

Selectively Strippable Silyl-Containing Aerospace Topcoats Using Environmentally Friendly Fluoride Salts

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TABLE OF CONTENTS

1. OBJECTIVE	1
2. BACKGROUND	1
3. MATERIALS AND METHODS	5
3.1 Synthetic Schemes and Procedures for Synthesis of Diphenyl Silyl Diols	6
3.2 Synthesis of Silyl-PU Coatings from Silyl Diols.....	13
4. RESULTS AND DISCUSSION.....	14
4.1 Coating Synthesis and Properties	14
4.2 Exposure of Coatings to Chemical Stimuli	24
4.3 Selective Removal of Topcoats from Primer.....	26
5. CONCLUSION AND IMPLICATIONS FOR FUTURE RESEARCH.....	28
6. LITERATURE CITED.....	29
7. APPENDICIES.....	32
7.1 Appendix 1 – ATR-IR Spectra of Silyl-PU Coating PU6	32
7.2 Appendix 2 – ATR-IR Spectra of Silyl-PU Coating PU5	33
7.3 Appendix 3 – Removal of Silyl-PU Coating PU9 from Epoxy Primer with 1.0 M TBAF (Acetone)	34
7.4 Appendix 4 – Removal of Silyl-PU Coating PU10 from Epoxy Primer with 1.0 M TBAF (Acetone)	35

SCHEMES

Scheme 1 — Synthesis of 2,2'-(diphenylsilanediyl)bis(ethan-1-ol) (3) for use as silyl diol starting material.	6
Scheme 2 — Synthesis of diphenyl silyl diols with extended chains (4-7) and double extended chains (8-10) for use in Silyl-PU coatings.	6

FIGURES

Figure 1 — Removal of polyurethane topcoats on Navy aircraft using a) a methylene chloride based chemical stripper and b) hand-sanding with abrasive paper.	2
Figure 2 — Silyl-PU network (with silyl trigger shown in blue expansion box) and mechanism of disassembly via cascading bond cleavage within polymeric chains upon activation with fluoride ion.	3
Figure 3 — Complete disassembly of a clear Silyl-PU after 5 days immersion in static 1.0 M TBAF (THF) at room temperature. The network is outlined in red for visual indication.	4
Figure 4 — Synthesis of Silyl-PU networks (coatings) from an aliphatic isocyanate (HDI oligomer) and extended or double extended chain silyl diol. The silicon atom (i.e. trigger) in the silyl diols and coating network is highlighted in red.	15
Figure 5 — Appearance of Silyl-PU based on silyl diol crystallinity and miscibility with HDI oligomer(s) during cure.	16
Figure 6 — Thermal degradation profile of Silyl-PU (PU1-PU10) and polyurethane control (PU11) coatings.	18
Figure 7 — Glass transition temperature (T_g) of Silyl-PU (PU1-PU10) and polyurethane control (PU11) coatings.	19
Figure 8 — Percent elongation of Silyl-PU (PU1-PU10) and polyurethane control (PU11) coatings.	20
Figure 9 — Tensile strength of Silyl-PU (PU1-PU10) and polyurethane control (PU11) coatings.	20
Figure 10 — Visual of Silyl-PU coating flexibility: a) PU9 (left) and PU10 (right) after cylindrical mandrel bend, and b) PU9 (left) and PU10 (right) after GE Impact.	22
Figure 11 — Adhesion results of Silyl-PU coatings over non-chromate epoxy: a) PU9 after Cross-Cut (top) and X-Cut (bottom) tests, and b) PU10 after Cross-Cut (top) and X-Cut (bottom) tests.	23
Figure 12 — Color change of polyurethane coatings after 500 hours of Xenon-Arc WOM exposure.	24
Figure 13 — a) Photographs of PU8 over pretreated AA before (left) and after 15 minutes (right) of immersion at room temperature in static 1.0 M TBAF (THF), where the red dashed line indicates immersion height, and b) proposed mechanism of partial chain disassembly in PU8 upon reaction with fluoride ion.	25
Figure 14 — Photographs of polyurethane coatings over pretreated AA before and after immersion at room temperature in static 1.0 M TBAF (THF): a) PU9 before (left) and after 30 minutes (right), b) PU10 before (left) and after 30 minutes (right), and c) PU11 control before (left) and after 6 hours (right). The red dashed line indicates immersion height.	26
Figure 15 — Time-lapse photographs of polyurethane coatings (as topcoats) over non-chromate epoxy primer before and after immersion at room temperature in static 1.0 M TBAF (THF): a) PU9 before (left), after 10 minutes (center), and after 20 minutes (right), b) PU10 before (left), after 10 minutes (center), and after 20 minutes (right). The red dashed line indicates immersion height.	27
Figure 16 — ATR-IR spectra of non-chromate epoxy primer: non-coated control (top), after removal of Silyl-PU topcoat PU9 (middle), and after removal of Silyl-PU topcoat PU10 (bottom).	27
Figure 17 — Illustration of a gray topcoat on an F/A-18 aircraft being selectively removed with a fluoride salt composition and toothbrush rather than toxic methylene chloride. The yellow area represents intact hexavalent chromium containing epoxy primer after selective removal of the topcoat.	28

TABLES

Table 1 — Glass transition temperature (T_g) of Silyl-PU when unexposed and after exposure in various static chloride ion stimuli for 1 week at room temperature.	4
Table 2 — Formulation and appearance of Silyl-PU coatings.	16
Table 3 — Onset degradation temperature of Silyl-PU and polyurethane control coatings.	17
Table 4 — Surface hardness and performance property testing of Silyl-PU and polyurethane control coatings.	21
Table 5 — Time required for complete removal of Silyl-PU coatings from pretreated AA substrate upon immersion in 1.0 M TBAF (THF).	25

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ABSTRACT

The polyurethane topcoats used on the exterior of DoD aircraft and ground support equipment (GSE) are removed with hazardous chemical strippers, such as methylene chloride, abrasive materials, such as blast media and sand paper, or thermal ablation. However, all of these methods also damage the underlying non-metallic substrate (e.g. anti-corrosive epoxy primer, carbon fiber reinforced composite) upon removal of the topcoat. Furthermore, a chemical stripper that is environmentally friendly, can selectively remove the polyurethane topcoat with minimal applications, and will not damaging the underlying non-metallic substrate does not currently exist. Herein, we have successfully demonstrated, as a proof-of-concept, that stimuli-responsive silyl-containing polyurethane (Silyl-PU) coatings can provide similar thermal, mechanical, and performance properties (e.g. up to 60% GE Impact flexibility) as a MIL-PRF-85285 qualified polyurethane topcoat, yet also be selectively and completely removed (within 20 minutes) from a strongly adhered epoxy primer using an environmentally friendly fluoride salt solution under mild conditions at room temperature (figure A1). Removal of the topcoat did not affect the chemical structure of the epoxy primer according to infrared analysis. The Silyl-PU technology, as a topcoat on aircraft, could prevent exposure of hazardous materials (e.g. hexavalent chromium based epoxy primer) to workers and the environment by maintaining an intact primer upon selective removal of the topcoat, thereby reducing costs associated with hazardous waste disposal and reapplication of the primer.

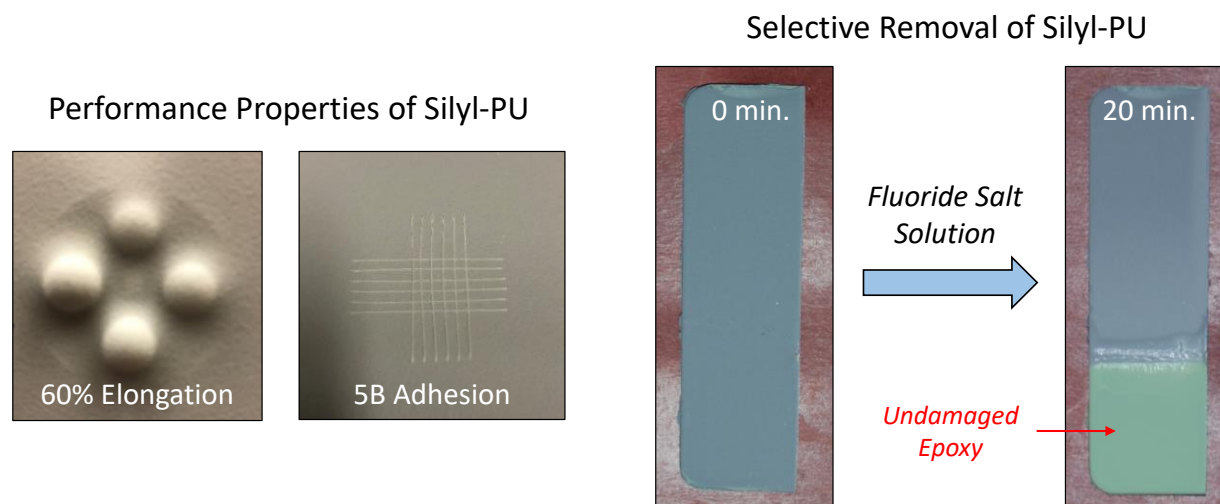


Fig. A1 — Example performance properties and selective removal (from epoxy primer) of low-gloss gray silyl-containing polyurethane (Silyl-PU) topcoat.

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LIMITED SCOPE FINAL REPORT: SELECTIVELY STRIPPABLE SILYL-CONTAINING AEROSPACE TOPCOATS USING ENVIRONMENTALLY FRIENDLY FLUORIDE SALTS (SERDP WP20-1106)

1. OBJECTIVE

The objective of this limited scope project was to develop novel stimuli-responsive silyl-containing polyurethane topcoats that possess similar properties (i.e. thermal, mechanical, weatherability) as current DoD aircraft topcoats, then demonstrate, as a proof-of-concept, that these topcoats can be selectively removed from a strongly adhered substrate (e.g. epoxy primer) using a mild and environmentally friendly fluoride salt solution. The fluoride salt solution should not damage or remove the underlying substrate, thereby demonstrating that the topcoat is selectively strippable. Furthermore, the fluoride salt should not alter the chemical structure or mechanical properties of the substrate upon removal of the topcoat.

2. BACKGROUND

The topcoats utilized on the exterior of Navy, Marine Corps, and Air Force aircraft (i.e. fixed and rotary wing) and ground support equipment (GSE) are two-component (2K) polyurethanes that are qualified to MIL-PRF-85285 performance requirements.[1] These topcoats are formed from the chemical reaction of hydroxyl- and isocyanate-functional molecules to generate highly crosslinked polymeric networks that contain carbamate (i.e. urethane) linkages. Formation of these crosslinked networks result in durable coatings with excellent hydrocarbon resistance, mechanical and thermal properties, and resistance to ultraviolet (UV) degradation from sunlight. However, the network of covalent bonds and tangled polymeric chains in polyurethanes cannot be easily degraded, and hence the coating cannot be easily removed from an asset, without using toxic and/or harsh chemicals, abrasive materials, or thermal treatments.

Polyurethane topcoats used on the exterior of DoD aircraft are chemically stripped with formulas that generate large quantities of hazardous waste, release significant amounts of hazardous air pollutants (HAPs) and/or volatile organic compounds (VOCs) into the air, and contaminate water due to washing the aircraft after applications.[2a,b] Methylene chloride strippers are the most effective and least expensive method of chemically removing coatings because they rapidly swell, soften, and delaminate the crosslinked polymeric networks (figure 1a).[3] However, methylene chloride is extremely hazardous, resulting in numerous health issues upon inhalation or dermal exposure. These issues include mental confusion, lightheadedness, nausea, vomiting, damage to the heart and liver, cancer, and even death due to asphyxiation.[4a,b] As a result, in 1997 the Occupational Safety and Health Administration (OSHA) reduced the permissible exposure limit (PEL) of methylene chloride to 12.5 ppm in an 8-hour workday. Furthermore, in March of 2019 the Environmental Protection Agency (EPA) banned the sale of methylene chloride paint removers to consumers, although they continued to allow its use in commercial applications for the foreseeable future.[5a-c]

Commercial alternatives to methylene chloride include N-methyl-pyrrolidone (NMP), benzyl alcohol, and benzyl alcohol blends with hydrogen peroxide or formic acid.[6a-e] Formic acid and NMP are both considered hazardous and their industrial use is regulated. Benzyl alcohol is less hazardous than methylene chloride, NMP, and formic acid, yet is slower acting and requires multiple applications to fully remove coatings from an aircraft, thus generating greater quantities of hazardous waste, increasing water consumption and contamination, reducing operational readiness, and increasing maintenance costs to the DoD. Furthermore, none of these chemical strippers can selectively remove the topcoat from non-metallic substrates (e.g. anti-corrosive epoxy primer, carbon fiber reinforced composite) or sealants because they

will damage said materials, and acidic strippers are prohibited for use on aircraft because they have shown to cause embrittlement of high-strength steel and corrode magnesium.



Figure 1 — Removal of polyurethane topcoats on Navy aircraft using a) a methylene chloride based chemical stripper and b) hand-sanding with abrasive paper.

Paint companies have proposed using an intermediate coating over primers and composites so that neutral benzyl alcohol could be used to selectively strip the topcoat.[7] However, this would add another coating to the system, would not eliminate the use of benzyl alcohol, would increase the number of stripper applications, increase the amount of contaminated water, and increase costs to the DoD due to labor and materials. Furthermore, any cracks in the intermediate coating would result in damage to the underlying substrate. Unfortunately, a chemical stripper that is environmentally friendly, can selectively remove the polyurethane topcoat with minimal applications, and will not damage the underlying non-metallic substrate does not currently exist.

Abrasive media and thermal ablation are alternative methods of removing polyurethane topcoats, yet each have their issues. Paint stripping via plastic blast media (PMB) requires special environmental containment, generates hazardous airborne particles, and removes both the topcoat and primer. In addition, this process is prohibited from use on aircraft with thin and sensitive substrates. Hand-sanding is less damaging to substrates, but is extremely time-consuming, labor-intensive, and still generates hazardous airborne particles. Currently, the polyurethane topcoat on the MV-22 Osprey is removed via hand-sanding in effort to minimize damage to the underlying copper mesh infused polymeric composite (figure 1b), although damage due to improper sanding techniques has resulted in expensive and time-intensive repairs. Thermal ablation via lasers generates minimal waste and has proven to be an efficient method for the de-painting of Air Force aircraft.[8-11] However, lasers are expensive and must be properly maintained, they require highly-trained individuals or articulating robotic arms, and coatings on complex geometries (e.g. fasteners, areas adjoining wings and fuselage) can be difficult to remove, thereby impacting painting operations. Furthermore, the effects of laser de-painting on the underlying metal alloys and composites have not been fully characterized and the risk exists for potentially damaging base substrates due to localized heating, which could negatively affect the structural integrity of an aircraft. Aside from costs, the latter remains the biggest concern for implementing lasers to remove coatings on Navy aircraft.

The polyurethane topcoats used on the exterior of DoD aircraft and GSE were not designed to be selectively stripped, and there are zero examples in the literature that describe a crosslinked polymeric coating being selectively degraded and removed from a strongly adhered substrate using a mild chemical treatment at room temperature. For several decades, academic research has focused on designing crosslinked networks that possess labile bonds and linkages to facilitate chemical degradation.[12] For example, olefinic bonds

in epoxy-amine networks were cleaved with potassium permanganate in acetic acid, tertiary carbamate groups in epoxy-amine networks were cleaved with heated solutions of mineral acids, and poly(hexahydrotriazine) (PHT) networks that were formed from aromatic diamines and paraformaldehyde under thermal conditions were disassembled by reversing to the diamines in a strong solution of sulfuric acid.[13-15] However, in all of these examples, highly acidic (i.e. $\text{pH} < 2$) solutions, and often elevated temperatures, were required to initiate bond cleavages, the cleavages were localized and primarily single bonds, and degradation was uncontrollable. Furthermore, none of these technologies are feasible for use as aircraft topcoats because they lack the structure and properties (e.g. flexibility, weatherability) required for high-performance coatings.

To address these limitations, researchers at the U.S. Naval Research Laboratory (NRL) developed novel stimuli-responsive crosslinked networks that can degrade on-demand when treated with a selective chemical stimulus under mild conditions at room temperature.[16-18] These materials, called silyl-containing polyurethanes (Silyl-PUs) (figure 2), were formed from the reaction between aliphatic isocyanates and silyl-centered diols or triols. The networks are highly cross-linked, tough, and possessed good thermal and hydrolytic stability. The silyl linkages within these networks are activated (i.e. triggered) with mild and environmentally friendly fluoride salts to initiate a cascade of bond breakages that enables the networks to rapidly disassemble, in multiple directions, and into several small molecules (figure 2). The time of Silyl-PU disassembly is based on the electrophilicity of the silicon atom and the number of cascable bonds in the appendages of the silyl diol or triol,[19] in addition to the cross-link density and glass transition temperature (T_g) of the network.

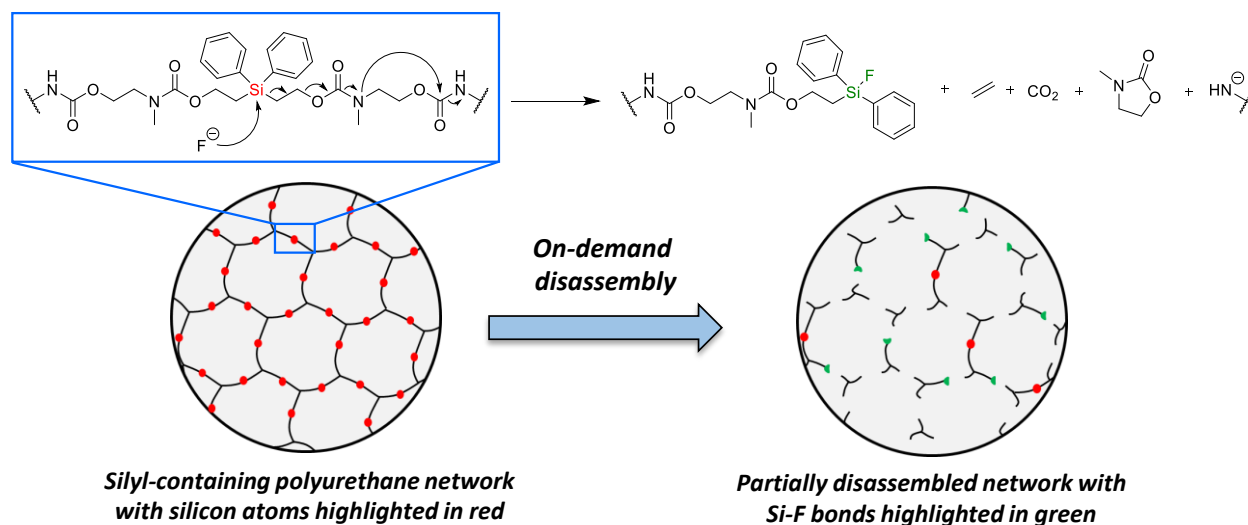


Figure 2 — Silyl-PU network (with silyl trigger shown in blue expansion box) and mechanism of disassembly via cascading bond cleavage within polymeric chains upon activation with fluoride ion.

A Silyl-PU network with a glass transition temperature (T_g) of 51.6 °C and thickness of about 2 mm demonstrated complete disassembly in less than 5 days when immersed in a static (i.e. non-stirred) solution of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) at room temperature (figure 3), whereas complete disassembly occurred in less than 24 hours under dynamic (i.e. stirred) conditions. Silyl-PUs immersed solely in THF did not disassemble. These networks were also resistant to disassembly in aqueous fluoride, strong acid, and strong base solutions, which demonstrates their hydrolytic stability and robustness compared to other degradable crosslinked networks in the literature. Furthermore, these networks were resistant to disassembly when exposed to a chloride ion stimulus, such as tetrabutylammonium chloride (TBACl) in THF (Table 1), thus demonstrating their potential for applications in the marine environment.

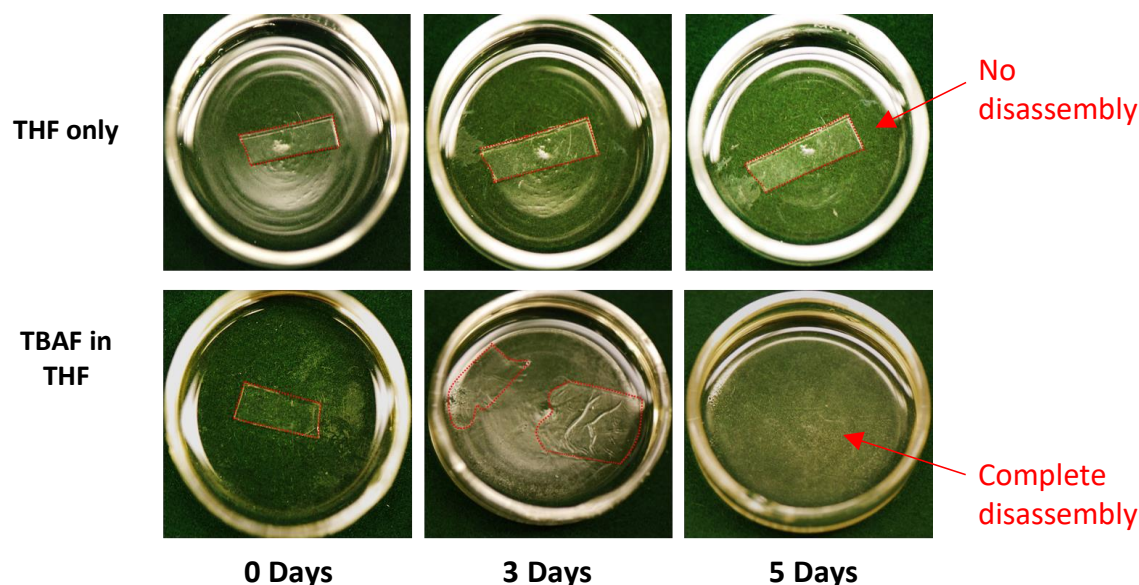


Figure 3 — Complete disassembly of a clear Silyl-PU after 5 days immersion in static 1.0 M TBAF (THF) at room temperature. The network is outlined in red for visual indication.

Table 1 — Glass transition temperature (T_g) of Silyl-PU when unexposed and after exposure in various static chloride ion stimuli for 1 week at room temperature.

Chloride Ion Stimulus	Unexposed T_g (°C)	T_g after 1 week of exposure (°C)
1.0 M TBACl (THF)	51.6	51.3
1.0 M HCl (aq.)	51.6	49.1

Mixtures of flexible aliphatic isocyanates and silyl-centered diols resulted in the formation of Silyl-PU with reduced crosslink density and T_g s ranging from 35-43 °C. These networks were observed to completely disassemble within 24 hours of immersion in a static solution of 1.0 M TBAF (THF) at room temperature, compared to 5 days for the network in Figure 3. However, these Silyl-PU still possessed T_g values far above the range of 18-25 °C, which is common for MIL-PRF-85285 qualified polyurethane aircraft topcoats, they lacked the necessary mechanical properties (e.g. elongation, tensile strength) for a topcoat, and the silyl-centered diols were incompatible with the aliphatic isocyanates without incorporating solvent and elevated temperatures to facilitate network formation. Furthermore, these Silyl-PU were not doped with solid particles to form a pigmented and/or filled coating, nor were they fabricated into 50-75 micron thick coatings via spray application or film forming bar.

Herein, we discuss the synthesis of novel extended and double extended chain silyl diols for use in clear and pigmented Silyl-PU coatings. The thermal, mechanical, and performance properties of these coatings were then determined, including their degree of disassembly and removal from substrates (e.g. pretreated aluminum, epoxy primer) when exposed to different solutions of chemical stimuli at room temperature. All results were compared to a MIL-PRF-85285 qualified polyurethane topcoat that is currently used on Navy and Air Force aircraft.

3. MATERIALS AND METHODS

Pentane-1,5-diol, *N,N'*-disuccinimidyl carbonate (DSC), pyridinium *para*-toluenesulfonate (PPTS), dimethylaminopyridine (DMAP), 2-((tert-butyldimethylsilyl)oxy)ethanol, 5-((tert-butyldimethylsilyl)oxypentanol), ethylene glycol, *N*-methylethanolamine, triethylamine (TEA), 0.5 M 9-borabicyclo[3.3.1]nonane (9-BBN) solution in tetrahydrofuran (THF), sodium hydroxide, hydrogen peroxide solution (30 Wt.% in water), butyl acetate, dibutyltin dilaurate, and 1.0 M vinyl magnesium bromide solution in THF were purchased from Sigma-Aldrich. Diphenyldichlorosilane was purchased from Gelest. The aliphatic isocyanates, which are oligomers of 1,6-hexamethylene diisocyanate, were purchased from Covestro. Titanium dioxide (TiO₂) pigment was purchased from Chemours as R-960 grade, whereas carbon black pigment was purchased from Birla Carbon as Raven 14. Micronized polypropylene powder, which was used as a filler, was purchased from Micro Powders. Deuterated solvents, such as DMSO-*d*₆ and Chloroform-*d*, were purchased from Sigma-Aldrich. All chemicals were utilized as received unless noted otherwise. Anhydrous THF was dried under molecular sieves for 24 hours.

Thin layer chromatography (TLC) was performed on EMD silica gel 60 F254 plates from Sigma-Aldrich, while column chromatography was performed using flash grade silica gel (SiO₂, 32-63μm) from Sigma-Aldrich. Thin layer chromatography (TLC) was used in conjunction with column chromatography to purify all synthesized molecules. 3x6x0.020-inch aluminum alloy panels were purchased from Q-Lab, followed by chromic acid anodization by Almag Plating Corporation. 3x6x0.010-inch tinplated steel panels were purchased from Q-Lab. Poly(vinylfluoride) (PVF) release paper was purchased from DuPont as Tedlar® TMR20SM3. The MIL-PRF-23377, Type I, Class N (non-chromate) epoxy primer was purchased from Deft / PPG Industries as 02GN084.[20] A MIL-PRF-85285, Type IV qualified camouflage gray polyurethane topcoat was used as the control coating.[1]

NMR spectra were performed on a Bruker 400 MHz NMR spectrometer and worked-up using Topspin. ¹³C NMR were recorded at 100 MHz. *J* coupling values are represented in Hz. NMR data is reported as follows: chemical shift (δ), multiplicity (bs = broad singlet, bt = broad triplet, singlet = singlet, d = doublet, t = triplet, q = quartet), coupling constant(s) in Hz, and integration. High resolution mass spectrometry (HRMS) was performed on a PerkinElmer AXION 2 time of flight (TOF) with direct sample analysis (DSA) source in positive mode.

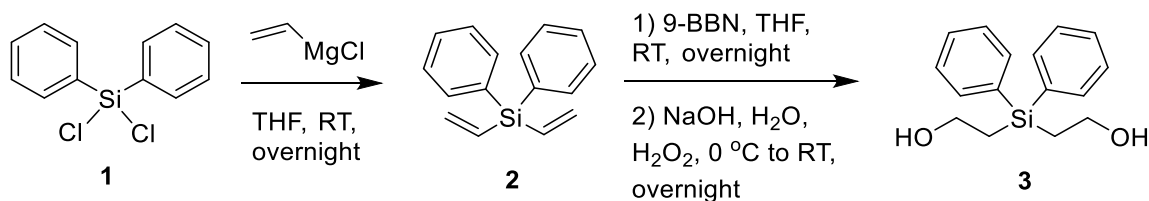
Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy was performed on a Nicolet iS50-FT-IR with iS50 ATR attachment equipped and a diamond ATR crystal from Thermo Scientific with 64 scans compiled for each spectrum. Spectra were recorded from 4000 – 500 cm⁻¹ with a resolution of 2 cm⁻¹, and were analyzed using the Nicolet OMNIC software suite.

Thermal analysis was performed on TA Instruments Discovery Differential Scanning Calorimeter (DSC) to determine glass transition temperature (*T*_g). Two successive ramps were performed from -50 °C to 170 °C at a rate of 10°C/min., from which measurements were made on the second run. Samples were run in triplicate and standard deviation was obtained for each set. Thermogravimetric analysis (TGA) was performed on a TA Instruments Discovery TGA at a heating rate of 10°C/min. under N₂ from room temperature to 700 °C. Degradation onset temperature was assigned at the temperature at which 90% mass remained. TA Instruments Trios software was used to analyze DSC and TGA data.

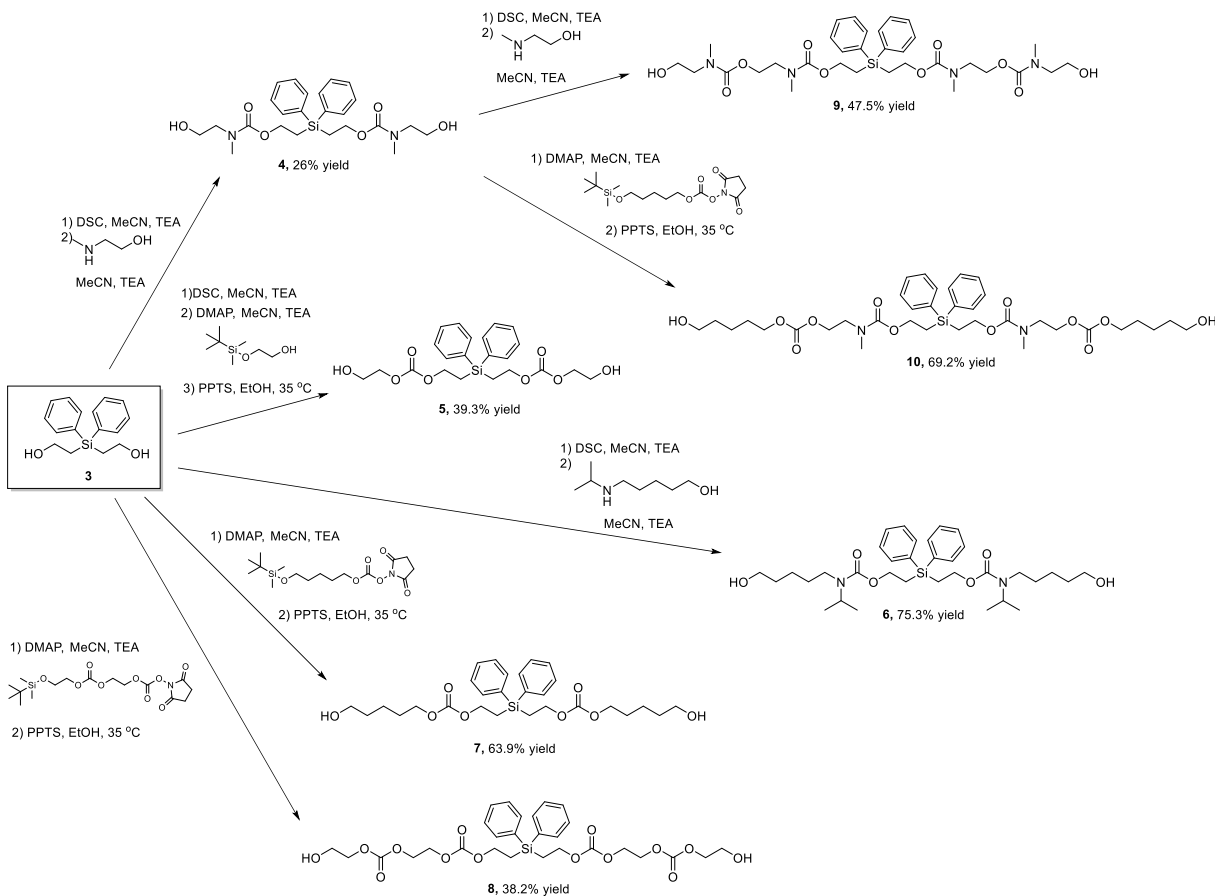
Tensile testing was performed on a Texture Technologies TA.XT Plus Texture Analyzer to determine Young's modulus, ultimate tensile strength at break, and percent elongation at break. Samples were run at 10 mm per minute and had an area of 2.8 cm². All samples were performed in at least triplicate to obtain standard deviation.

Immersion experiments in solutions of chemical stimuli at room temperature were conducted using small pieces (i.e. dimensions of approximately 7.2 cm length by approximately 1.5 cm width) of the coatings over treated and/or epoxy-primed aluminum alloy panels.

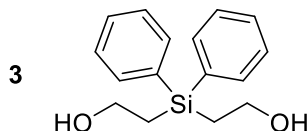
3.1 Synthetic Schemes and Procedures for Synthesis of Diphenyl Silyl Diols



Scheme 1 — Synthesis of 2,2'-(diphenylsilanediyl)bis(ethan-1-ol) (3) for use as silyl diol starting material.



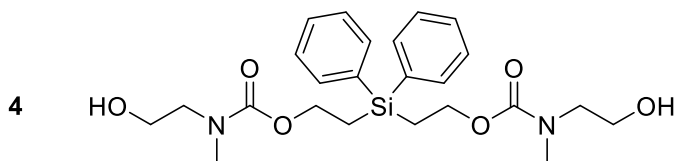
Scheme 2 — Synthesis of diphenyl silyl diols with extended chains (4-7) and double extended chains (8-10) for use in Silyl-PU coatings.



2,2'-(Diphenylsilanediyl)bis(ethan-1-ol) (3):

Diphenyldichlorosilane (**1**) (1.9 mL, 9.1 mmol) was added to 1.0 M vinylmagnesium bromide solution in THF (20 mL, 20 mmol) at 0° C. After 10 min. the cooling bath was removed and the mixture was stirred at room temperature for 15 hours. Aqueous ammonium chloride (30 mL) was added, followed by water, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (100 mL). The combined organics were dried with MgSO₄ and concentrated to give a yellow oil. The resulting mixture was purified using column chromatography (100% hexane) to furnish diphenyldivinylsilane (**2**) (1.97 g) as an oil in 92% yield. ¹H NMR (300 MHz, CDCl₃, Me₄Si, 25 °C): δ = 7.55 ppm (m, 4H), 7.39 (m, 6H), 6.55, 6.48, 6.31, 6.26, 5.85, 5.79. ¹³C NMR (75 MHz, CDCl₃, Me₄Si): δ = 136.61, 135.71, 134.46, 134.07, 129.62, 128.05. HRMS (EI) *m/z*: [M]⁺ calcd for C₁₆H₁₆Si, 236.1216; found 236.1008. This compound has been previously reported.[16]

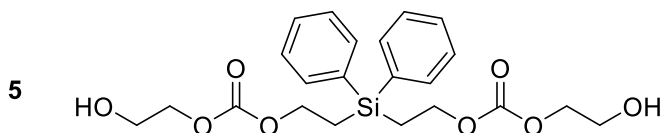
A solution of diphenyldivinylsilane (**2**) (2.2 g, 9.4 mmol) in 15 mL of THF was added dropwise to a 0.5 M solution of 9-BBN in THF (47.2 mL, 23.6 mmol) and the resulting mixture was stirred at room temperature for 4 hours, followed by the addition of water (30 mL) and 3.0 M aqueous sodium hydroxide solution (30 mL). Subsequently, aqueous hydrogen peroxide solution (30 Wt.%, 30 mL) was added dropwise at 0 °C within 15 minutes and the reaction mixture was heated to reflux for 3 hours. Upon cooling to room temperature, the aqueous layer was saturated with potassium carbonate, the organic layer was removed and the aqueous layer was extracted with ethyl acetate (100 mL). The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture was purified using column chromatography (100% ethyl acetate) to furnish silyl diol **3** (1.4 g) as a clear crystal in 83% yield. ¹H NMR (300 MHz, CDCl₃, Me₄Si, 25 °C): δ = 8.15 ppm (m, 4H), 7.24 (m, 6H), 4.29 (t, *J* = 7.6 Hz, 4H), 1.12 (t, *J* = 7.6 Hz, 4H). ¹³C NMR (75 MHz, CDCl₃, Me₄Si): δ = 155.54, 152.44, 145.39, 125.30, 121.82, 67.35, 16.15. HRMS (EIC) *m/z*: [M + Na]⁺ calcd for C₁₆H₂₀O₂SiNa, 295.1125; found 295.1125. This compound has been previously reported.[16]



(Diphenylsilanediyl)bis(ethane-2,1-diyl) bis((2-hydroxyethyl)(methyl)carbamate) (4):

Triethylamine (1.02 mL, 7.34 mmol) was added to 2,2'-(diphenylsilanediyl)bis(ethan-1-ol) (0.52 mg, 1.83 mmol) in 100 mL acetonitrile, followed by *N,N'*-disuccinimidyl carbonate (0.9 g, 3.67 mmol). The reaction was stirred at room temperature for overnight. The reaction was concentrated and extracted using ethyl acetate (100 mL) and saturated sodium bicarbonate (50 mL). The organic layer was concentrated after dried over magnesium sulfate. The resulting mixture produced a precipitate and was filtered with ethyl acetate to furnish Bis(2,5-dioxopyrrolidin-1-yl) ((diphenylsilanediyl)bis(ethane-2,1-diyl)) bis(carbonate) (0.4 g) as a white powder in 40% yield. ¹H NMR (300 MHz, DMSO-*d*₆, Me₄Si): δ = 7.43 ppm (m, 4H), 7.31 (m, 6H), 4.28 (t, *J* = 8.6 Hz), 2.66 (s, 8H), 1.69 (t, *J* = 8.6 Hz). ¹³C NMR (75 MHz, DMSO-*d*₆, Me₄Si): δ = 170.39, 151.60, 134.57, 133.22, 130.52, 128.77, 69.82, 25.81, 13.54. The parent ion could not be obtained via HRMS analysis.

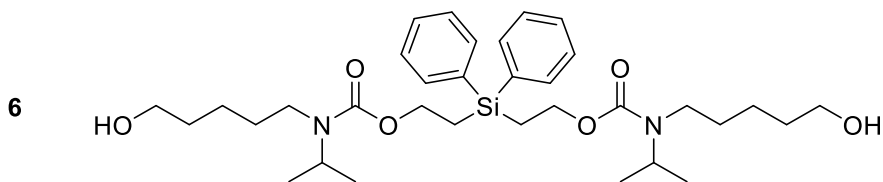
A solution of N-methylethanolamine (2.0 mL, 31.4 mmol) and triethylamine (4.1 mL, 29.4 mmol) was prepared in acetonitrile (60 mL). Bis(2,5-dioxopyrrolidin-1-yl) ((diphenylsilanediyl)bis(ethane-2,1-diyl)) bis(carbonate) (6.5 g, 11.7 mmol) was then added to the solution and was stirred overnight at room temperature. The reaction mixture was concentrated, dissolved in dichloromethane, and washed with sodium bicarbonate, 3.0 M sodium hydroxide, and brine. The organic layer dried over magnesium sulfate and concentrated under reduced pressure. The resulting mixture was purified using column chromatography (95:5 dichloromethane:methanol) to furnish silyl diol **4** (2.8 g) as a clear liquid in 51% yield. ^1H NMR (300 MHz, CDCl_3 , Me_4Si , 25 °C): δ = 7.37 ppm (m, 4H), 7.21 (m, 6H), 4.07 (t, J = 8.3 Hz, 4H), 3.51 (bt, 2H), 3.44 (bt, 2H), 3.40 (bs, 2H), 3.18 (bt, 2H), 3.07 (bt, 2H), 2.74 (s, 3H), 2.62 (s, 3H), 1.48 (t, J = 8.3 Hz, 4H). ^1H NMR (300 MHz, DMSO-d_6 , Me_4Si , 70 °C): δ = 7.41 (m, 4H), 7.28 (m, 6H), 4.23 (s, 2H), 3.98 (t, J = 8.3 Hz), 3.34 (bt, 4H), 3.05 (bt, 4H), 2.65 (s, 6H), 1.48 (t, J = 8.3 Hz). ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si , 25 °C): δ = 157.43, 156.77, 134.64, 134.03, 62.89, 60.34, 51.45, 50.71, 35.43, 34.94, 25.37, 14.33. ^{13}C NMR (75 MHz, DMSO-d_6 , Me_4Si , 70 °C): δ = 155.32, 134.01, 133.94, 129.09, 127.57, 61.48, 58.63, 50.40, 34.31, 13.57. HRMS (EIC) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_6\text{Si}$, 497.2084; found 497.2086.



(Diphenylsilanediyl)bis(ethane-2,1-diyl) bis(2-hydroxyethyl) bis(carbonate) (5):

2-((tert-butyldimethylsilyl)oxy)ethan-1-ol (17.6 mL, 90.0 mmol) and bis(2,5-dioxopyrrolidin-1-yl) ((diphenylsilanediyl)bis(ethane-2,1-diyl)) bis(carbonate) (15.06 g, 30.0 mmol) were added to a 1-L round bottom flask containing 400 mL acetonitrile and a stir bar. Triethylamine (16.7 mL, 120.0 mmol) was then added to the round bottom flask, followed by 4-dimethylaminopyridine (3.60 g, 30.0 mmol). The reaction was stirred for 48 hours at 40 °C. The reaction mixture was concentrated *in vacuo* to afford a yellow oil. The oil was dissolved in CH_2Cl_2 (100 mL) and washed with 1.0 M NH_4Cl (aq) (3 X 100 mL). The organic layer was isolated and concentrated *in vacuo* to afford Bis(2-((tert-butyldimethylsilyl)oxy)ethyl) ((diphenylsilanediyl)bis(ethane-2,1-diyl)) bis(carbonate) as a yellow oil (15.3 g, 75.3 % yield). ^1H NMR (400 MHz, DMSO , 25 °C): δ = 7.57-7.54 (m, 4H, *ortho*), 7.45-7.39 (m, 6H, *meta* & *para*), 4.28 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{Si}-$), 4.18 (t, 4H, J = 5.2 Hz, $-\text{SiOCH}_2\text{CH}_2\text{O}-$), 3.83 (t, 4H, J = 5.2 Hz, $-\text{SiOCH}_2\text{CH}_2\text{O}-$), 1.172 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{Si}-$), 0.93 (s, 18H, $(\text{CH}_3)_3\text{C}(\text{CH}_2)\text{Si}-$), 0.10 (s, 12H, $(\text{CH}_3)_3\text{C}(\text{CH}_2)\text{Si}-$); ^{13}C NMR (100 MHz, DMSO , 25 °C): δ = 154.98, 134.78, 133.96, 130.29, 128.60, 81.31, 65.38, 61.29, 26.13, 18.33, 13.74, -4.96. Parent ion could not be found.

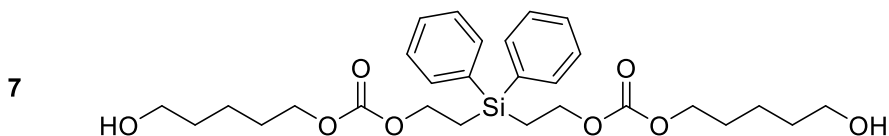
Pyridinium para-toluenesulfonate (2.26 g, 9.0 mmol) was added to a 500-mL round bottom flask containing 300 mL ethanol and a stir bar. Bis(2-((tert-butyldimethylsilyl)oxy)ethyl) ((diphenylsilanediyl)bis(ethane-2,1-diyl)) bis(carbonate) (15.3 g, 22.6 mmol) was then added to the flask with a stir bar. The solution was stirred for 72 hours at 35 °C. The reaction mixture was concentrated *in vacuo* to afford a colorless, clear oil. The oil was dissolved in CHCl_3 (100 mL) and washed with water (3 X 50 mL). The organic layer was isolated and concentrated under reduced pressure to afford a clear oil. Purification by column chromatography (95:5 CH_2Cl_3 : CH_3OH) afforded silyl diol **5** as a clear, colorless oil (3.99 g, 39.3 % yield). ^1H NMR (400 MHz, DMSO , 25 °C): δ = 7.55-7.39 (m, 10H, aromatic), 4.85 (t, J = 5.6 Hz, 2H, $\text{HOCH}_2\text{CH}_2\text{O}-$), 4.17 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{Si}-$), 4.02 (t, J = 5.2 Hz, 4H, $\text{HOCH}_2\text{CH}_2\text{O}-$), 3.56-3.52 (q, J = 5.2 Hz, 4H, $\text{HOCH}_2\text{CH}_2\text{O}-$), 1.68 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{Si}-$); ^{13}C NMR (100 MHz, DMSO , 25 °C): δ = 155.06, 134.84, 133.99, 130.32, 128.65, 69.56, 65.34, 59.32, 13.73. HR-MS (MALDI) m/z : $[\text{M} + \text{MeOH} + \text{H}]$ calcd for $\text{C}_{22}\text{H}_{28}\text{O}_8\text{Si}$: 503.5607; found 544.0926.



(Diphenylsilanediyl)bis(ethane-2,1-diyl) bis((5-hydroxypentyl)(isopropyl)carbamate) (6):

5-Aminopentanol (15.1 g, 146.0 mmol) was added to a 1-L round bottom flask containing 350 mL of dry acetone. Molecular sieves 4 Å (16.0 g) were added to the flask. The solution was stirred for 24 hours at room temperature. The reaction mixture was concentrated *in vacuo* to afford a clear oil. The oil was dissolved in dry ethanol (500 mL). Sodium borohydride (5.62 g, 0.1485) was slowly added to the flask at 0 °C. The reaction was stirred for 24 hours. The reaction was quenched by adding in CH₃OH (50 mL). The mixture was concentrated *in vacuo* to afford a clear, colorless oil. The colorless oil was dissolved in CHCl₃ (100 mL) and rinsed with water (3 X 50 mL). The organic layer was isolated and solvent removed under reduced pressure to afford 5-(isopropylamino)pentanol as a clear, colorless oil (14.84 grams, 70.0% yield). The product crystallized after sitting at room temperature in the flask for 1 hour. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 3.51 (t, 2H, J= 6.4 Hz, HOCH₂CH₂-), 2.71 (h, 1H, J= 6.4 Hz, -NCH(CH₃)₂), 2.52 (t, 2H, J=7.2 Hz, -NCH₂CH₂-), 1.54-1.38 (overlapped m, 4H, HOCH₂CH₂CH₂CH₂CH₂N- & HOCH₂CH₂CH₂CH₂CH₂N-), 1.33 (m, 2 H, HOCH₂CH₂CH₂CH₂CH₂N-), 0.99 (d, 6H, J= 6.4 Hz, -NCH(CH₃)₂); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 61.73, 48.69, 47.27, 32.50, 29.84, 23.59, 22.73. Parent ion could not be found. This compound has previously been synthesized

Bis(2,5-dioxopyrrolidin-1-yl) ((diphenylsilanediyl)bis(ethane-2,1-diyl)) bis(carbonate) (15.00 g, 27.1 mmol) was added to a 500-mL round bottom flask containing acetonitrile (300 mL) and a stir bar. 5-(Isopropylamino)pentan-1-ol (9.44 g, 65.0 mmol) and triethylamine (3.76 mL, 26.9 mmol) were added to the flask. The solution was stirred for 24 h at room temperature. The reaction mixture was concentrated *in vacuo* to afford a yellow oil. The oil was dissolved in CHCl₃ (150 mL) and washed with water (3 X 100 mL). The organic layer was isolated and solvent removed under reduced pressure to afford silyl diol **6** as a light-yellow oil (12.55 g, 75.3 % yield). ¹H NMR (400 MHz, DMSO, 25 °C): δ = 7.53-7.52 (m, 4H, *ortho*), 7.43-7.38 (m, 6H, *meta* & *para*), 4.37 (broad t, 2H, , HOCH₂CH₂CH₂CH₂CH₂N-), 4.06 (t, 4H, J=8.0 Hz, -OCH₂CH₂Si-), 4.02 (m, 2H, -NCH(CH₃)₂), 2.93 (m, 4H, -NCH₂CH₂-), 1.59 (t, 4H, J= 8.0 Hz, -OCH₂CH₂Si-), 1.46-1.33 (overlapped m, 8H, HOCH₂CH₂CH₂CH₂CH₂N- & HOCH₂CH₂CH₂CH₂CH₂N-), 1.22 (m, 4H, HOCH₂CH₂CH₂CH₂CH₂N-), 1.03 (broad m, 12H, -NCH(CH₃)₂); ¹³C NMR (100 MHz, DMSO, 25 °C): δ = 155.54, 134.83, 134.70, 130.10, 128.55, 79.66, 62.22, 61.14, 42.71, 32.82, 29.83, 23.56, 20.92, 14.03. HR-MS (ESI) *m/z*: [M+H] calcd for C₃₄H₅₄N₂O₆Si: 615.3878; found 615.3000.



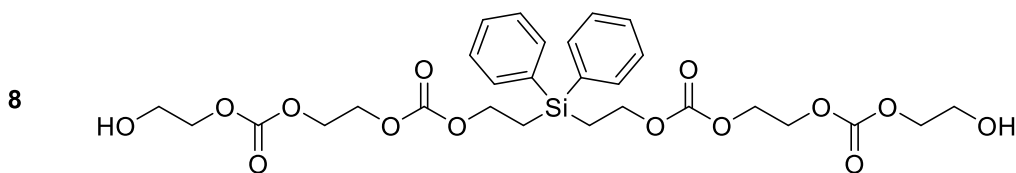
(Diphenylsilanediyl)bis(ethane-2,1-diyl) bis(5-hydroxypentyl) bis(carbonate) (7):

Disuccinimidyl carbonate (26.7 g, 104.0 mmol) and triethylamine (9.7 mL, 69.6 mmol) were added to a 250-mL round bottom flask containing CHCl₃ (175 mL) and a stir bar. 5-((tert-butyl)dimethylsilyl)oxy)pentan-1-ol (17.2 mL, 69.6 mmol) was then added to the flask and stirred for 16 hours at room temperature. The reaction mixture was washed with water (3 X 50 mL) to afford 5-((tert-butyl)dimethylsilyl)oxypentyl (2,5-dioxopyrrolidin-1-yl) carbonate as an orange oil (21.4 g, 85.0% yield).

^1H NMR (400 MHz, DMSO, 25 °C): δ = 4.34 (t, J = 6.4 Hz, 2H, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 3.59 (t, 2H, J = 6.4 Hz, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 2.81 (s, 4H, $-(\text{C}=\text{O})\text{CH}_2\text{CH}_2(\text{C}=\text{O})-$), 1.69 (m, 2H, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.49 (m, 2H, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.38 (m, 2H, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$) 0.86 (s, 9H, $(\text{CH}_3)_3\text{C}(\text{CH}_2)\text{Si}-$), 0.03 (s, 6H, $(\text{CH}_3)_3\text{C}(\text{CH}_2)\text{Si}-$); ^{13}C NMR (100 MHz, DMSO, 25 °C): δ = 170.28, 151.77, 79.62, 71.74, 62.69, 32.12, 28.07, 26.26, 25.80, 21.82, 18.38, -4.91. Parent ion could not be found.

2,2'-(diphenylsilanediyl)bis(ethan-1-ol) (11.05 g, 41.0 mmol) and 5-((tert-Butyldimethylsilyl)oxy)pentyl (2,5-dioxopyrrolidin-1-yl) carbonate (35 g, 97.4 mmol) were added to a 250-mL round bottom flask containing dry acetonitrile (150 mL) and a stir bar. Triethylamine (5.6 mL, 41.0 mmol) was added to the flask followed by 4-dimethylaminopyridine (1.50 g, 12.2 mmol). The reaction was stirred for 72 hours at 40 °C. The reaction mixture was concentrated *in vacuo* to afford a yellow oil. The oil was dissolved in chloroform (100 mL) and washed with water (3 X 50 mL). The organic layer was concentrated *in vacuo* to afford a yellow oil. Purification by column chromatography (95:5 CH_2Cl_2 : CH_3OH) afforded Bis(5-((tert-butyl dimethylsilyl)oxy)pentyl)((diphenylsilanediyl)bis(ethane-2,1-diyl)) bis(carbonate) as a clear, colorless oil (17.23 grams, 55.8% yield). ^1H NMR (400 MHz, DMSO, 25 °C): δ = 7.53-7.51 (m, 4H, *ortho*), 7.43-7.38 (m, 6H, *meta* & *para*), 4.15 (t, 4H, J =8.0 Hz, $-\text{OCH}_2\text{CH}_2\text{Si}-$), 3.99 (t, 4H, J =6.4 Hz, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 3.56 (t, 4H, J = 6.4 Hz $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.65 (t, 4H, J =8.0 Hz, $-\text{OCH}_2\text{CH}_2\text{Si}-$), 1.56 (m, 4H, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.45 (m, 4H, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.32 (m, 4H, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 0.85 (s, 18H, $(\text{CH}_3)_3\text{C}(\text{CH}_2)\text{Si}-$), 0.01 (s, 12H, $(\text{CH}_3)_3\text{C}(\text{CH}_2)\text{Si}-$); ^{13}C NMR (100 MHz, DMSO, 25 °C): δ = 154.95, 134.79, 134.09, 130.24, 128.59, 67.75, 65.22, 62.72, 32.24, 28.35, 26.25, 22.06, 18.37, 13.72, -4.88. HR-MS (MALDI) m/z : $[\text{M}+\text{Na}]$ calcd for $\text{C}_{40}\text{H}_{68}\text{O}_8\text{Si}_3$: 783.4114; found 783.4109.

Pyridinium para-toluenesulfonate (1.66 g, 6.6 mmol) was added to a 500-mL round bottom flask containing ethanol (220 mL) and a stir bar. Bis(5-((tert-butyl dimethylsilyl)oxy)pentyl)((diphenylsilanediyl)bis(ethane-2,1-diyl)) bis(carbonate) (16.73 g, 22.0 mmol) was then added to the flask with a stir bar. The solution was stirred for 48 h at 35 °C. The reaction mixture was concentrated *in vacuo* to afford a colorless, clear oil. The oil was dissolved in CHCl_3 (100 mL) and washed with water (3 X 50 mL). The organic layer was isolated and concentrated under reduced pressure to afford a clear oil. Purification by column chromatography (9:1 CH_2Cl_3 : CH_3OH) afforded silyl diol **7** as a clear, colorless oil (8.04 g, 63.9 % yield). ^1H NMR (400 MHz, DMSO, 25 °C): δ = 7.53-7.52 (m, 4H, *ortho*), 7.45-7.39 (m, 6H, *meta* & *para*), 4.39 (t, 2H, J = 5.2 Hz, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 4.15 (t, 4H, J =8.0 Hz, $-\text{OCH}_2\text{CH}_2\text{Si}-$), 3.99 (t, 4H, J =6.4 Hz, $-\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 3.37 (overlapped m, 4H $-\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.66 (t, 4H, J =8.0 Hz, $-\text{OCH}_2\text{CH}_2\text{Si}-$), 1.55 (m, 4H, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.41 (m, 4H, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 1.31 (m, 4H, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$); ^{13}C NMR (100 MHz, DMSO, 25 °C): δ = 154.99, 134.82, 134.18, 130.31, 128.62, 67.83, 65.28, 60.96, 32.46, 28.48, 22.24, 13.71. HR-MS (MALDI) m/z : $[\text{M}+\text{Na}]$ calcd for $\text{C}_{28}\text{H}_{40}\text{O}_8\text{Si}$: 555.2384; found 555.2390.



Ethane-1,2-diyl (1-hydroxy-4,9-dioxo-13,13-diphenyl-3,5,8,10-tetraoxa-13-silapentadecan-15-yl) (2-hydroxyethyl) bis(carbonate) (8):

N,N'-Disuccinimidyl carbonate (8.2 g, 32.0 mmol) and triethylamine (3.0 mL, 21.0 mmol) were added to a 100-mL round bottom flask containing CHCl_3 (50 mL) and a stir bar 2-((tert-butyl dimethylsilyl)oxy)ethan-

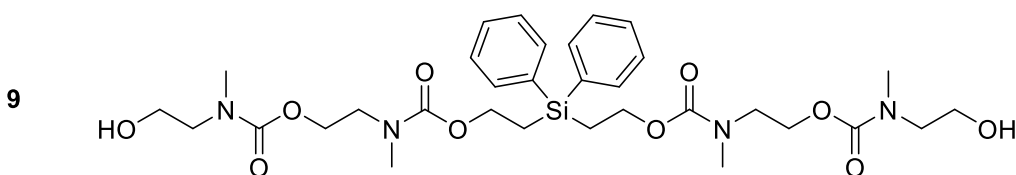
1-ol (4.1 mL, 21.0 mmol) was then added to the flask and stirred for 16 hours at room temperature. The reaction mixture was washed with water (3 X 50 mL) to afford 2-((tert-butyldimethylsilyl)oxy)ethyl (2,5-dioxopyrrolidin-1-yl) carbonate as an orange oil (6.43 g, 96.7% yield). The product begins to crystallize after one day sitting in the flask. ^1H NMR (400 MHz, DMSO, 25 °C): δ = 4.39 (t, J =4.2 Hz, 2H, -SiOCH₂CH₂O-), 3.86 (t, J =4.2 Hz, 2H, -SiOCH₂CH₂O-), 2.80 (s, 4H, -(C=O)CH₂CH₂(C=O)-), 0.87 (s, 9H, (CH₃)₃C(CH₂)Si-), 0.07 (s, 6H, (CH₃)₃C(CH₂)Si-); ^{13}C NMR (100 MHz, DMSO, 25 °C): δ = 170.27, 151.93, 72.82, 60.96, 26.20, 25.80, 18.400, -4.96. HR-MS (MALDI) m/z : [M+K] calcd for C₁₁H₂₄O₅Si: 303.4883; found 303.1025.

2-((tert-butyldimethylsilyl)oxy)ethyl (2,5-dioxopyrrolidin-1-yl) carbonate (60 g, 189.0 mmol) and ethylene glycol (15.25 g, 245.7 mmol) were added to a 1-L round bottom flask with a stir bar. Triethylamine (26.3 mL, 189.0 mmol) was added to the flask followed by 4-dimethylaminopyridine (6.93 g, 56.7 mmol). The solution was stirred for 48 hours at 40 °C. The solvent was removed under reduced pressure to afford a yellow oil. The oil was dissolved in CHCl₃ (400 mL) and rinsed with water (3 X 100 mL). The organic layer was isolated and concentrated *in vacuo* to afford 2-((tert-Butyldimethylsilyl)oxy)ethyl (2-hydroxyethyl) carbonate as a yellow oil (40.43 g, 80.9 % yield). ^1H NMR (400 MHz, DMSO, 25 °C): δ = 4.87 (t, J =5.2 Hz, 2H, HOCH₂CH₂O-), 4.12 (t, J =4.4 Hz, 2H, HOCH₂CH₂O-), 4.07 (t, J = 4.4 Hz, 2H, -SiOCH₂CH₂O-), 3.77 (t, J = 4.4 Hz, 2H, -SiOCH₂CH₂O-), 3.57 (q, J = 4.8 Hz, 2H, HOCH₂CH₂O-), 0.86 (s, 9H, (CH₃)₃C(CH₂)Si-), 0.04 (s, 6H, (CH₃)₃C(CH₂)Si-); ^{13}C NMR (100 MHz, DMSO, 25 °C): δ = 155.27, 69.69, 65.77, 61.32, 59.31, 26.19, 18.40, -4.92. HR-MS (DSA) m/z : [M+H] calcd for C₂₄H₄₁N₃O₉Si: 544.2684; found 544.2697.

Disuccinimidyl carbonate (49.62 g, 193.7 mmol) was added to a 500-mL round bottom flask containing acetonitrile (375 mL) and a stir bar. 2-((tert-Butyldimethylsilyl)oxy)ethyl (2-hydroxyethyl) carbonate (39.43 g, 149.1 mmol) and triethylamine (20.8 mL, 149.1 mmol) were added to the flask and stirred for 16 hours at room temperature. The reaction mixture was concentrated *in vacuo* to afford a yellow oil. The oil was dissolved in CHCl₃ (250 mL) and washed with water (3 X 100 mL). The organic layer was concentrated under reduced pressure to afford 2-((tert-Butyldimethylsilyl)oxy)ethyl(2,5-dioxopyrrolidin-1-yl)ethane-1,2-diyl bis(carbonate) as yellow oil (15.6 g, 25.8 % yield). ^1H NMR (400 MHz, DMSO, 25 °C): δ = 4.56 (m, 2H, -O(C=O)OCH₂CH₂O-), 4.38 (m, 2H, -O(C=O)OCH₂CH₂O-), 4.16 (t, J = 4.4 Hz, 2H, -SiOCH₂CH₂O-), 3.79 (t, J = 4.4 Hz, 2H, -SiOCH₂CH₂O-), 2.81 (s, 4H, -(C=O)CH₂CH₂(C=O)-), 0.86 (s, 9H, (CH₃)₃C(CH₂)Si-), 0.04 (s, 6H, (CH₃)₃C(CH₂)Si-); ^{13}C NMR (100 MHz, DMSO, 25 °C): δ = 173.22, 170.94, 155.31, 69.69, 69.13, 61.33, 59.31, 26.20, 25.68, 18.41, -4.91. HR-MS (MALDI) m/z : [M+H] calcd for C₁₆H₂₇NO₉Si: 406.1527; found 406.1647.

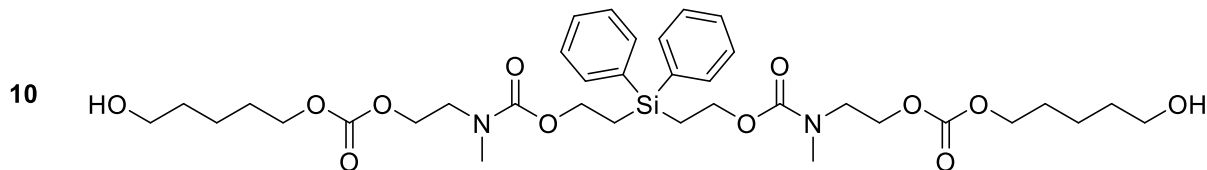
2,2'-(diphenylsilanediyl)bis(ethan-1-ol) (4.20 g, 16.1 mmol) and 2-((tert-Butyldimethylsilyl)oxy)ethyl(2,5-dioxopyrrolidin-1-yl)ethane-1,2-diyl bis(carbonate) (15.0 g, 37.0 mmol) were added to a 250-mL round bottom flask containing dry acetonitrile (50 mL) and a stir bar. Triethylamine (2.24 mL, 16.1 mmol) was added to the flask followed by 4-dimethylaminopyridine (0.59 g, 4.8 mmol). The reaction was stirred for 48 hours at 30 °C. The reaction mixture was concentrated *in vacuo* to afford a yellow oil. The oil was dissolved in chloroform (75 mL) and washed with water (3 X 30 mL). The organic layer was concentrated *in vacuo* to afford a yellow oil. Purification by column chromatography (50:50 Hexanes:Ethyl Acetate) afforded 2-((tert-Butyldimethylsilyl)oxy)ethyl ethane-1,2-diyl (2,2,3,3-tetramethyl-8,13-dioxo-17,17-diphenyl-4,7,9,12,14-pentaoxa-3,17-disilanonadecan-19-yl) bis(carbonate) as a clear, colorless oil (12.73 grams, 92.7% yield). ^1H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.54-7.51 (m, 4H, *ortho*), 7.44-7.38 (m, 6H, *meta* & *para*), 4.37-4.19 (overlapped m, 16H, -O(C=O)OCH₂CH₂O- & -O(C=O)OCH₂CH₂O- & -SiOCH₂CH₂O- & -SiCH₂CH₂O(C=O)O-), 3.84 (t, J = 4.6 Hz, 4H, -SiOCH₂CH₂O-), 1.70 (m, 4H, -SiCH₂CH₂-), 0.90 (s, 18H, (CH₃)₃C(CH₂)Si-), 0.08 (s, 6H, (CH₃)₃C(CH₂)Si-); ^{13}C NMR (100 MHz, CDCl₃, 25 °C): δ = 155.00, 145.77, 134.63, 133.01, 130.06, 128.30, 69.18, 65.67, 65.24, 65.10, 61.02, 25.83, 18.29, 14.25, -5.37. Parent ion could not be found.

Pyridinium *para*-toluenesulfonate (1.12 g, 4.5 mmol) was added to a 250-mL round bottom flask containing ethanol (150 mL) and a stir bar. 2-((tert-Butyldimethylsilyl)oxy)ethyl ethane-1,2-diyl (2,2,3,3-tetramethyl-8,13-dioxo-17,17-diphenyl-4,7,9,12,14-pentaoxa-3,17-disilanonadecan-19-yl) bis(carbonate) (12.73 g, 14.9 mmol) was then added to the flask with a stir bar. The solution was stirred for 48 hours at 35 °C. The reaction mixture was concentrated *in vacuo* to afford a colorless, clear oil. The oil was dissolved in CHCl₃ (100 mL) and washed with water (3 X 50 mL). The organic layer was isolated and concentrated under reduced pressure to afford a clear oil. Purification by column chromatography (9:1 CHCl₃:CH₃OH) afforded silyl diol **8** as a clear, colorless oil (3.56 g, 38.2 % yield). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.51-7.49 (m, 4H, *ortho*), 7.42-7.35 (m, 6H, *meta* & *para*), 4.32-4.22 (overlapped m, 16H, -O(C=O)OCH₂CH₂O- & -O(C=O)OCH₂CH₂O- & HOCH₂CH₂O- & -SiCH₂CH₂O(C=O)O-), 3.79 (m, J= 4.6 Hz, 4H, HOCH₂CH₂O-), 2.96 (t, J= 6.0 Hz, 2H, HOCH₂CH₂O-), 1.67 (m, 4H, -SiCH₂CH₂-); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 155.03, 154.84, 134.62, 133.09, 130.05, 128.29, 69.63, 65.81, 65.53, 65.10, 60.53, 14.12. HR-MS (ESI) *m/z*: [M+Na] calcd for C₂₈H₃₆O₁₄Si: 647.2000; found 647.1797.



(Diphenylsilanediyl)bis(ethane-2,1-diyl)bis((2-((2-hydroxyethyl)(methyl)carbamoyl)oxy)ethyl)(methyl)carbamate) (9**):**

(Diphenylsilanediyl)bis(ethane-2,1-diyl) bis((2-hydroxyethyl)(methyl)carbamate) (**4**) (9.98 g, 42.0 mmol) and triethylamine (34.0 mL, 243.9 mmol) were added to a 500-mL round bottom flask containing 200 mL dry acetonitrile. *N,N'*-disuccinimidyl carbonate (42.5 g, 165.9 mmol) was then added to the flask with a stir bar and allowed to stir for 16 hours at room temperature. TLC was used to determine reaction completion. The reaction mixture was concentrated *in vacuo* to afford a yellow liquid. The liquid was dissolved in chloroform (200 mL) and washed with a saturated aqueous NaCl solution (3 X 50 mL). The organic layer was concentrated *in vacuo* to afford a yellow liquid. The liquid was dissolved in acetonitrile (200 mL). Triethylamine (29.3 mL, 210.0 mmol) was added to the flask, followed by *N*-methylethanolamine (13.5 mL, 168.0 mmol). The reaction mixture was stirred at room temperature for 16 hours. TLC was used to determine reaction completion. The mixture was concentrated *in vacuo* to afford a yellow oil. Purification by column chromatography (9:1 CH₂Cl₂:CH₃OH) afforded silyl diol **9** as a clear, yellow/orange oil (8.8 grams, 72.6% yield). ¹H NMR (400 MHz, DMSO, 25 °C): δ = 7.56 (m, 2H,), 7.41-7.39 (m, 3H), 4.65 (m, 3H), 4.08 (t, J= 7.8 Hz, 6H), 3.44 (q, J= 12.4, 6 Hz, 6H), 3.19 (m, 6H), 2.82 (s, 9H), 1.33 (t, J= 7.4 Hz, 6H); ¹³C NMR (100 MHz, DMSO, 25 °C): δ = 156.06, 134.22, 129.99, 128.50, 128.40, 62.32, 59.49, 51.30, 53.62, 14.09. HR-MS (DSA) *m/z*: [M+H] calcd for C₂₄H₄₁N₃O₉Si: 544.2684; found 544.2697



(Diphenylsilanediyl)bis(ethane-2,1-diyl) bis((2-(((5-hydroxypentyl)oxy)carbonyl)oxy)ethyl)(methyl)carbamate) (10**):**

(Diphenylsilanediyl)bis(ethane-2,1-diyl) bis((2-hydroxyethyl)(methyl)carbamate) (10.82 g, 22.8 mmol) and 5-((tert-Butyldimethylsilyl)oxy)pentyl (2,5-dioxopyrrolidin-1-yl) carbonate (20.5 g, 57.0 mmol) were added to a 500-mL round bottom flask containing acetonitrile (230 mL) and a stir bar. Triethylamine (4.77 mL, 34.2 mmol) was added to the flask, followed by 4-dimethylamino pyridine (1.40 g, 11.4 mmol). The reaction was stirred for 72 hours at 50 °C. The reaction mixture was concentrated *in vacuo* to afford a yellow oil. The oil was dissolved in CHCl₃ (250 mL) and washed with DI water (3 X 100 mL). The organic layer was isolated and concentrated *in vacuo* to afford a yellow oil. Purification by column chromatography (9:1 CH₂Cl₂:CH₃OH) afforded (Diphenylsilanediyl)bis(ethane-2,1-diyl) bis(methyl(2,2,3,3-tetramethyl-11-oxo-4,10,12-trioxa-3-silatetradecan-14-yl)carbamate) as a clear, colorless oil (14.06 grams, 64.0% yield). ¹H NMR (400 MHz, DMSO, 25 °C): δ = 7.52-7.51 (m, 4H, *ortho*), 7.43-7.37 (m, 6H, *meta* & *para*), 4.12-4.02 (overlapped m, 12H, -OCH₂CH₂Si- & -OCH₂CH₂N- & -SiOCH₂CH₂CH₂CH₂CH₂O-), 3.54 (t, 4H, J=6.0 Hz, -SiOCH₂CH₂CH₂CH₂CH₂O-), 3.40-3.32 (m, 4H, -OCH₂CH₂N-), 2.78-2.69 (ds, 6H, -NCH₃), 1.64-1.49 (overlapped m, 8H, -OCH₂CH₂Si- & -SiOCH₂CH₂CH₂CH₂CH₂O-), 1.42 (m, 4H, -SiOCH₂CH₂CH₂CH₂CH₂O-), 1.30 (m, 4H, -SiOCH₂CH₂CH₂CH₂CH₂O-), 0.84 (s, 18H, (CH₃)₃C(CH₂)Si-), 0.02 (s, 12H, (CH₃)₃C(CH₂)Si-). Parent ion could not be found.

Pyridinium para-toluenesulfonate (1.50 g, 5.8 mmol) was added to a 250-mL round bottom flask containing ethanol (150 mL) and a stir bar. (Diphenylsilanediyl)bis(ethane-2,1-diyl) bis(methyl(2,2,3,3-tetramethyl-11-oxo-4,10,12-trioxa-3-silatetradecan-14-yl)carbamate) (14.06 g, 14.6 mmol) was then added to the flask with a stir bar. The solution was stirred for 48 h at 35 °C. The reaction mixture was concentrated *in vacuo* to afford a colorless, clear oil. The oil was dissolved in CHCl₃ (100 mL) and washed with water (3 X 50 mL). The organic layer was isolated and concentrated under reduced pressure to afford a clear oil. Purification by column chromatography (95:5 CH₂Cl₃:CH₃OH) afforded silyl diol **10** as a clear, colorless oil (7.41 g, 69.2 % yield). ¹H NMR (400 MHz, DMSO, 25 °C): δ = 7.52-7.51 (m, 4H, *ortho*), 7.43-7.38 (m, 6H, *meta* & *para*), 4.38 (t, 2H, J= 5.2 Hz, HOCH₂CH₂CH₂CH₂CH₂O-), 4.12-4.02 (overlapped m, 12H, -OCH₂CH₂Si- & -OCH₂CH₂N- & HOCH₂CH₂CH₂CH₂CH₂O-), 3.40-3.32 (m, 4H, -OCH₂CH₂N-), 2.78-2.69 (ds, 6H, -NCH₃), 1.64-1.49 (overlapped m, 8H, -OCH₂CH₂Si- & HOCH₂CH₂CH₂CH₂CH₂O-), 1.39 (m, 4H, -HOCH₂CH₂CH₂CH₂CH₂O-), 1.29 (m, 4H, HOCH₂CH₂CH₂CH₂CH₂O-); ¹³C NMR (100 MHz, DMSO, 25 °C): δ = 155.96, 154.98, 134.79, 130.10, 128.52, 68.07, 65.31, 62.63, 60.94, 55.35, 47.74, 47.07, 34.98, 34.57, 32.44, 28.44, 28.22, 26.25, 22.18, 14.03. HR-MS (MALDI) *m/z*: [M+Na] calcd for C₃₆H₅₄N₂O₁₂Si: 757.3338; found 757.3358.

3.2 Synthesis of Silyl-PU Coatings from Silyl Diols

Clear (colorless) Silyl-PU coatings were synthesized by mixing each diphenyl silyl diol with the aliphatic isocyanate at a 1.05:1.0 ratio (hydroxyl to isocyanate functionality) in a plastic cup, followed by addition of butyl acetate (to make a 82-86 Wt.% solution) and 0.50 Wt.% dibutyltin dilaurate (DBTDL) (on binder solids) as a catalyst. The formulas were then applied over the bare chromic acid anodized AA 2024-0 panels, PVF-wrapped tinplate panels, and bare tinplate steel panels using a 3 mil (76.2 micron) drawdown bar. The topcoats were allowed to cure under ambient conditions (65-75 °F, 40-60% R.H.) for 10-14 days before being tested. Dry film thickness (DFT) of the clear topcoats were 2.0-2.5 mils (50.8-63.5 microns).

The low-gloss gray Silyl-PU coating was synthesized by mixing a diphenyl silyl diol with TiO₂, carbon black, and micronized polypropylene in a plastic cup, followed by addition of an aliphatic isocyanate blend at a 1.05:1.0 ratio (hydroxyl to isocyanate functionality). The formula was then diluted with butyl acetate to make a 70-75 Wt.% mixture, followed by addition of 0.30 Wt.% DBTDL (on total solids) as a catalyst. The formula was spray-applied onto bare chromic acid anodized AA 2024-0 panels, PVF-wrapped tinplate panels, bare tinplate steel panels, and epoxy-primed panels using high-volume, low-pressure (HVLP) spray equipment. The coating was allowed to cure under ambient conditions (65-75 °F, 40-60% R.H.) for 10-14 days before being tested. DFT of the coating was 2-3 mils (50.8-76.2 microns).

The gloss white Silyl-PU coating was synthesized by mixing a diphenyl silyl diol with TiO_2 in a plastic cup, followed by addition of the aliphatic isocyanate (or isocyanate blend) at a 1.05:1.0 ratio (hydroxyl to isocyanate functionality). The formula was then diluted with butyl acetate to make a 80-85 Wt.% mixture, followed by addition of 0.35 Wt.% DBTDL (on total solids) as a catalyst. The topcoat formula was spray-applied onto bare chromic acid anodized AA 2024-0 panels, PVF-wrapped tinplate panels, bare tinplate steel panels, and epoxy-primed panels using high-volume, low-pressure (HVLP) spray equipment. The coating was then allowed to cure under ambient conditions (65-75 °F, 40-60% R.H.) for 10-14 days before being tested. DFT of the coating was 2-3 mils (50.8-76.2 microns).

A MIL-PRF-85285, Type IV camouflage gray polyurethane aircraft topcoat, for use as a control, was spray-applied onto bare chromic acid anodized AA 2024-0 panels, PVF-wrapped tinplate panels, bare tinplate steel panels, and epoxy-primed panels using high-volume, low-pressure (HVLP) spray equipment. The topcoat was then allowed to cure under ambient conditions (65-75 °F, 40-60% R.H.) for 10-14 days before being tested. DFT of the topcoat was 2-3 mils (50.8-76.2 microns).

4. RESULTS AND DISCUSSION

4.1 Coating Synthesis and Properties

Silyl-centered diols with extended (4-7) and double extended (8-10) aliphatic chains were synthesized for use as crosslinkers in silyl-containing polyurethane coatings (figure 4). These diols were synthesized based on previous research from our group where we showed the length of covalently bound appendages and an increase in cleavable bonds resulted in an increased rate of network disassembly.[16] The silyl diols possessed phenyl groups attached to silicon, which provide greater electronegativity compared to methyl groups, and the aliphatic chains included N-alkyl carbamate and/or carbonate linkages, in addition to ethylene and pentylene segments, to determine how diol structure affected coating properties and the time of coating disassembly. Furthermore, these silyl diols were synthesized to resemble the size and structure of diols used in MIL-PRF-85285 polyurethane topcoats, which in theory would reduce the glass transition temperature of Silyl-PU coatings by provide greater aliphatic character and reduced crosslink density.

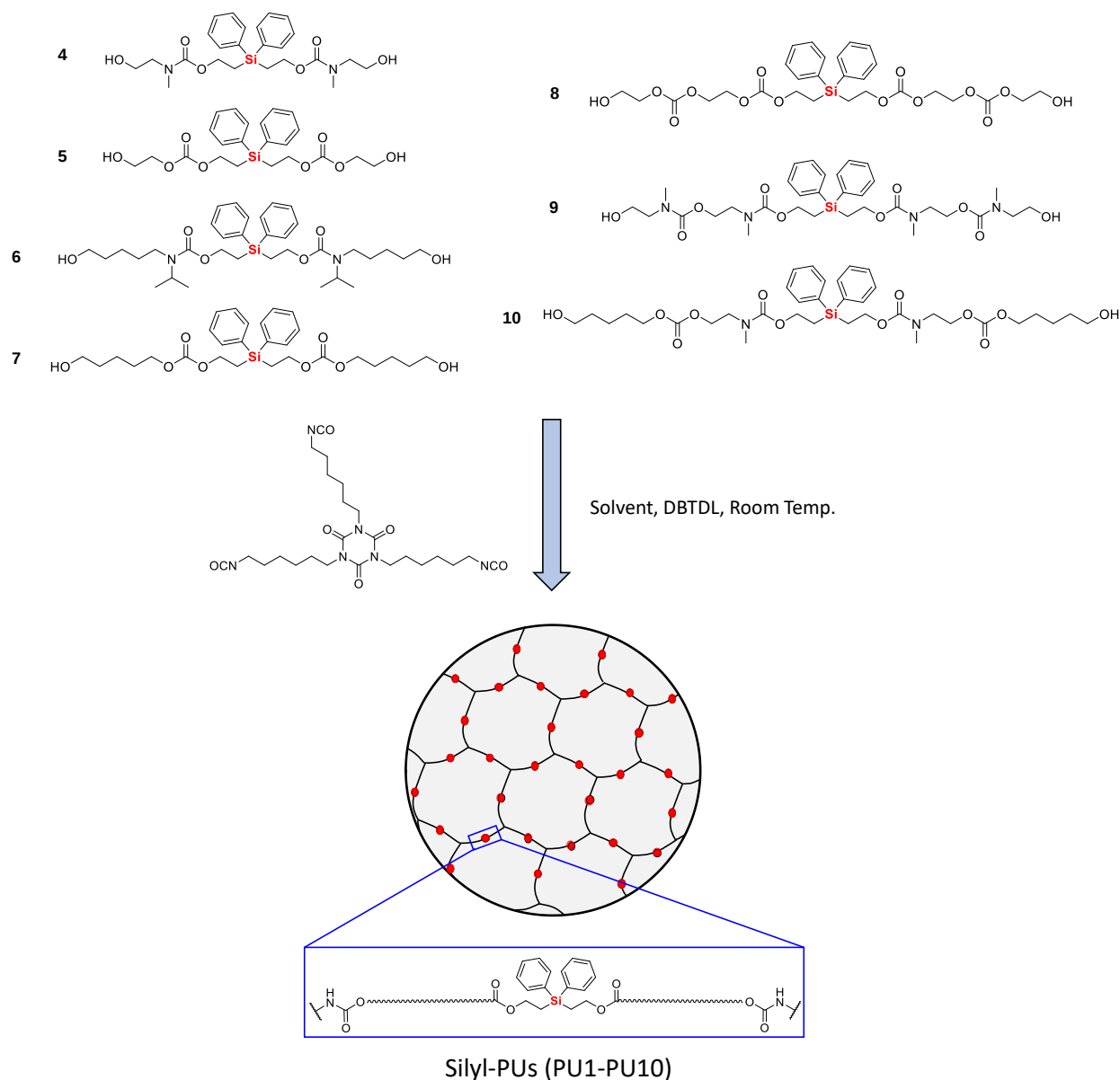
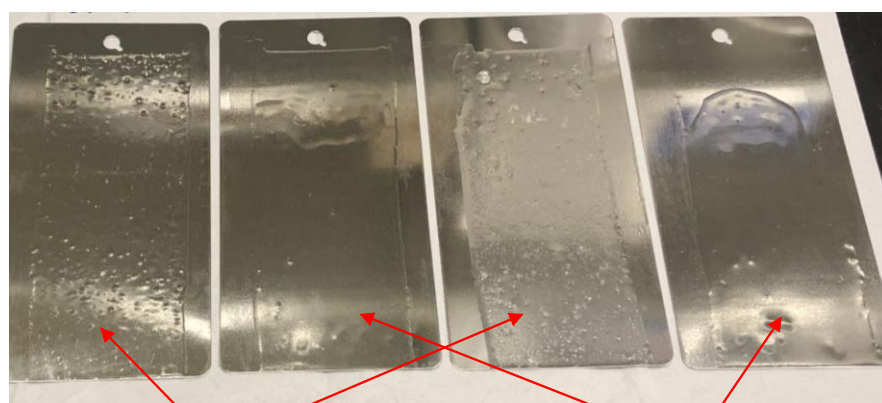


Figure 4 — Synthesis of Silyl-PU networks (coatings) from an aliphatic isocyanate (HDI oligomer) and extended or double extended chain silyl diol. The silicon atom (i.e. trigger) in the silyl diols and coating network is highlighted in red.

Silyl-PU coatings **PU1-PU10** were synthesized by reacting each silyl diol (**4-10**) with an aliphatic isocyanate (HDI oligomer), or 50/50 blend of aliphatic isocyanates, in solvent at room temperature, then forming coatings via drawdown bar or HVLP spray application (see Section 3.2). All Silyl-PUs were synthesized using a 5% molar excess of hydroxyl (-OH) functionality to consume all isocyanate (-NCO) groups. **PU1-PU8** were colorless (clear) coatings, whereas **PU9** and **PU10** were pigmented/filled to form low-gloss (1.40 gloss units (GU) at 60° angle) gray and gloss (93.5 GU at 60° angle) white finishes, respectively (table 2). **PU1**, which was fabricated from silyl diol **4**, showed regions of segregation during curing (crosslinking) due to low miscibility with HDI oligomers; however, all other silyl diols were miscible with the HDI oligomer(s) and provided colorless homogeneous networks (figure 5). A MIL-PRF-85285 camouflage (1.8 GU at 60° angle) gray polyurethane topcoat (**PU11**), which does not contain silyl linkages, was fabricated for use as a control topcoat via HVLP spray method.

Table 2 — Formulation and appearance of Silyl-PU coatings.

Silyl Diol	Aliphatic Isocyanate	Coating	Pigment and Filler	Appearance	Gloss Units at 60 Degree Angle
4	HDI oligomer	PU1	No	Colorless	N/A
5	HDI oligomer	PU2	No	Colorless	N/A
6	HDI oligomer	PU3	No	Colorless	N/A
7	HDI oligomer	PU4	No	Colorless	N/A
8	HDI oligomer	PU5	No	Colorless	N/A
9	HDI oligomer	PU6	No	Colorless	N/A
9	50/50 blend of HDI oligomers	PU7	No	Colorless	N/A
10	HDI oligomer	PU8	No	Colorless	N/A
9	50/50 blend of HDI oligomers	PU9	Yes	Low-gloss gray	1.40 GU
9	50/50 blend of HDI oligomers	PU10	Yes	Gloss white	93.5 GU



Silyl diol **4** crystallized during cure and had limited miscibility with HDI oligomer(s), thereby providing hazy coatings

Silyl diol **9** did not crystallize during cure and was miscible with HDI oligomer(s), thereby providing clear coatings

Figure 5 — Appearance of Silyl-PUs based on silyl diol crystallinity and miscibility with HDI oligomer(s) during cure.

Spectroscopic and thermal analysis provided confirmation of polyurethane coating formation. Attenuated total reflectance infrared (ATR-IR) spectroscopy of **PU1-PU10** confirmed the formation of carbamate (i.e. urethane) linkages as shown by the carbonyl stretch around 1680 cm^{-1} , a N-H stretch around 3300 cm^{-1} , and an in-plane carbamate bend around 1525 cm^{-1} . The Si-C bond stretch was located around 765 cm^{-1} for all coatings, whereas a stretch around 1740 cm^{-1} was observed for coatings that possessed carbonate linkages

(see Appendices 1 and 2). An isocyanate peak at 2270 cm^{-1} was not detected due to complete consumption as a result of excess hydroxyl functionality. Thermogravimetric analysis (TGA) of silyl-containing polyurethanes **PU1-PU10** showed onset degradation temperatures of $210.2\text{--}301.7\text{ }^{\circ}\text{C}$ (table 3), which is typical of crosslinked polymeric networks, and the majority of clear Silyl-PU coatings showed a similar degradation profile (figure 6). Clear coating **PU7**, which is based on a blend of HDI oligomers, did not show a difference in onset degradation temperature or degradation profile compared to coating **PU6**, which is based on a single HDI oligomer, thereby indicating the structure of the oligomer did not affect thermal stability. Above $225\text{ }^{\circ}\text{C}$, greater weight loss was observed for coatings based on silyl diols with all carbonate linkages and ethylene chains (**PU2** and **PU5**), and **PU5**, which is based on double extended silyl diol **8**, was the greater of the two due to an increased number of degradable linkages. The reduced thermal stability of these Silyl-PUs compared to other clear coatings is due to reduced thermal stability of carbonate linkages compared to N-alkyl carbamate linkages.[21,22] **PU1** also showed increased weight loss above $225\text{ }^{\circ}\text{C}$, although this coating was non-homogenous and likely possessed reduced crosslink density compared to other Silyl-PUs. Furthermore, **PU9**, the low-gloss gray Silyl-PU coating, and **PU10**, the gloss white Silyl-PU coating, possessed onset degradation temperatures of $288.7\text{ }^{\circ}\text{C}$ and $287.4\text{ }^{\circ}\text{C}$, respectively, which were nearly identical to the MIL-PRF-85285, Type IV camouflage gray polyurethane control (**PU11**) at $285.6\text{ }^{\circ}\text{C}$. However, beyond $350\text{ }^{\circ}\text{C}$, pigmented coatings **PU9-PU11** demonstrated reduced weight loss compared to the clears, although the remaining weight can be attributed to the inorganic solid particles in the network. It is worth noting that Silyl-PU coatings **PU9** and **PU10** contained TiO_2 , whereas the camouflage gray polyurethane control contained TiO_2 and amorphous silica.

Table 3 — Onset degradation temperature of Silyl-PU and polyurethane control coatings.

Coating	Onset Degradation Temperature ($^{\circ}\text{C}$)
PU1	229.5
PU2	210.2
PU3	301.7
PU4	300.9
PU5	189.1
PU6	282.4
PU7	279.3
PU8	276.4
PU9	288.7
PU10	287.4
PU11	285.5

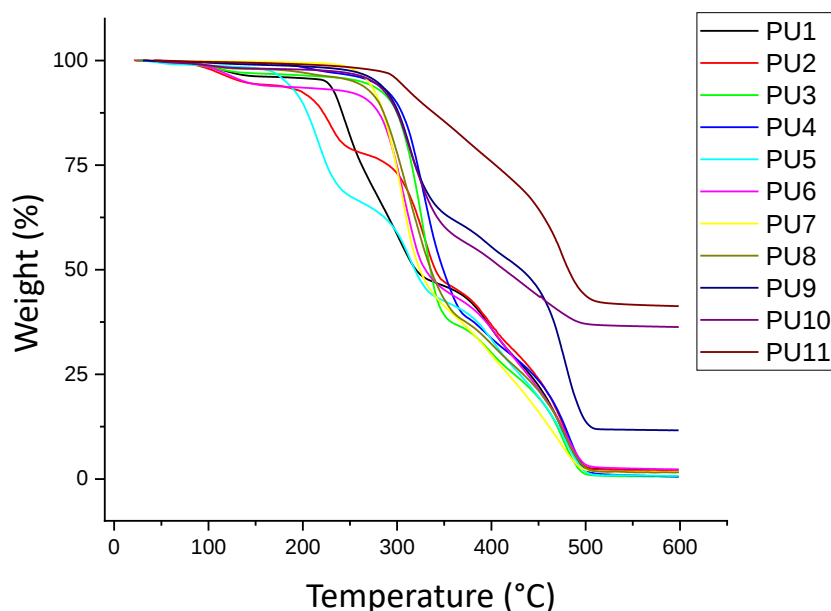


Figure 6 — Thermal degradation profile of Silyl-PU (**PU1-PU10**) and polyurethane control (**PU11**) coatings.

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) of polyurethane coatings, whereas tensile testing was performed to determine coating elongation, ultimate tensile strength, and Young's Modulus. The T_g of the clear Silyl-PU (**PU1-PU8**) ranged from 21.4-44.8 °C, whereas the pigmented Silyl-PU and polyurethane control were 21.5 °C (**PU9**), 20.8 °C (**PU10**), and 20.1 °C (**PU11**), respectively (figure 7). The greatest T_g was observed for **PU2**, which is likely due to the short chain of silyl diol **5** providing increased crosslink density. However, **PU1**, which is based on silyl diol **4** and also contains a short chain, demonstrated a T_g of 29.5 °C due to reduced crosslinks resulting from incompatibilities within the network. Coatings based on silyl diols with pentylene linkages (**PU3**, **PU4** and **PU8**) showed reduced T_g s compared to **PU2** due to increased bond rotations within the aliphatic chains, whereas the T_g of **PU4** was lower than **PU3** due to decreased hydrogen bonding within the network as a result of the carbonate linkages. A similar trend was observed for **PU5** ($T_g = 35.5$ C) and **PU6** ($T_g = 38.9$ C), which are based on extended chain silyl diols with two carbonate or two N-methyl carbamate linkages within each appendage, respectively. Incorporation of the 50/50 blend of HDI oligomers in **PU7** resulted in a T_g of 21.4 °C, which was a significant decrease compared to the T_g of 38.9 °C for **PU6** with a single HDI oligomer, and can be attributed to increased bond rotations within the linear aliphatic chains of the second oligomer. The addition of pigments and fillers to **PU7**, in effort to form low-gloss gray coating **PU9** and gloss white coating **PU10**, resulted in minor T_g changes, even with **PU10** containing about 31 Wt.% of TiO_2 on total solids. However, these additions enabled T_g s that were within the target range of 18-25 °C and nearly identical to the polyurethane control (**PU11**, $T_g = 20.1$ °C).

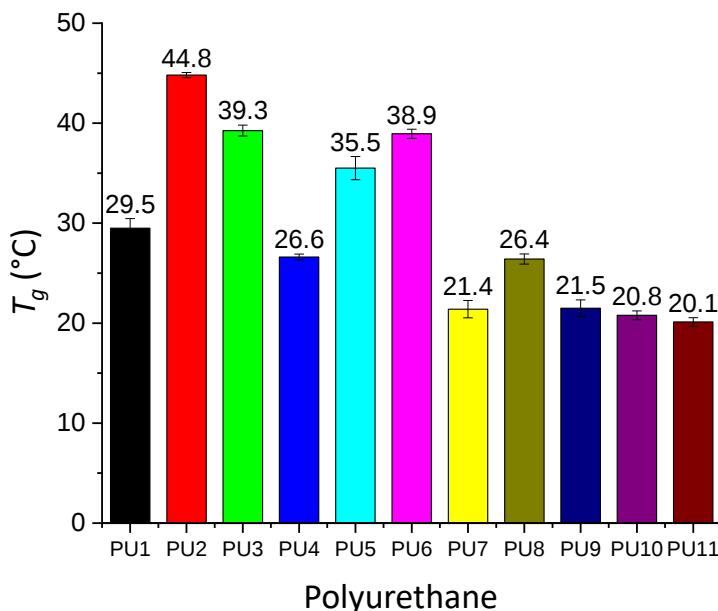


Figure 7 — Glass transition temperature (T_g) of Silyl-PU (**PU1-PU10**) and polyurethane control (**PU11**) coatings.

Silyl-PU coatings possessed elongation values of 4.80-327.0%, with **PU5** demonstrating the lowest elongation and **PU8** demonstrating the greatest (figure 8). The elongation of for **PU8** is due to silyl diol **10** having aliphatic pentylene segments and the longest chain of any diol, thereby forming a coating with reduced crosslink density and increased chain conformations due to less hindered bond rotations. On the contrary, **PU5**, which is based on silyl diol **8** and contains two carbonate linkages within each appendage, provided the lowest elongation, likely due to reduced bond rotations and intramolecular hydrogen bonding between carbonate groups. **PU6**, which is based on silyl diol **9** and contained two N-methyl carbamate linkages within each appendage, demonstrated nearly double the elongation at 9.46%. It remains unclear why **PU6**, which had a greater T_g than **PU5** and should possess reduced chain conformations due to increased hydrogen bonding between carbamate linkages, demonstrated a greater elongation value, although it is possible the silyl diol chains obtained a slightly more favorable confirmation during coating formation and/or the coating possessed a slight reduction in crosslink density compared to **PU5**. However, **PU3**, which is based on silyl diol **6** and contains a pentylene chain and single N-isopropyl carbamate linkage within each appendage, possessed both greater elongation (153.9%) and a greater T_g than **PU4**, which is based on silyl diol **7**. Incorporation of the HDI oligomer blend in **PU7** resulted in an elongation of 262.8%, which is an increase of 2678% from **PU6**. This increase can be attributed to the flexible aliphatic segments in the second oligomer, in addition to a slightly reduction in crosslink density for the coating. Furthermore, the addition of pigments and filler to **PU7** resulted in elongation values of 146.1% and 147.9% for **PU9** and **PU10**, respectively, which was expected due to a reduction in crosslink density. Interestingly, the latter coatings possessed nearly six times the elongation of the polyurethane control (**PU11**), which demonstrated a value of only 24.9% elongation, even though the T_g values of the three coatings were relatively similar.

As expected, coatings with greater elongation were less tough, in general, than those with lower elongation values as indicated by their tensile strength (figure 9). For instance, **PU5** and **PU6**, which had low elongation, possessed the greatest tensile strength at 37.6 MPa and 78.1 MPa, respectively, which is excellent toughness and above the limit of 30 MPa reported for most crosslinked polyurethanes.[23-25] However, **PU7** and **PU8**, which had the greatest elongation, also demonstrated tensile strength values of 25.1 MPa and 21.4 MPa, respectively. These values were greater than most Silyl-PU coatings, yet similar to the value of 28.9 MPa for the polyurethane control (**PU11**). Silyl-PU coatings with pigments and filler

exhibited a lower tensile strength (**PU9** = 5.46 MPa, **PU10** = 15.4 MPa) compared to the control, although the gloss white Silyl-PU coating (**PU10**), which possessed three times the amount of TiO_2 compared to **PU9**, had nearly triple the tensile strength. The chemical composition of pigments and fillers used in the polyurethane control are unknown. However, the total amount of inorganic material is likely between 40 and 50 Wt.% as indicated by the TGA degradation profile in Figure 6, which is greater than the 31 Wt.% of TiO_2 used in **PU10**. Increased network toughness due to reinforcement with TiO_2 and/or other hydroxyl-functional fillers (e.g. amorphous silica) has been previously reported and is commonly used to enhance the properties of polyurethane materials.[26]

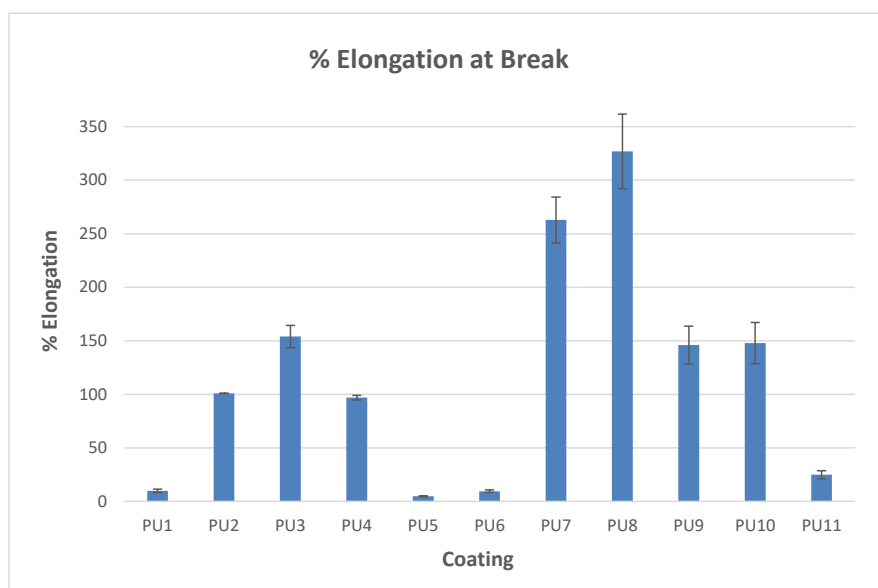


Figure 8 — Percent elongation of Silyl-PU (**PU1-PU10**) and polyurethane control (**PU11**) coatings.

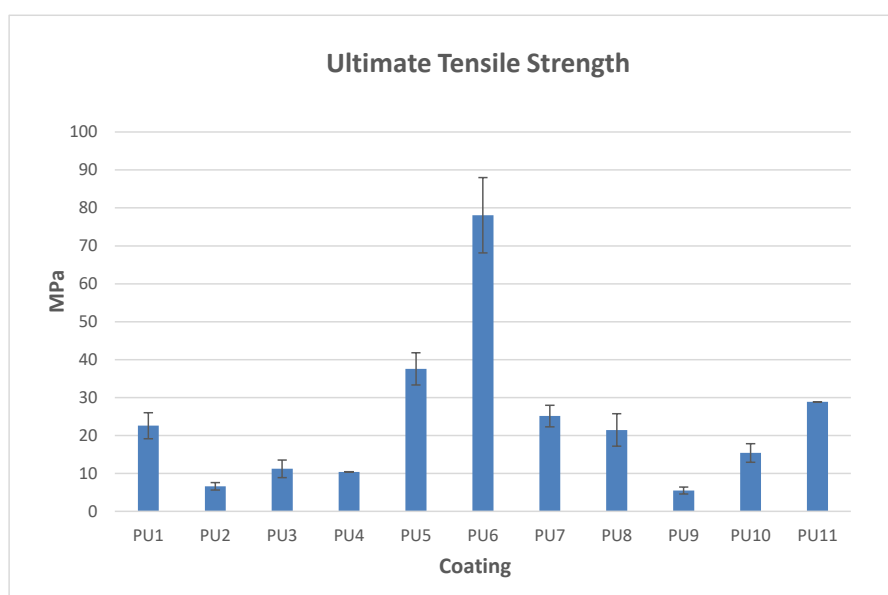


Figure 9 — Tensile strength of Silyl-PU (**PU1-PU10**) and polyurethane control (**PU11**) coatings.

The surface hardness of the colorless and pigmented polyurethane coatings was determined with a König Pendulum hardness instrument, whereas coating performance properties (e.g. mandrel bend, GE Impact, adhesion, weatherability) were evaluated using American Society for Testing and Material (ASTM) standards per MIL-PRF-85285 requirements. As shown in Table 4, pendulum hardness values ranged from 8-127 oscillations, with **PU1** being the softest and **PU5** being the hardest coating. The softness for **PU1** is likely due to its non-homogenous network and hence reduced crosslink density, whereas the hardness of **PU5** can be attributed to high crosslink density and increased hydrogen bonding character between the carbonate linkages within network chains. **PU2** and **PU4** had the second and third hardest surfaces at 73 and 62 oscillations, respectively. Both coatings possessed carbonate linkages within the network, although **PU4** also possessed aliphatic pentylene segments. **PU6**, which possessed N-methyl carbamate linkages, had one of the lowest surface hardness values at 13 oscillations, even though this coating was tough and possessed a greater T_g value than most coatings. Silyl-PU coatings **PU9** and **PU10**, which possess inorganic pigments and filler, demonstrated hardness values of 26 and 13 oscillations, respectively, and were similar to the polyurethane control at 25 oscillations. However, it was interesting that **PU10**, which contained nearly three times the amount of TiO_2 compared to **PU9**, had a lower surface hardness. Shore A hardness values for all coatings were also determined, although these values were within a narrow range of 95-98, thereby limiting the ability to distinguish differences in hardness between samples.

Table 4 — Surface hardness and performance property testing of Silyl-PU and polyurethane control coatings.

Coating	König Pendulum Hardness (osc.)	0.25-Inch Cylindrical Mandrel Bend	MEK Solvent Resistance (double rubs)	Room Temperature Flexibility via GE Impact
PU1	8	No cracking	100 – no marring	20-40% elongation
PU2	73	No cracking	100 – no marring	60% elongation
PU3	27	No cracking	100 – no marring	60% elongation
PU4	62	No cracking	100 – no marring	60% elongation
PU5	127	No cracking	100 – no marring	60% elongation
PU6	13	No cracking	100 – no marring	40% elongation
PU7	38	No cracking	100 – no marring	60% elongation
PU8	14	No cracking	100 – slight marring	60% elongation
PU9	26	No cracking	100 – no marring	60% elongation
PU10	13	No cracking	100 – no marring	60% elongation
PU11	25	No cracking	100 – no marring	40% elongation

The room temperature flexibility of coatings was determined via a 0.25-inch cylindrical mandrel bend according to ASTM D522 and a GE Impact according to ASTM D6905 (table 4).[27,28] None of the coatings exhibited cracking when bent over the 0.25-inch mandrel, indicating that sufficient chain

realignment occurred during slow stretching of the coatings (figure 10a). However, the GE Impact test, which rapidly deforms a coating, resulted in 20-40% elongation for **PU1**, **PU6**, and **PU11** (control), whereas all other Silyl-PU demonstrated 60% elongation. Clear coatings **PU1** and **PU6** possessed N-methyl carbamate linkages, which limited chain rearrangements, and hence deformation, due to strong intramolecular hydrogen bonding. However, **PU11** is supposed to possess a minimal of 40% elongation per MIL-PRF-85285, and clear **PU6** demonstrated equivalent performance. The enhanced flexibility for the other Silyl-PU, especially those with pigments and filler (**PU9** and **PU10**), can be attributed to reduced crosslink density and increased aliphatic chains resulting from incorporation of the second HDI oligomer. Figure 10b shows photographs of low-gloss gray **PU9** and gloss white **PU10** after the GE Impact test.

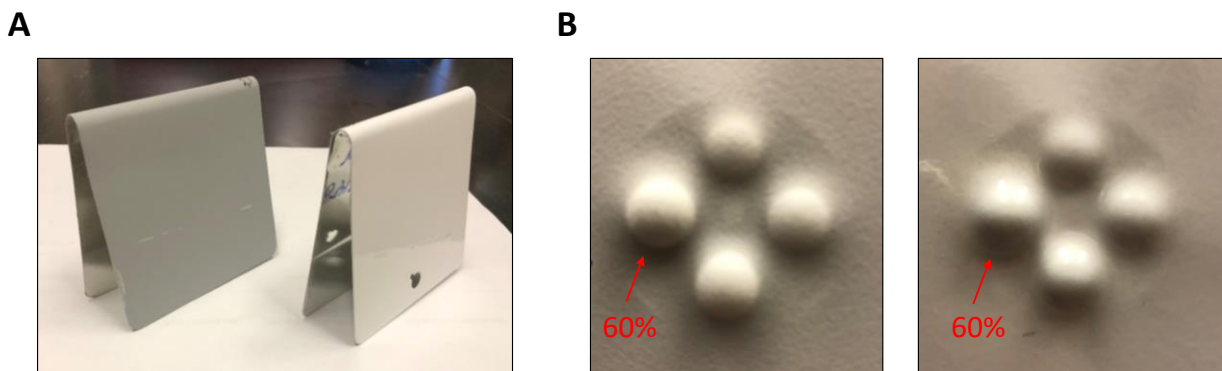


Figure 10 — Visual of Silyl-PU coating flexibility: a) **PU9** (left) and **PU10** (right) after cylindrical mandrel bend, and b) **PU9** (left) and **PU10** (right) after GE Impact.

All coatings demonstrated resistance to cut-through when exposed to 100 double rubs with a methyl ethyl ketone (MEK) soaked rag according to ASTM D5402, and **PU8** was the only coating that showed slight surface marring.[29] This demonstrated that all coatings were highly crosslinked and their polymer chains were not easily solvated with MEK. Fluid resistance (e.g. JP-5 jet fuel, hydraulic fluid) testing per MIL-PRF-85285 was not performed on any of the coatings, nor was strippability testing with a methylene chloride or benzyl alcohol based paint remover.

Coatings **PU9** and **PU10** applied over the MIL-PRF-23377, Class N (non-chromate) epoxy primer were evaluated for adhesion according to ASTM D3359, Methods A and B.[30] As shown in Figure 11, both coatings demonstrated a 5A rating (no peeling or removal) when X-Cut (Method A) adhesion was evaluated, and both coatings demonstrated a 5B rating (0% removal) when Cross-Cut (Method B) adhesion was evaluated. The polyurethane control (**PU11**) over the same primer showed $\geq 4A$ and $\geq 4B$ ratings via X-Cut and Cross-Cut adhesion tests, respectively, thus demonstrating the Silyl-PU can provide excellent adhesion to a DoD-grade epoxy primer that is used on aircraft.

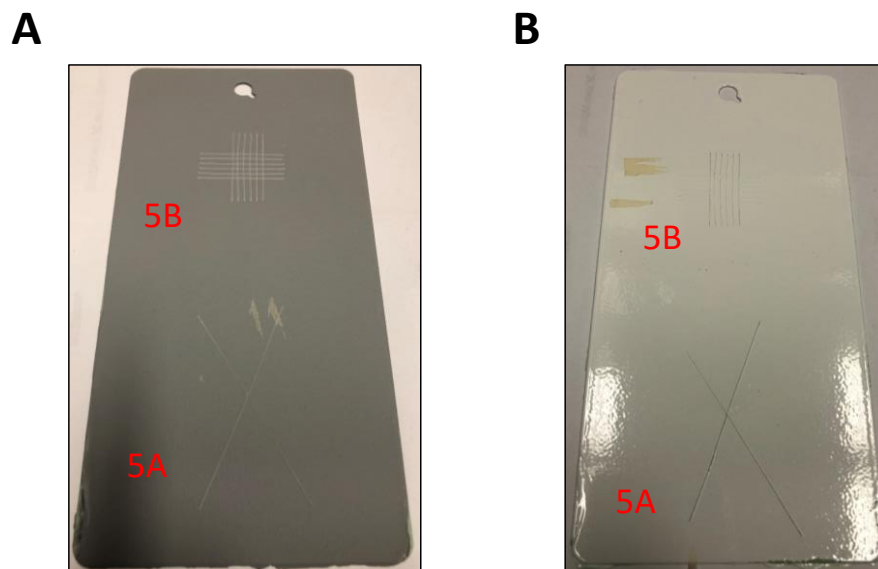


Figure 11 — Adhesion results of Silyl-PU coatings over non-chromate epoxy: a) **PU9** after Cross-Cut (top) and X-Cut (bottom) tests, and b) **PU10** after Cross-Cut (top) and X-Cut (bottom) tests.

Silyl PU coatings **PU9** and **PU10**, in addition the MIL-PRF-85285, Type IV polyurethane control, were exposed for a total of 500 hours in a Xenon-Arc Weatherometer (WOM) chamber according to ASTM G155, Cycle 1.[31] This accelerated weathering test, which simulates exposure to sunlight, was performed to determine degradation resistance of the Silyl-PU. During this test, the coatings were exposed to a cycle of 102 minutes of light (340 nm wavelength) at an irradiance of 0.35 W/m², followed by 18 minutes of light and deionized (DI) water spray. After 250 and 500 hours, the coatings were removed and their color and gloss were determined via ASTM D2244 and D523, respectively.[32,33] As shown in Figure 12, after 500 hours **PU9** had a color change (ΔE) of 0.99 and gloss values of 1.1 GU at 60 degrees and 1.8 GU at 85 degrees, whereas the **PU10** had a color change of 0.78 and a gloss of 58.2 GU at 60 degrees after the same period. The polyurethane control (**PU11**) demonstrated a color change of 1.07 with gloss values of 1.8 GU at 60 degrees and 6.8 GU at 85 degrees after 500 hours, which is above the MIL-PRF-85285 requirement of $\Delta E \leq 1.0$ for these coatings. **PU9** showed a nominal change in gloss after 500 hours, as did the control, whereas **PU10** showed a 37.7% decrease in gloss at 60 degrees after this period. The Silyl-PU did not contain stabilizers (e.g. UV-absorbers) to increase color and gloss stability, which are present in all MIL-PRF-85285 polyurethanes. Nonetheless, this test demonstrated that Silyl-PU coatings can provide similar performance to a non-silyl containing polyurethane. Per MIL-PRF-85285, **PU9** meets the weatherability requirement for a Type I camouflage aircraft topcoat, whereas **PU10** meets the Type I color change requirement for a gloss aircraft topcoat, but would need to retain a gloss of 80 GU after 500 hours to meet the gloss requirement.

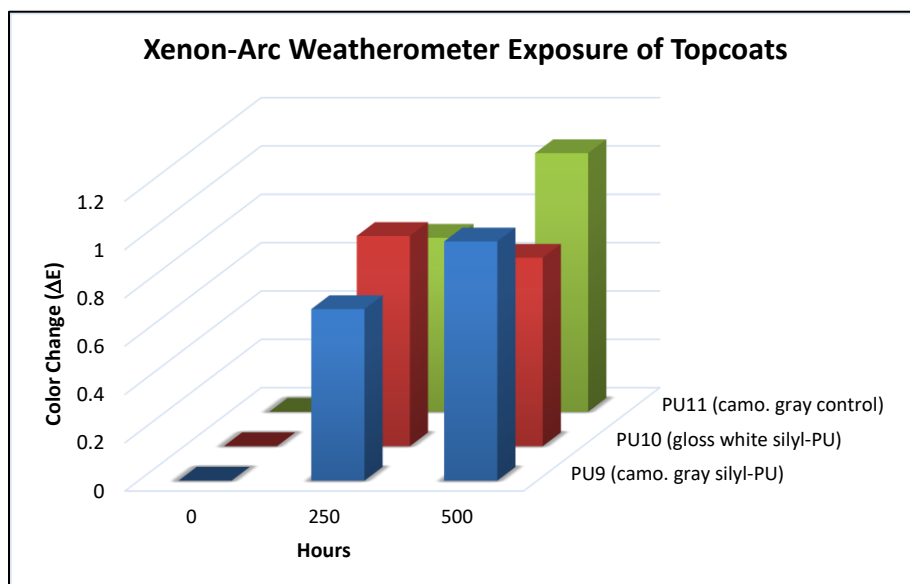


Figure 12 — Color change of polyurethane coatings after 500 hours of Xenon-Arc WOM exposure.

4.2 Exposure of Coatings to Chemical Stimuli

Clear and pigmented Silyl-PU coatings were immersed in a solution of fluoride salt, which is a mild reagent, under static (non-stirring) conditions at room temperature to evaluate their time and degree of removal from the pretreated aluminum alloy. This was accomplished using a 1.0 M solution of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) solvent. As shown in Table 5, the majority of coatings were disassembled and completely removed within 30-60 minutes of static exposure, although **PU8** required only 15 minutes, whereas **PU1** required 120 minutes. The faster removal for **PU8** is due to the presence of several bonds and linkages (e.g. carbamate, carbonate) that can degrade via cascading bond cleavage upon activation of the silyl trigger with fluoride ion, in addition to enhanced solvent interactions due to the presence of pentylene chains and a lower T_g compared to the other clear coatings. On the contrary, the slower disassembly for **PU1** is due to the presence of fewer cleavable bonds and linkages, including reduced chain swelling with THF due to the non-homogeneous nature of the sample. Figure 13a shows removal of **PU8** from the substrate after 15 minutes, and the proposed mechanism of partial chain disassembly for **PU8** is shown in Figure 13b. It has yet to be determined if the oxyanion generated during disassembly of **PU8** reacts intermolecularly with the tethered carbamate linkage to form an 8-membered cyclic carbonate, as this reaction is thermodynamically and entropically unfavorable.

Table 5 — Time required for complete removal of Silyl-PU coatings from pretreated AA substrate upon immersion in 1.0 M TBAF (THF).

Coating	Time of Removal (minutes)
PU1	120
PU2	30
PU3	75
PU4	30
PU5	30
PU6	60
PU7	60
PU8	15
PU9	30
PU10	30

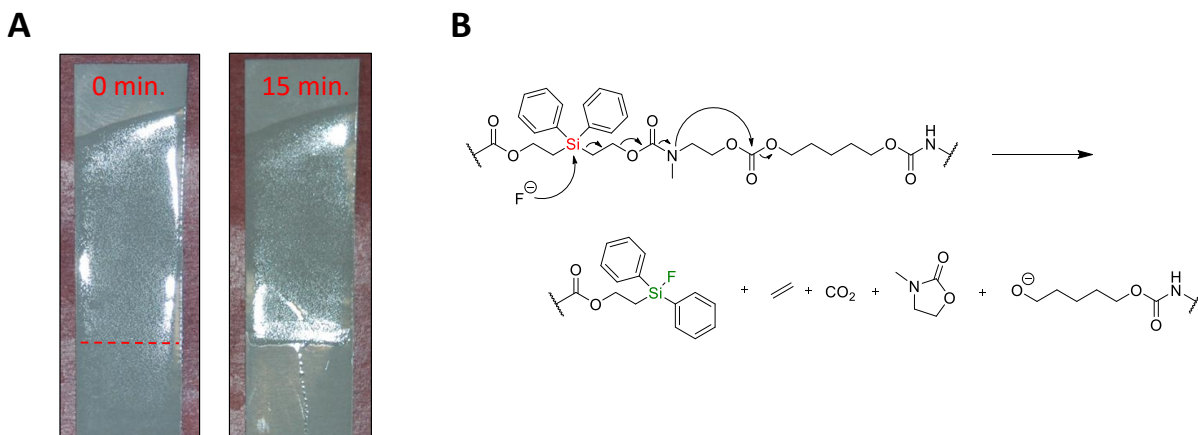


Figure 13 — a) Photographs of **PU8** over pretreated AA before (left) and after 15 minutes (right) of immersion at room temperature in static 1.0 M TBAF (THF), where the red dashed line indicates immersion height, and b) proposed mechanism of partial chain disassembly in **PU8** upon reaction with fluoride ion.

Pigmented and filled Silyl-PU coatings (**PU9** and **PU10**) were completely removed from the pretreated AA substrate within 30 minutes with static 1.0 M TBAF (THF), which was twice as fast as the clear version (**PU6**) of these coatings (figures 14a and 14b). The faster time of disassembly and removal is likely due to their reduced crosslink density, and hence greater swelling with THF, as a result of adding solid particles to the matrix. However, exposure of the polyurethane control (**PU11**) to static 1.0M TBAF (THF) for 6 hours did not result in removal of the coating (figure 14c). The control did show some minor staining due to the TBAF solution, but there was no evidence of blistering, softening, peeling, or other deformities. This demonstrates the ability of the Silyl-PU coatings to be selectively disassembled and removed from a substrate compared to a DoD-grade polyurethane coating.

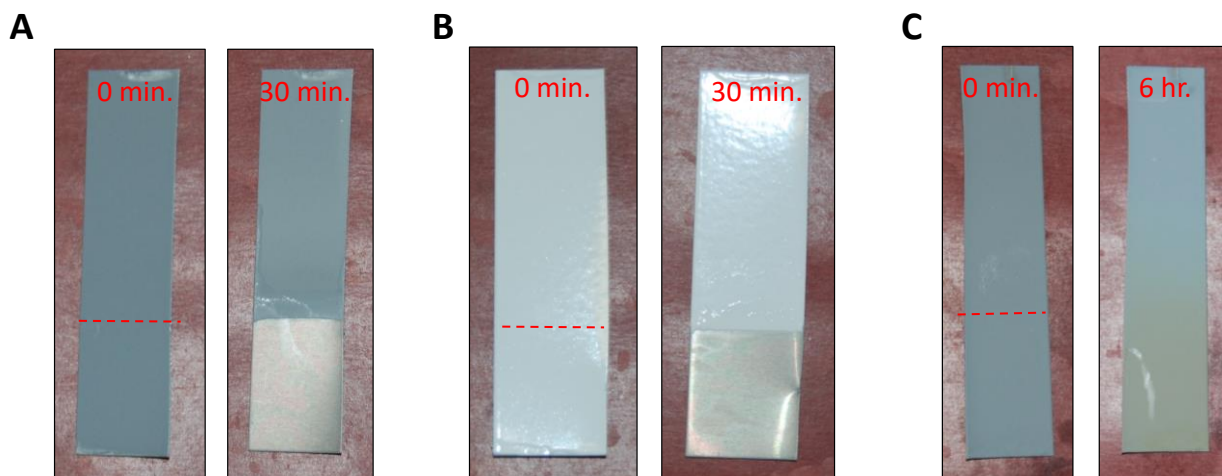


Figure 14 — Photographs of polyurethane coatings over pretreated AA before and after immersion at room temperature in static 1.0 M TBAF (THF): a) **PU9** before (left) and after 30 minutes (right), b) **PU10** before (left) and after 30 minutes (right), and c) **PU11** control before (left) and after 6 hours (right). The red dashed line indicates immersion height.

In addition, immersion of **PU9** and **PU10** in 1.0 M aqueous hydrochloric acid (HCl), 1.0 M aqueous sodium hydroxide (NaOH), 1.0 M aqueous sodium chloride (NaCl) and 1.0 M tetrabutylammonium chloride (TBACl) in THF for 3 hours, and in some instances up to 24 hours, resulted in zero damage to the coatings, showing that the coatings are resistance to disassembly with strong acid, strong base, and chloride-containing salt solutions, in addition to possessing good hydrolytic stability. Unlike harsh acid and base solutions, fluoride ion (fluoride) is a mild and relatively benign chemical reagent. Fluoride is commonly found in drinking water and is essential to maintaining strong bones,[34,35] and numerous brands of commercial toothpaste contain fluoride in effort to prevent cavities in children and adults.[36]

4.3 Selective Removal of Topcoats from Primer

Silyl-PU coatings **PU9** and **PU10**, as topcoats over the green-colored MIL-PRF-23377, Class N (non-chromate) epoxy primer, were evaluated for time and degree of disassembly upon immersion in static 1.0 M TBAF (THF) and 1.0 M TBAF (acetone) solutions at room temperature. As shown in Figures 15a, the majority of the low-gloss gray Silyl-PU topcoat (**PU9**) was removed after 10 minutes, with only minute amounts of the coating remaining on the surface. Complete removal was observed after 20 minutes. For the gloss white Silyl-PU topcoat (**PU10**), a limited amount of coating was removed after 10 minutes, whereas 20 minutes was required for complete removal (figure 15b). The faster time of disassembly for **PU9** and **PU10** over the non-chromate primer, as compared to the coatings over the pretreated AA substrates, can be attributed to the mechanism of binding to the substrates. The pretreated AA panels possess numerous hydroxyl groups due to the chromic acid anodizing treatment, thereby providing sufficient functional groups to form covalent bonds and strong adhesion to the Silyl-PU. However, strong adhesion to the epoxy primer is likely attributed to mechanical bond formation as a result of over-coating with the Silyl-PU within 24 hours of primer application, thereby enabling the outer layers of the coatings to diffuse and their polymer chains to tangle. Exposure of **PU9** and **PU10** to a static solution of 1.0 M TBAF in acetone at room temperature resulted in complete removal of the coatings within 250 minutes (4 hours, 10 min.), thus demonstrating that alternative and “greener” solvents can be used for the removal process (see Appendices 3 and 4). The longer time for removal in acetone compared to THF is likely due to reduced solubility of the network chains with acetone as the disassembly process occurred, in addition to reduced activity of the fluoride ion due to the presence of water in acetone.

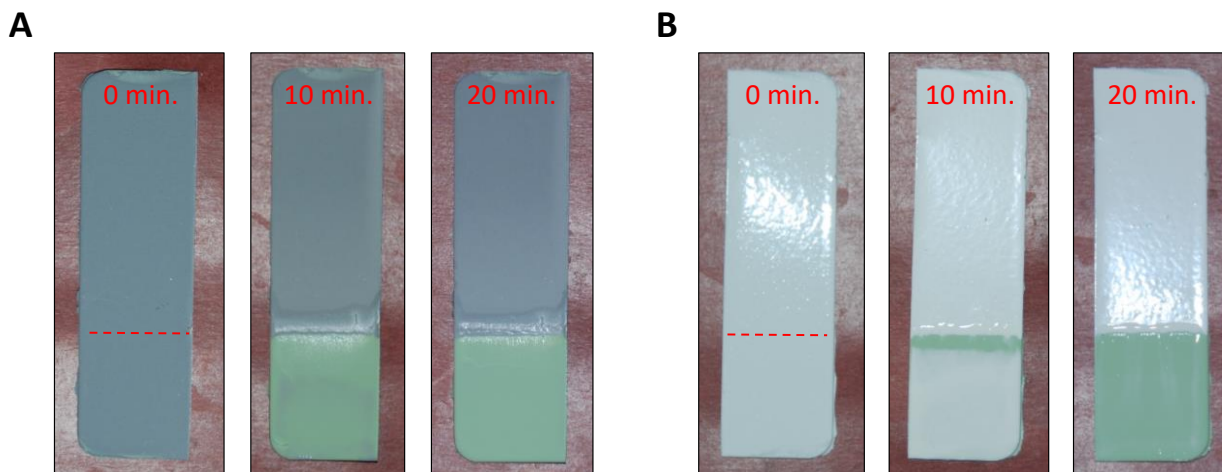


Figure 15 — Time-lapse photographs of polyurethane coatings (as topcoats) over non-chromate epoxy primer before and after immersion at room temperature in static 1.0 M TBAF (THF): a) **PU9** before (left), after 10 minutes (center), and after 20 minutes (right), b) **PU10** before (left), after 10 minutes (center), and after 20 minutes (right). The red dashed line indicates immersion height.

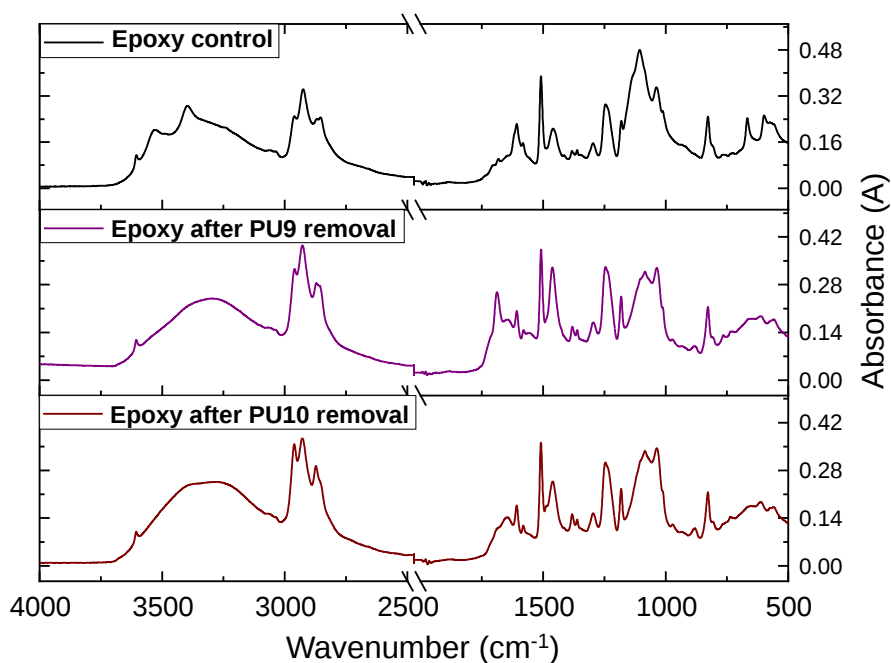


Figure 16 — ATR-IR spectra of non-chromate epoxy primer: non-coated control (top), after removal of Silyl-PU topcoat **PU9** (middle), and after removal of Silyl-PU topcoat **PU10** (bottom).

ATR-IR analysis of the non-chromate epoxy primer after Silyl-PU topcoat removal showed that none of the chemical bonds in the epoxy coating had changed when compared to a pristine (non-coated) primer, thereby demonstrating the primer was undamaged by the fluoride salt solution (figure 16). Mechanical properties of the epoxy primer after were not evaluated because an entire 3x6-inch panel of removed Silyl-PU would be required to conduct a cylindrical mandrel bend or GE Impact test, and a sufficient volume of fluoride salt solution could not be made due to limited commercial quantities of TBAF and delays in product receipt, in addition to its high concentration in THF and acetone solutions.

5. CONCLUSION AND IMPLICATIONS FOR FUTURE RESEARCH

Herein, we have successfully demonstrated, as a proof-of-concept, that stimuli-responsive silyl-containing polyurethane coatings (Silyl-PUs) can be designed to provide similar thermal, mechanical, and performance properties (e.g. GE Impact flexibility, MEK solvent resistance) as a MIL-PRF-85285, Type IV qualified camouflage gray polyurethane topcoat used on Navy and Air Force aircraft. Furthermore, when pigmented and filled to generate low gloss gray and gloss white Silyl-PUs the coatings exhibited similar weatherability as the qualified polyurethane topcoat, in addition to excellent adhesion to a MIL-PRF-23377, Class N (non-chromate) epoxy primer. However, the pigmented and filled Silyl-PUs, when exposed to a mild and relatively benign fluoride salt solution of TBAF in THF or acetone, were completely disassembled and removed within 20 or 250 minutes, respectively. Removal of the topcoats revealed the underlying non-chromate epoxy primer, which was not chemically damaged by the stimulus according to infrared analysis. Immersion of the polyurethane control coating in these fluoride salt solutions resulted in no damage (e.g. blisters, wrinkling) or removal of the coating, thus illustrating that the Silyl-PUs are selectively activated. Attempts to remove the Silyl-PUs with strong acid, strong base, and chloride-containing salt solutions were unsuccessful. The success of this limited scope project has enabled maturation of the technology to a TRL of 3-4.

This technology has potential applications as selectively removable topcoats, which could leave an underlying primer or composite intact upon removal. This would prevent the exposure of hazardous materials (e.g. hexavalent chromium) to workers and the environment, in addition to reducing costs for hazardous waste disposal and reapplication of the primer or fabrication of a new composite component. The concept of a selectively strippable topcoat is illustrated in Figure 17, where the gray topcoat on an F/A-18 aircraft is selectively activated and removed with a fluoride salt composition. The toothbrush is included to enhance the concept of removal via “fluoride”, which is commonly found in toothpaste.[36]

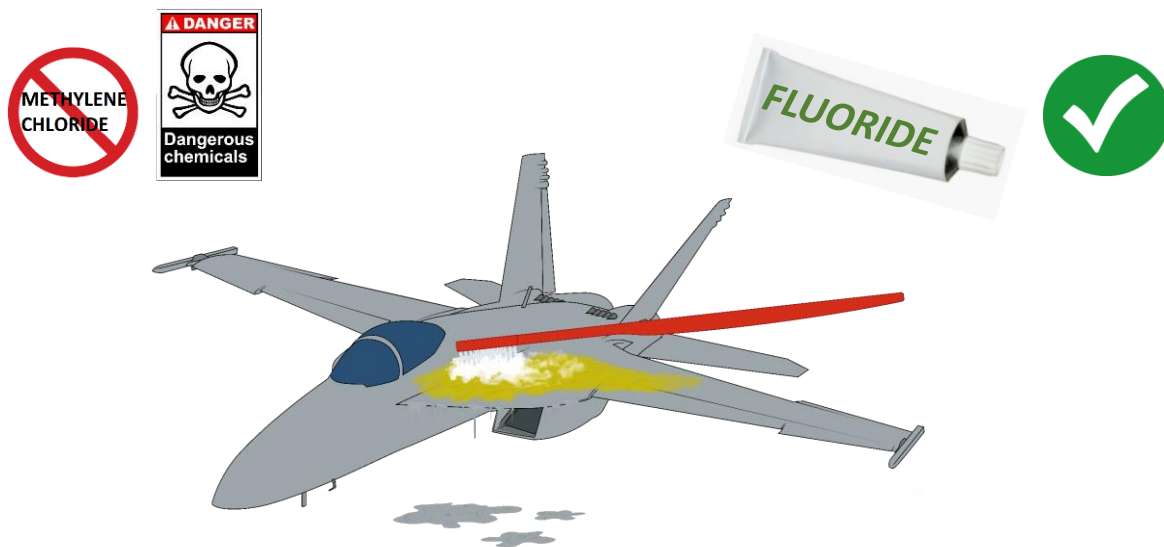


Figure 17 — Illustration of a gray topcoat on an F/A-18 aircraft being selectively removed with a fluoride salt composition and toothbrush rather than toxic methylene chloride. The yellow area represents intact hexavalent chromium containing epoxy primer after selective removal of the topcoat.

Currently, the main issue hindering scale-up of the technology is the synthesis of 2,2'-(diphenylsilanediyl)bis(ethan-1-ol) (**3**), which is the starting silyl diol (see Section 3.1). This diol is not commercially available and is synthesized on a gram scale by NRL using large quantities of hydroboration

and oxidation reagents, including time-consuming purification methods, which are not optimal for producing kilogram quantities of material. In effort to resolve this issue an alternative pathway for synthesis of silyl diol **3**, optimally in a single step from diphenyldivinylsilane (**2**), must be developed. We have attempted to use hydrosilylation reaction conditions to synthesize silyl diol **3**, which have resulted in low yields thus far, although limited time was spent on this issue because it was outside the scope of the project. This issue could be addressed during a follow-on 3-year SERDP project, as well as locating a manufacturer to synthesize large quantities of the silyl diol.

A second issue that must be overcome to mature the technology is formulation of a fluoride salt composition that possesses properties of a paint stripper and meets MIL-R-81294 requirements. During this project we were only able to evaluate fluoride salt compositions in the form of solutions, and we have yet to evaluate solvents other than THF and acetone. An ideal stripper must possess thixotropic and other properties, which would require the use of alternative solvents, various additives, and potentially the use of alternative fluoride salts. Furthermore, it remains unknown if a subsequent polyurethane topcoat can be sufficiently adhered to the primer, without additional surface preparation, after removal of the first topcoat, nor is the number of topcoat and removal cycles known. These issues could also be addressed under a follow-on 3-year SERDP project.

A quart-sized solution of TBAF in acetone is currently being evaluated for sandwich corrosion and hydrogen embrittlement at NAWC-AD according to TT-R-2918 requirements.[2] However, the solution did not contain corrosion inhibitors, the viscosity was not optimal for a paint stripper, and acetone is not an ideal solvent for a stripper because it possesses a high evaporation rate. Furthermore, only one solution was provided to NAWC-AD due to limited quantities of commercially available TBAF. Test results will be reported in a future communication.

6. LITERATURE CITED

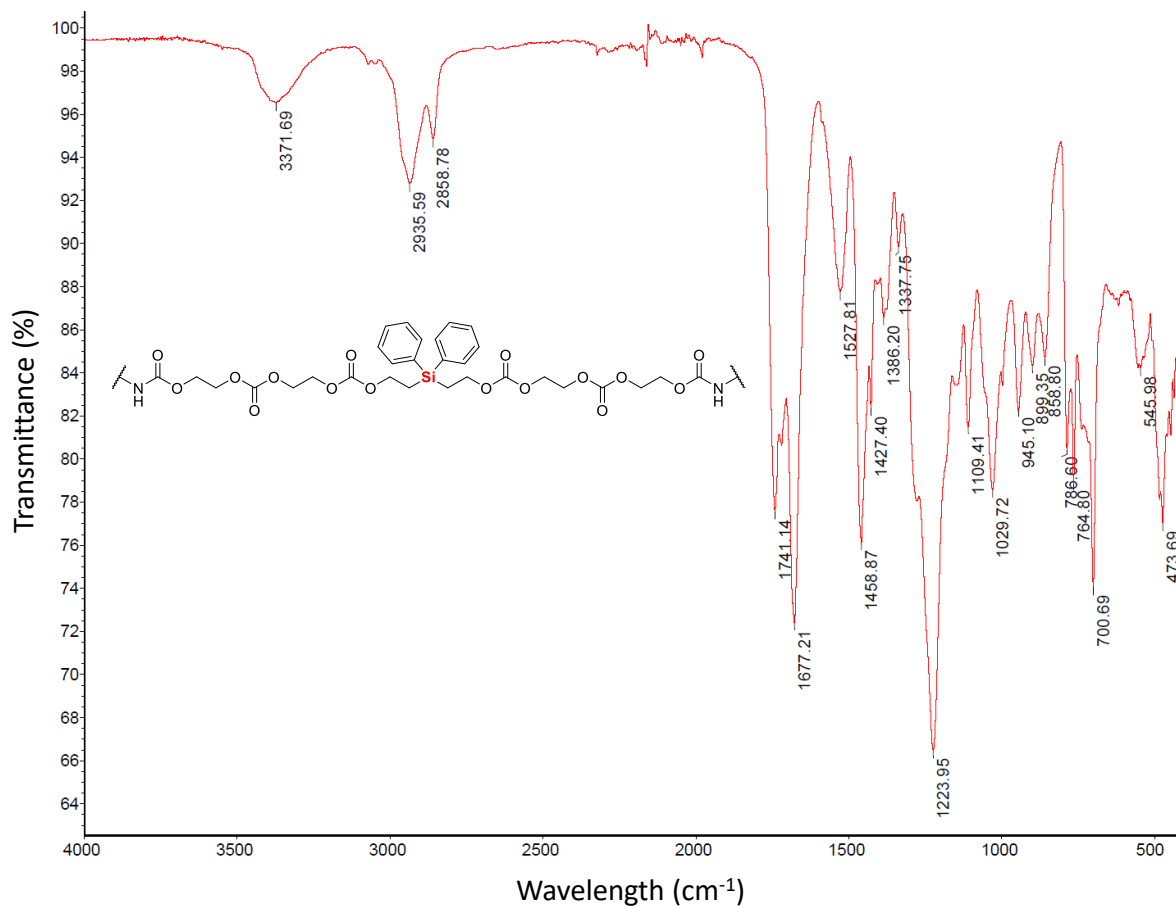
1. MIL-PRF-85285E Performance Specification, "Coating: Polyurethane, Aircraft and Support Equipment", 12 January 2012.
2. a) MIL-R-81294 Military Specification, "Remover, Paint, Epoxy, Polysulfide, and Polyurethane Systems", 31 December 1990; b) TT-R-2918A Federal Specification, "Remover, Paint, Non-Hazardous Air Pollutants (HAPS)", 19 March 2001.
3. J. Durkee, "Paint Stripping: It's Just Like Parts Cleaning", *Met. Finish* **2009**, 107, 49.
4. a) J. MacIsaac, R. Harrison, J. Krishnaswami, J. McNary, J. Suchard, M. Boysen-Osborn, H. Cierpich, L. Styles and D. Shusterman, "Fatalities Due to Dichloromethane in Paint Strippers: A Continuing Problem", *Am. J. Ind. Med.* **2013**, 56, 907, b) Occupational Safety and Health Administration, "Methylene Chloride", <https://www.osha.gov/methylene-chloride>, accessed 18 August 2021.
5. a) Occupational Safety and Health Administration (OSHA), "General Industry Standards (29 CFR 1910.1052) for Methylene Chloride", <https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1052>, accessed 18 August 2021, b) "EPA Bans All Retail Distribution of Methylene Chloride to Consumers for Paint and Coating Removal", 22 November 2019, <https://www.epa.gov/newsreleases/epa-bans-all-retail-distribution-methylene-chloride-consumers-paint-and-coating-removal>, accessed 18 August 2021, c) "EPA's Methylene Chloride Ban Excludes Workers", 18 March 2019, <https://www.webmd.com/lung/news/20190318/epa-methylene-chloride-ban-excludes-workers>, accessed 18 August 2021.
6. a) B. E. Erickson, "Replacing Methylene Chloride in Paint Strippers", *C&E News*, 11 June 2018, <https://cen.acs.org/safety/consumer-safety/Replacing-methylene-chloride-paint-strippers/96/i24>, accessed 18 August 2021, b) R. Pauli, "Alternative Processes to Methylene Chloride", 1996, <http://www.nmfr.org/pdf/pf0697b.htm>, accessed 18 August 2021, c) "Benzyl Alcohol Paint Stripping", August 2001, https://p2infohouse.org/ref/20/19926/P2_Opportunity_Handbook/5_9.html,

- accessed 18 August 2021, d) J. Escobar, “Aircraft De-painting: Variety of Products Available to Remove Paint From Your Aircraft”, 1 March 2002, <https://www.aviationpros.com/home/article/10387618/aircraft-depainting-variety-of-products-available-to-remove-paint-from-your-aircraft>, accessed 18 August 2021.
7. PPG Aerospace, “Selectively Strippable System”, http://www.ppgaerospace.com/getmedia/2f5ac92b-1b96-4796-aa7f-864f1ed9a7d6/PPG_AS_SSS_10-2013.pdf, accessed 18 August 2021.
 8. US Army TACOM-ARDEC, “Laser Cleaning and Coatings Removal”, SERDP WP-139, completed October 1998.
 9. G. Mongelli, “Portable Laser Coating Removal System (PLCRS)”, ESTCP WP-200027, completed September 2005.
 10. T. Hoehman, “Robotic Laser Coating Removal System (RLCRS)”, ESTCP WP-200526, completed August 2008.
 11. A. Fletcher, “High-Speed, Substrate Safe Low Observable Coating Laser Stripping”, SERDP WP-2146, completed November 2016
 12. S. Ma and D. C. Webster, “Degradable Thermosets Based on Labile Bonds or Linkages: A Review”, *Prog. Polym. Sci.* **2018**, 76, 65.
 13. J. R. Griffith, “Epoxy Resins Containing a Specific Vulnerability”, *ACS Symp. Ser.* **1979**, 114, 259.
 14. S. L. Buchwalter and L. L. Kosbar, “Cleavable Epoxy Resins: Design for Disassembly of a Thermoset”, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, 34, 249.
 15. J. M. Garcia, G. O. Jones, K. Virwani, B. D. McCloskey, D. J. Boday, G. M. ter Huurne, H. W. Horn, D. J. Coady, A. M. Bintaleb, A. M. S. Alabdulrahman, F. Alsewailem, H. A. A. Almegren and J. L. Hedrick, “Recyclable, Strong Thermosets and Organogels via Paraformaldehyde Condensation with Diamines”, *Science* **2014**, 344, 732.
 16. G. C. Daniels, E. Camerino, J. H. Wynne and E. B. Iezzi, “Cross-Linked Networks that Selectively and Controllably Disassemble On-Demand via Cascading Bond Cleavage”, *Mater. Horiz.* **2018**, 5, 831.
 17. E. B. Iezzi, E. Camerino, G. Daniels and J. H. Wynne, “Silyl-Containing Alcohols and Amines for Thermosets that Disassemble On-Demand”, U.S. Patent 10,730,993, 4 August 2020.
 18. E. B. Iezzi, E. Camerino, G. C. Daniels, J. H. Wynne, Silyl-containing polyurethanes that selectively disassemble with fluoride salts. *Coatings Tech.* **2020**, 17, 26.
 19. E. Camerino, G. C. Daniels, J. H. Wynne and E. B. Iezzi, “Synthesis and Kinetics of Silyl-Containing Ethoxycarbonyls using Fluoride Ions”, *RSC Adv.* **2018**, 8, 1884.
 20. MIL-PRF-23377K Performance Specification, “Primer Coatings: Epoxy, High-Solids”, 7 June 2012.
 21. Y. Fernandes, A. Brya, S. De Persis, “Thermal Degradation Analyses of Carbonate Solvents used in Li-Ion Batteries”, *J. Power Sources* **2019**, 414, 250.
 22. N. J. Daly, F. Ziolkowski, “The Thermal Decompositions of Carbamates. IV. The Ethyl *N*-Methyl-Carbamate System”, *Int. J. Chem. Kinet.* **1980**, 12, 241.
 23. E. Hablot, D. Zheng, M. Bouquey, L. Avérous, “Polyurethanes based on castor oil: kinetics, chemical, mechanical and thermal properties”, *Macromol. Mater. Eng.* **2008**, 293, 922.
 24. P. J. Driest, D. J. Dijkstra, D. Stamatiadis, D. W. Grijpma, “The trimerization of isocyanate-functionalized prepolymers: an effective method for synthesizing well-defined polymer networks”, **2019**, 40, 1800867.
 25. V. V. Gite, P. P. Mahulikar, D. G. Hundiware, “Preparation and properties of polyurethane coatings based on acrylic polyols and trimer of isophorone diisocyanate”, *Prog. Org. Coat.* **2010**, 68, 307.
 26. S. Shia, D. Shena, T. Xua, Y. Zhang, “Thermal, optical, interfacial and mechanical properties of titanium dioxide/shape memory polyurethane nanocomposites”, *Compos. Sci. Technol.* **2018**, 164, 17.
 27. ASTM D522, “Standard Test Method Mandrel Bend Test of Attached Organic Coatings”, Test Method B (Cylindrical Mandrel), 15 September 1993.
 28. ASTM D6905, “Standard Test Method for Impact Flexibility of Organic Coatings”, 10 May 2003.
 29. ASTM D5402, “Standard Practice for Assessing the Solvent Resistance of Organic Coatings Using Solvent Rubs”, 15 May 1993.

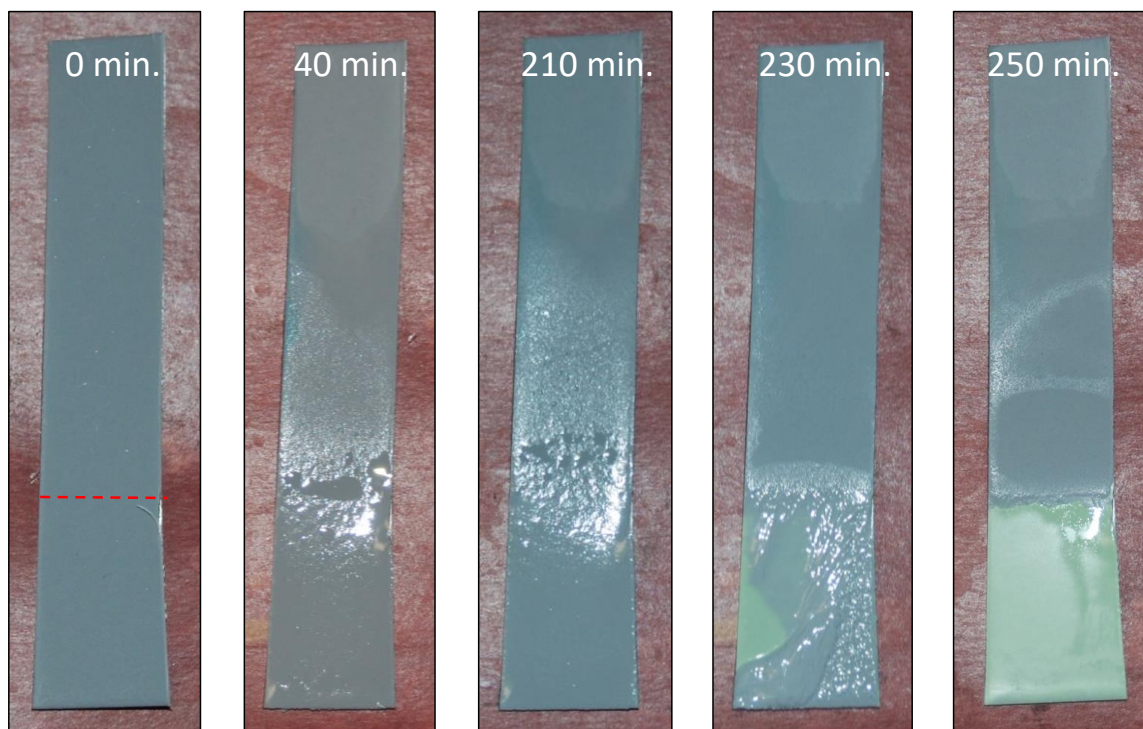
30. ASTM D3359, “Standard Test Method for Measuring Adhesion by Tape Test”, Method A (X-Cut) and Method B (Cross-Cut), 10 August 2002.
31. ASTM G155, “Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials”, 1 October 2005.
32. ASTM D2244, “Standard Practice for Calculation of Color Tolerance and Color Differences from Instrumentally Measured Color Coordinates”, 10 June 2002.
33. ASTM D523, “Standard Test Method for Specular Gloss”, 31 March 1989.
34. Environmental Protection Agency, “Review of the Fluoride Drinking Water Regulation”, <https://www.epa.gov/dwsixyearreview/review-fluoride-drinking-water-regulation>, accessed 7 September 2021.
35. Center for Disease Control and Prevention, “Water Fluoridation Additives”, <https://www.cdc.gov/fluoridation/engineering/wfadditives.htm>, accessed 7 September 2021.
36. American Dental Association, “Fluoridation FAQs”, <https://www.ada.org/en/public-programs/advocating-for-the-public/fluoride-and-fluoridation/fluoridation-faq>, accessed 7 September 2021.

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7.2 Appendix 2 – ATR-IR Spectra of Silyl-PU Coating PU5



7.3 Appendix 3 – Removal of Silyl-PU Coating PU9 from Epoxy Primer with 1.0 M TBAF (Acetone)



7.4 Appendix 4 – Removal of Silyl-PU Coating PU10 from Epoxy Primer with 1.0 M TBAF (Acetone)

