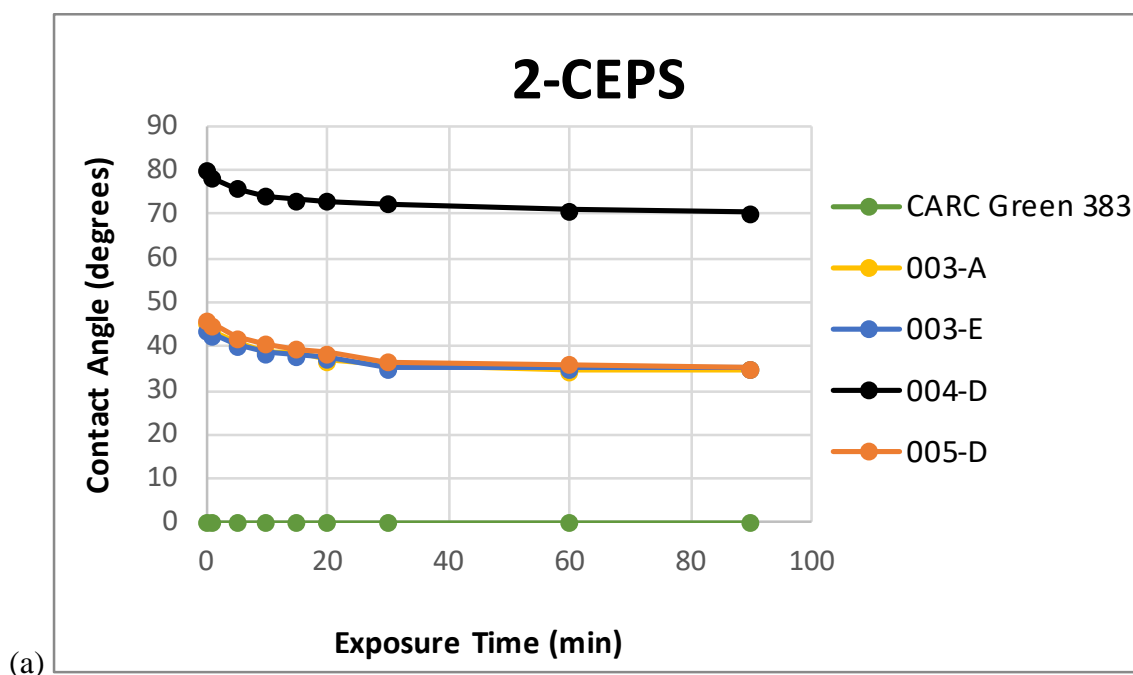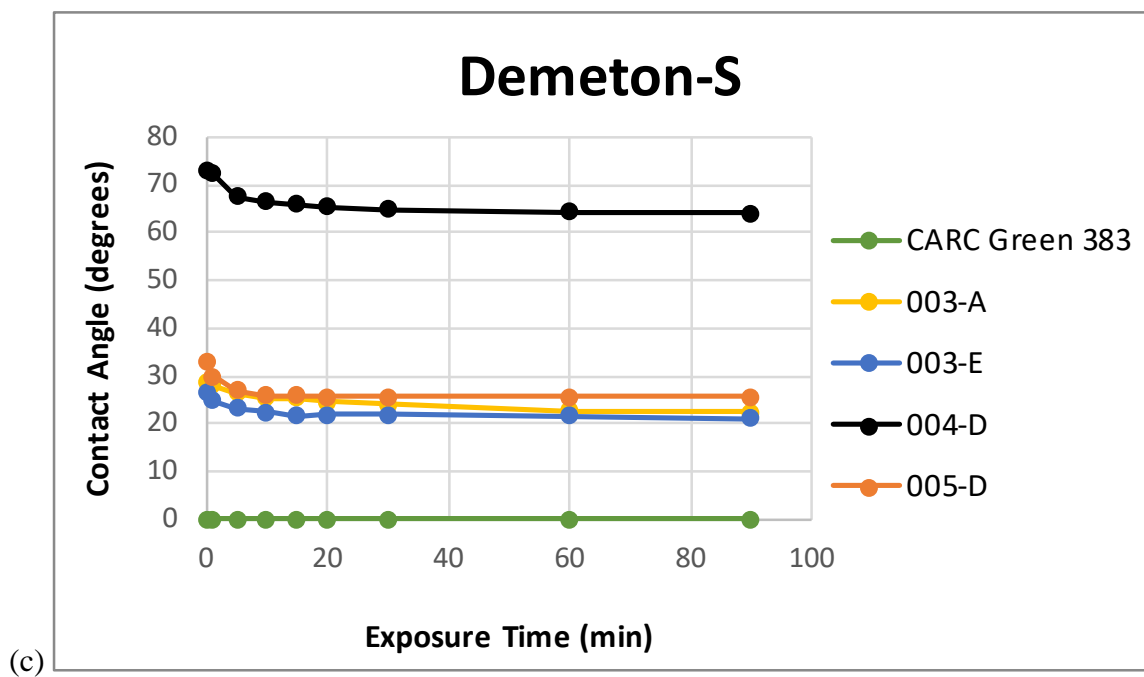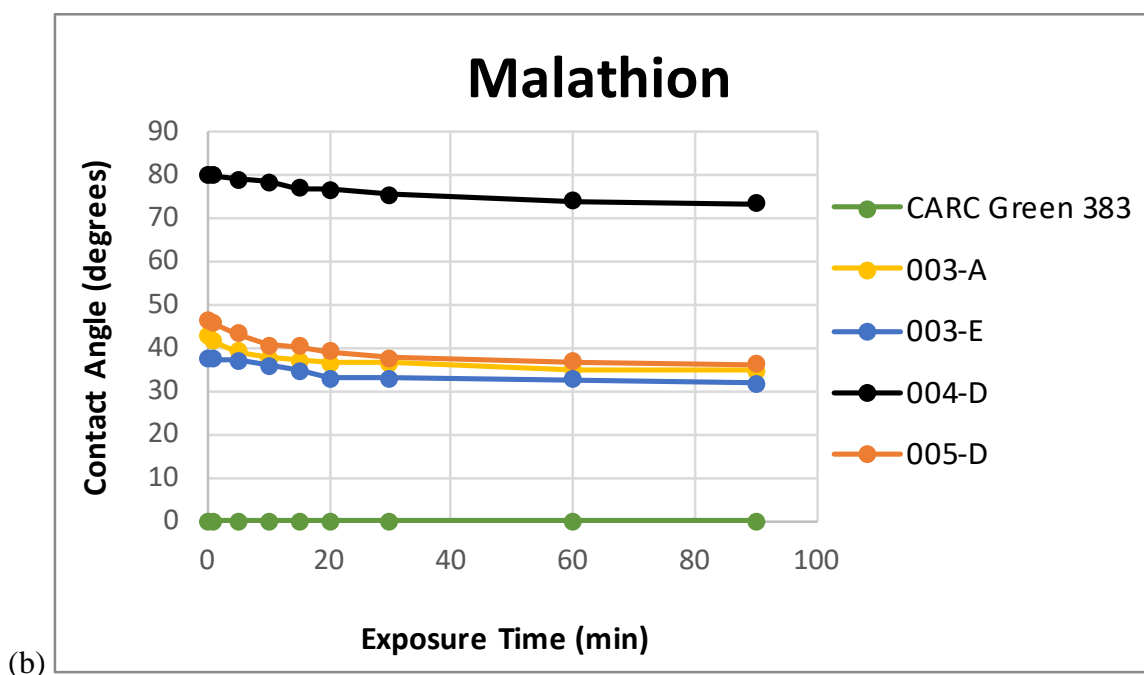
Figure 4.3: 90 minute exposure of CWAS. (a) 2-CEPS (b) Malathion (c) Demeton-S

4.4 Scanning Electron Microscope (SEM) Imaging – Surface Roughness and Porosity

SEM images of the organosilane formulations and CARC Green 383 were taken to find a correlation between surface roughness and contact angle. Samples were viewed at higher magnifications to check for porosity that could act as an entrance points for the CWAS. The first, second, and third column are magnifications of 150x, 1000x, and 2500x, respectively. SEM images are found in Figures 4.4 – 4.7.

Magnification of 150x was primarily used to compare the surface roughness of each sample. Higher magnification could not be used to analyze general surface roughness due to higher magnification being localized to a smaller surface area. Samples 003-F, 004-A, and 005-A displayed greater roughness and yet had lower UHP water contact angles.

Magnification at 1000x and 2500x was used to analyze the surface for any porosity. Formulation set 003 had increasing porosity with increasing wt% of matting agent, Pergopak M3, seen at 2500x magnification. Small localized areas of porosity were observed in samples sets 004 and 005.
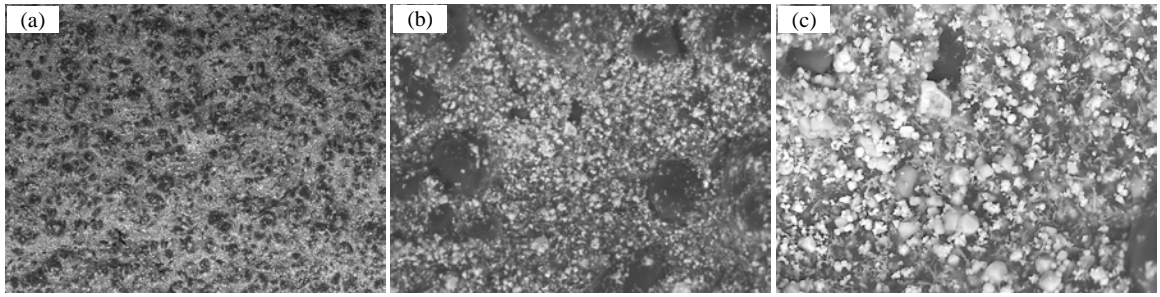
Figure 4.4: SEM surface analysis of CARC Green 383 at different magnifications (a) 150x (b) 1000x (c) 2500x
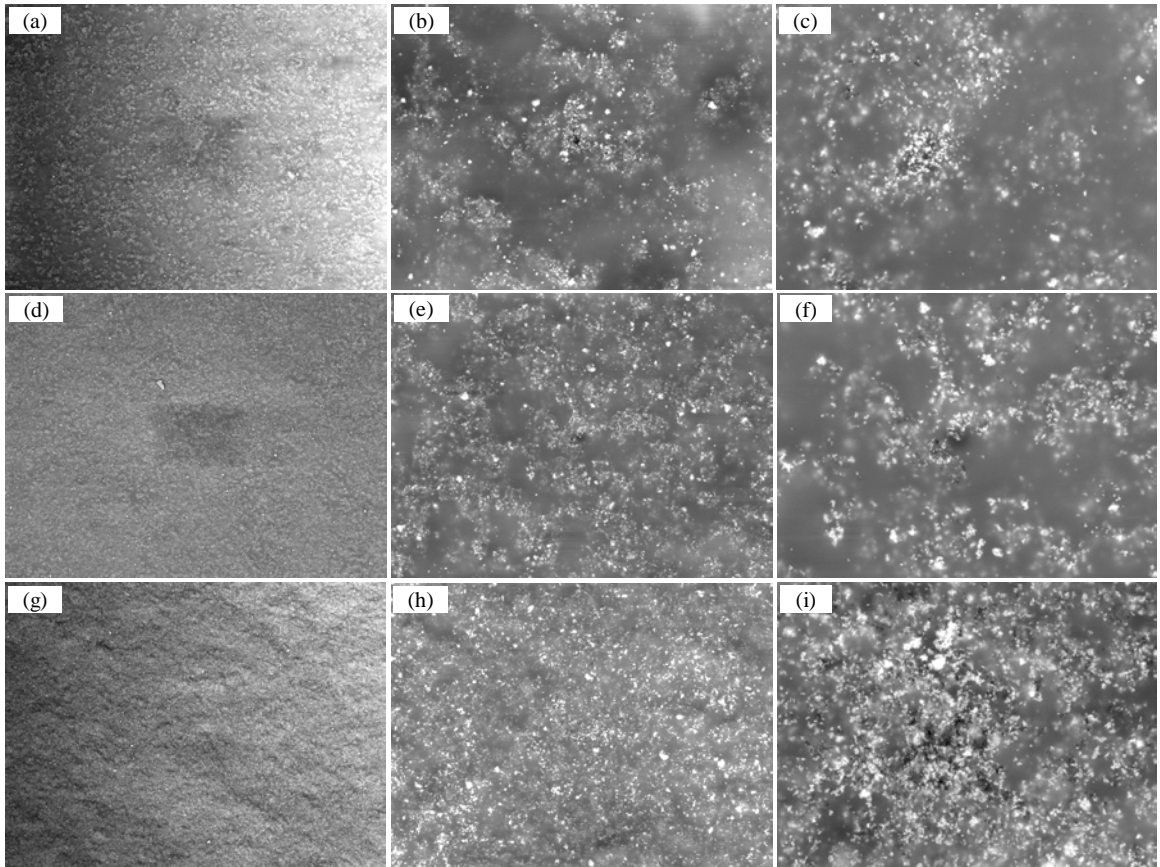
Figure 4.5: SEM Images of 003-A (a-c), 003-E (d-f), 003-F (g-i)
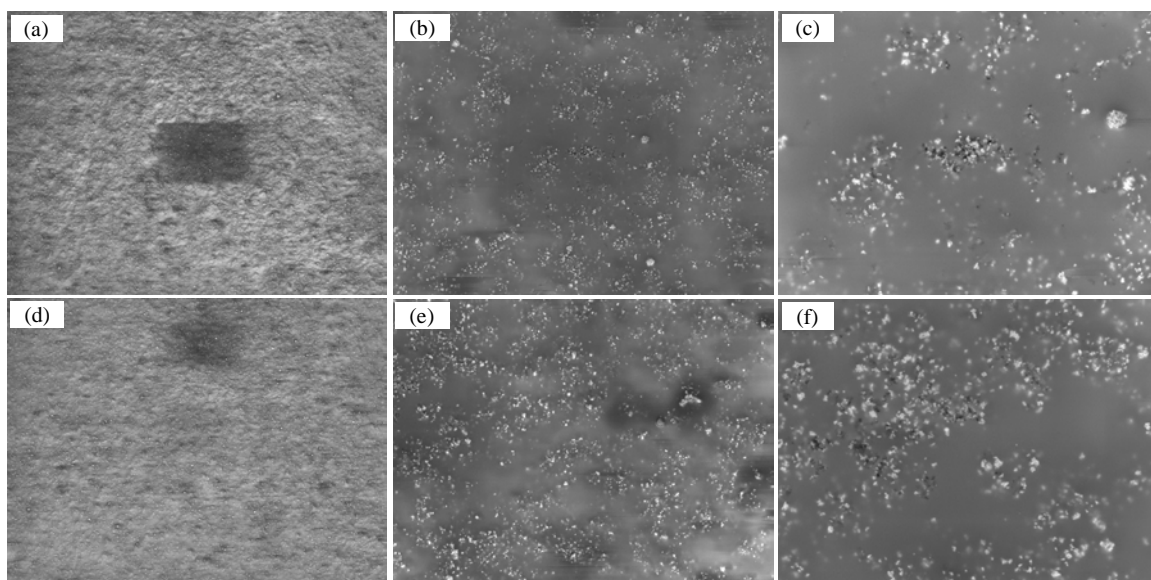
Figure 4.6: SEM Images of 004-A (a-c), 004-E (d-f)
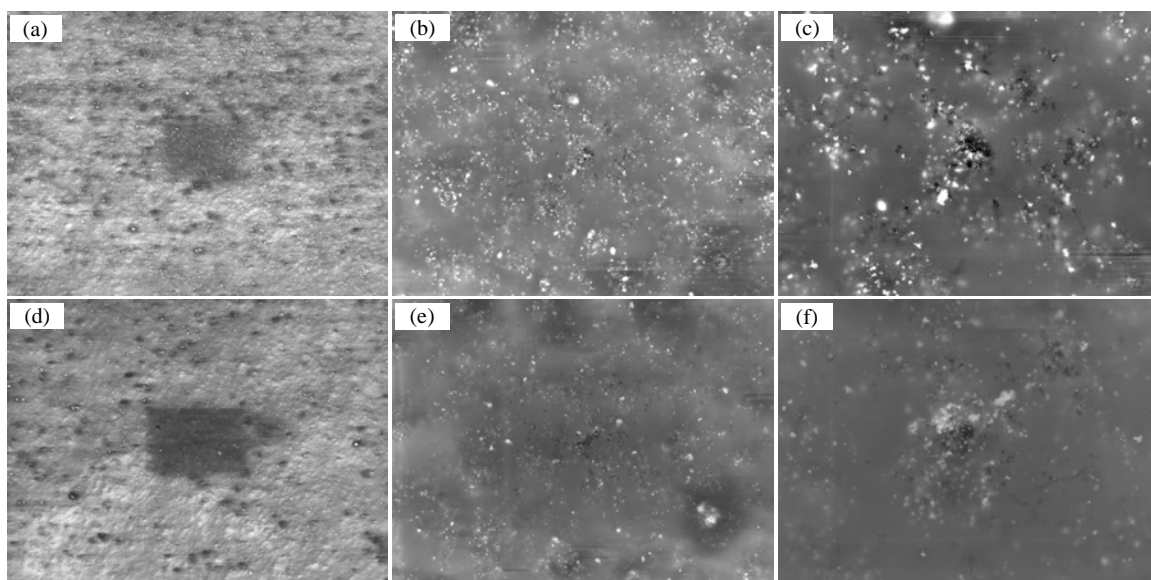
Figure 4.7: SEM Images of 005-A (a-c), 005-D (d-f)

5. SUMMARY

Comparison of various 2K epoxy-amine organosilane coating formulations to a currently qualified CARC coating, Green 383, was performed to test the chemical resistance of each coating against polar and non-polar liquids. UHP water (polar liquid), diiodomethane (dispersive liquid), and hexadecane (non-polar liquid) contact angles were measured as preliminary testing to understand the effect the ingredients had on chemical resistance. One goal was to identify the most effective epoxy:amine ratio, and based on preliminary testing, succeeding formulations were built off of the 1.1:1 ratio. Pigment, matting agent, and additives were then added one-by-one to identify the weight percent of each ingredient that enhanced the chemical resistance. Overall, all of the organosilane formulations had little variation in wettability. It was not until the introduction of the fluoroalkyl silane additive, that a major decrease in surface wettability was seen. Out of the four fluorinated additive formulations, 004-D displayed the lowest surface free energy and lowest wettability of all three liquids.

CARC Green 383 and select samples from formulation sets 003, 004, and 005 were exposed to three CWAS, 2-CEPS, Malathion, and Demeton-S, that were chosen based on structural similarities to live agents, Sulfur Mustard and VX. CWAS were exposed to the samples for 90 minutes with contact angle measurements at 0, 1, 5, 10, 15, 20, 30, 60, and 90 minutes to see if a coating could withstand absorption of the simulant for a period of time. Formulation 004-D outperformed the other samples with higher chemical resistance. All samples experienced an initial drop in contact angles for all

three simulants from 0 – 20 minutes. After approximately 20 minutes, the contact angles began to stabilize and plateau as seen in Figure 4.3 (a-c).

Surface roughness was analyzed using SEM imaging at 150x magnification. Initially, a hypothesis was made that increased surface roughness would result in higher contact angles, creating something representative of the lotus effect. The results were not supportive of this hypothesis, in fact, increased roughness resulted in an increase in surface wettability.

The current qualified product CARC Green 383 did not perform as well as the 2K epoxy-amine organosilane formulations. Contact angles for UHP water and diiodomethane resulted in a high surface free energy value. Green 383 also had poor chemical resistance against the CWAS, due to high wettability of the control, no static contact angle measurements could be recorded for any of the non-polar liquids.

It is important that a coating provides enhanced chemical against the CWA. If the live agent is exposed to the coating, it instantly penetrates the surface and begins to spread wider and deeper, making the decontamination process difficult. A more chemical resistant coating would prevent or limit absorption of CWA, making it easier to decontaminate and provide a longer service life for the military ground vehicles. If a coating is super omniphobic, it would possess contact angles greater than 150° for both polar and non-polar liquids. Chemical resistance to non-polar liquids, in this case CWA, and polar liquids like water would reduce corrosion degradation. Limiting interaction between the coating and CWA can minimize or prevent corrosion and off gassing of toxic byproducts. A developed coating that contains prodigious mechanical and chemical

properties would not only cut military expenditure, it could save military structures, and the health and lives of soldiers.

New ideas arose during analysis, opening up the opportunity for future testing and improvement of both the same and additional formulations. Although spray applications are the more common method for applying coatings within the field, primarily because of speed, ease of application, and cleanup, it is of interest to extend this research further and analyze different coating application methods. Spray application allows the solvent to escape the coating much faster as it atomizes from the spray tip and result in a thin coating and a shorter dry time. Using a stainless-steel film applicator bar to apply a coating applies a thicker single layer. A thicker paint layer will have a slower dry time because the solvent will reside in the coating longer.

Having a longer dry time enables the solvent to evaporate off much slower, allowing the molecules to achieve higher cross-link density. Not only will better cross-linking be achieved, but the additives will have more time to migrate to the surface of the coating in hopes of decreasing the wettability of the surface.

Fluoroalkylsilane, a highly electronegative molecule, is an example of why it is important to have an extended dry time. The fluorinated tail, which has a low affinity with the coating system, will migrate to the surface of the coating and act as a barrier against chemicals and significantly increase the chemical resistance of the coating.

Concluding this research, new ideas were formulated for future testing. Testing the effects of CWAS that are less structurally similar to the live agents, but are more similar in physiochemical properties? As mentioned before, testing spray versus

drawdown applications and extending the dry time of the coating to allow the additives to migrate to the surface and be more effective in decreasing the SFE. Lastly, working with different pigments using different particle sizes, and different additives including 1H,1H,2H,2H-Perfluorodecyltrimethoxysilane with higher fluorination and Trimethoxy(octadecyl)silane that possess a large aliphatic carbon chain.

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