NDSU NORTH DAKOTA STATE UNIVERSITY

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Please find enclosed the following documentation for ONR grant N00014-12-1-0482:

SF298
Final Technical Report

Sincerely,

Dean C. Webster
Professor and Chair

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14. ABSTRACT

To address the need for modern ship hull coatings that can reduce the accumulation of fouling organisms without using toxic chemicals, this project has focused on the exploration of coatings that self-stratify into a low surface energy top layer and a tough and durable bulk layer. The basic technology combines siloxane with polyurethane, with the siloxane providing the low surface energy surface and the polyurethane yielding good adhesion to the marine primer and an overall tough coating system. Variations on this technology have been explored and a number of promising coating compositions have been identified for further optimization.

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Abstract

To address the need for modern ship hull coatings that can reduce the accumulation of fouling organisms without using toxic chemicals, this project has focused on the exploration of coatings that self-stratify into a low surface energy top layer and a tough and durable bulk layer. The basic technology combines siloxane with polyurethane. First, the impact of damage on the properties of the siloxane-polyurethane (SiPU) coating system was explored and it was shown that siloxane is still prevalent on the surface after controlled abrasion. The use of silicone oil additives was shown to be able to improve the fouling-release properties of the SiPU coatings. Field testing at multiple test sites supported this conclusion. Approaches to generating coatings having amphiphilic surfaces are also showing promise as coatings that can resist adhesion for a wide variety of fouling organisms with several systems showing good results in laboratory assays. Finally, some initial work has been undertaken to explore a self-stratifying non-isocyanate polyurethane system and the preliminary results show that this is a promising approach for further investigation.

Technical Section

Technical Objectives

The project had two main focus areas: 1) Further exploration and development of the siloxane-polyurethane fouling-release coating system leading to a detailed understanding of the impact of coating design parameters on the morphology and performance of the coatings and 2) Exploration of methods to use the concept of self-stratification to develop tough coatings having an amphiphilic surface, to incorporate fouling deterrence into the coating system.

Technical Approach

The overall experimental strategy and approach to designing coatings formulations involves first carefully designing experiments to systematically explore a specific aspect of the chemistry or composition of the coatings; using either conventional laboratory methods or C/HT methods to prepare the polymers and coatings, as appropriate; screening the coatings for surface energy using contact angle measurements, pseudobarnacle adhesion, laboratory biological assays with marine bacteria (2 species), algae (2 species), and barnacles. As a general assessment of the coatings' stability in water, surface energy and pseudobarnacle measurements are made after the coatings have been immersed in water for at least a month. Additional screening assessments include thermal analysis using DSC, dynamic mechanical analysis using the parallel DMTA, and toughness measurements using our in-house puncture testing system. Field testing of promising compositions identified through the laboratory screening will be carried out at ONR-sponsored test sites.

Technical Progress

Background

This project built on the successful results obtained in the prior series of ONR-funded projects, the most recently being the Marine Coatings Productization project. In these past projects we developed the combinatorial and high throughput methodology for use in coatings synthesis and screening which included the development of a series of laboratory assays using marine organisms. The concept of self-stratification wherein a low surface energy component predominates on the surface of a coating system was shown to be a promising approach to the design of tough fouling-release coatings. The combinatorial and high throughput methodology was used effectively in identifying and optimizing the compositions by combining well-designed experiments with the suite of high throughput characterization methods.

The siloxane-polyurethane coating system consists of a reactive poly(dimethyl siloxane) (PDMS), a polyol, and a polyisocyanate. Experiments have shown that the aminoalkyl end group on the PDMS yields the best fouling-release performance and that higher molecular weight PDMS also results in better fouling-release properties. Initial experiments used a polycaprolactone polyol and additional studies were carried out to identify a suitable composition for a more hydrolytically-stable acrylic based polyol. Several different aliphatic polyisocyanates have been used in the formulation of coatings, but the best properties result with a cycloaliphatic polyisocyanate is used. Some experiments indicated that a monofunctional PDMS yielded better performance than a difunctional PDMS. However, recently, an experiment was carried out showing that changing the formulation (e.g. solvent) could lead to a coating using the difunctional PDMS that had good performance properties. Since the difunctional PDMS is easier to synthesize and lower in cost, this result shows that the difunctional PDMS can be successfully used to obtain the desired fouling-release properties.

A grooming study was carried out at FIT and showed that the siloxane-polyurethane system was mechanically robust and was able to maintain its fouling-release performance over many cycles of fouling and cleaning.

Since the surface composition of the siloxane-polyurethane coating system is comprised of PDMS, the fouling-release properties are similar to the of PDMS elastomer coatings. That is, there are some marine organisms, such as diatoms, that are able to adhere well to these coatings. The concept of an amphiphilic coating—wherein both hydrophobic and hydrophilic groups are present on the surface—has been shown by other researchers to be a promising approach to reducing the adhesion of a broad variety of marine fouling organisms. To make use of the amphiphilic coating concept in the self-stratifying coatings, we have explored several approaches for attaching hydrophilic groups to the PDMS while maintaining the presence of the reactive functional groups. In all cases we were able to demonstrate that the PDMS component was able to bring the hydrophilic group to the surface, leading to self-stratified coatings having amphiphilc surfaces. In all cases we observed that the release properties of diatoms was significantly improved, however, in some cases the release properties of green algae and barnacles was impaired. One system where PEG chains were grafted onto the PDMS backbone appeared to yield good release properties for all organisms. These concepts appear to be promising, however, further tuning and optimization of the compositions is needed.

Task 1. Further exploration of the siloxane-polyurethane coating system

a. Understand the release mechanism from siloxane-polyurethane coatings

This task was not carried out in order to focus on other activities.

b. Characterize siloxane-polyurethane stratification

XPS experiments were carried out using Ar ion milling to characterize the stratification of two different siloxane-polyurethane formulations that show different biofouling performance in different environments. The experiments showed a clear different in stratification between the two coating system with one having a very distinct overlayer of PDMS and the other showing that the PDMS was more uniformly mixed with the coating system as a function of depth. Details are presented in **Appendix A**. This methodology is continuing to be used in additional studies, such as the recently published study on silicone oil incorporation.

c. Explore siloxane-polyurethane coatings as groomable surfaces

To understand the effect of damage or cleaning on the surfaces of siloxane-polyurethane coatings, a controlled laboratory experiment has been carried out. In previous reports, the method used and some of the results describing the effects of abrasion on the surface properties and roughness of the surfaces has been reported. In this past year, additional analysis of the roughness of the coatings has been carried out as has additional bioassays to determine the effect of abrasion on fouling-release properties. Details are provided in a draft manuscript being prepared for publication: **Appendix B**.

d. Study the impact of PDMS architecture on surface properties and coatings performance

A study was carried out exploring the incorporation of phenyl silicone oils into the siloxane-polyurethane coating system. Briefly, a series of phenyl-containing silicone oils were added to a standard siloxane-polyurethane system to generate coatings with mobile surfaces to provide release to biofouling organisms due to interfacial slippage. The coatings were subjected to surface analysis using contact angle measurements and XPS experiments and then using laboratory biological assays. From the laboratory results, two coatings were selected for field testing at three different test sites and the results tended to confirm that the silicone oil did improve the fouling-release performance of the coatings. Details are provided in **Appendix C**, which is the manuscript accepted for publication in *ACS Applied Materials & Interfaces*.

Task 2. Design approaches to polyurethane coatings having amphiphilic surfaces

Since some work seems to indicate that amphiphilic surfaces—surfaces having mixed low and high surface energy components—may tend to deter a broad variety of fouling organisms, we have been exploring different approaches to implementing this concept with the self-stratified siloxane-polyurethane coatings system. One approach has been to attach hydrophilic groups to the siloxane used in the coatings so that the low surface energy siloxane will bring the hydrophilic components to the surface along with it. Approaches with carboxylic acid groups, zwitterionic groups, and PEG groups have been assessed, with the PEG approach the most promising (publication forthcoming). However attaching PEG chains to a functional siloxane proved challenging and is not likely to be commercially feasible. Thus, we are exploring alternative methods to join siloxane and hydrophilic groups together to create a polyurethane coating having an amphiphilic surface.

One approach that was explored was to create an isocyanate functional prepolymer where the siloxane and PEG components are pre-reacted and then mix this into the polyurethane coating system. An advantage of this approach is that we don't have a mixture of reaction kinetics occurring during film formation and therefore the properties of the coating might not be as sensitive to the film formation process. In addition, preliminary bioassays appear promising, showing that some coatings have good release of a broad variety of fouling organisms. Details are provided in **Appendix D**, which is the manuscript accepted for publication in *Journal of Coatings Technology and Research.*

In previous studies in our group, we had explored the use of siloxanes having grafted carboxylic acid groups as an approach to generating coatings having amphiphilic surfaces. The results of that study did indicate that the fouling organisms were responsive to the changes in surface chemistry, but an optimum coating having good release for a broad spectrum of organisms was not identified. In an attempt to further optimize that coating system, a study was carried out where the siloxane component of the siloxane-polyurethane consisted of mixtures of an acid functional siloxane along with the standard siloxane in order to vary the acid content of the coating surface. As with the previous study, an optimum coating system could note identified. Details of the study are provided in **Appendix E**.

A further study was carried out to explore the design of polyurethane systems having highly hydrophilic surfaces. Both polyethylene glycol and a zwitterionic compound were used as the hydrophilic component. Many of the coatings demonstrated rapid surface reconstruction from a hydrophobic to hydrophilic surface. The laboratory bioassays identified a number of coatings that had properties superior to the control siloxane-polyurethane system. The results are in **Appendix F**. This work will form the basis for work in the next project.

Task 3. Field testing of promising compositions

A set of experimental and control coatings was subjected to field testing at several different ONR field testing sites: California, Hawaii, and Singapore. In addition to two variations of the basic siloxane-polyurethane coatings, two coatings from the acid functional siloxane set (described in Appendix E) and two coatings from the silicone oil study (Appendix C) were included in the experimental matrix. The results for the silicone oil coatings and the controls are described in Appendix C. Neither of the acid functional siloxane coatings had good fouling-release performance and so that approach has now been abandoned.

Task 4: New Direction: Coatings based on Glycidyl Carbamate Technology

While the self-stratified siloxane-polyurethane coating system is showing great prospects as a tough and durable fouling-release coating, concerns have been raised over the use of isocyanates as a component of the coating system. Isocyanates can present a hazard to the workers applying the coatings (although proper engineering controls can mitigate this) and also isocyanate coatings may be sensitive to variations in ambient humidity. Therefore, the exploration of a non-isocyanate polyurethane system has been explored as an alternative. Glycidyl (GC) carbamate resins are epoxy functional resins that incorporate carbamate or urethane groups and the Webster research group has been exploring this technology for a number of years for high performance coatings in applications such as non-skid coatings for ship decks and primers for aircraft. An advantage of this technology is that the end users use epoxy-amine chemistry and are not exposed to isocyanates during coating application. Plus, the epoxy group appears to have a higher reactivity in curing with amines than a standard bisphenol-A epoxy, resulting in more rapid curing.

We started with synthesizing a siloxane-polyurethane coating system based on GC chemistry and have explored the effect of different amounts of siloxane and different amine crosslinkers on the properties of the coatings. This initial study is described in detail in **Appendix G**. Due to the generally positive results we have been obtaining with the amphiphilic coating approach, the work has been extended into the area of an amphiphilic system with siloxane being used for the hydrophobic component and poly(ethylene glycol) as the hydrophilic component. Some preliminary bioassays are promising and additional work with this approach will be carried out in the future. Details of the work are provided in **Appendix H**.

Progress Statement

During the course of the project we have had three graduate students and a number of undergraduate researchers carrying out the main research project along with Shane Stafslien and his staff providing the bioassays for the experimental coatings. Bioassays have also been conducted by the University of Newcastle. The work involving the abrasion of the siloxane-polyurethane (SPU) coatings was completed with the general finding that abrasion doesn't significantly reduce the amount of siloxane on the surface, however, some abrasives can induce a texture on the surface that can reduce barnacle adhesion. We have explored the use of phenyl containing silicone oils as a modifier for the SPU system and several coatings are promising. We have also further pursued previous approaches to amphiphilic surfaces in an attempt to further fine tune the surface composition to yield good release performance for a broader range of organisms. A new approach to amphiphilic coatings appears to be very promising. A set of six experimental selected from several different technologies and two control coatings were subjected to field testing. The results from these field tests have been interesting and similar performance was observed at the different field testing sites. To eliminate the use of polyisocyanates in the coating application process, we have been evaluating a new approach to self-stratified fouling-release coatings using glycidyl carbamate (GC) resins. GC resins are epoxy resins containing carbamate or urethane groups. They can be crosslinked with amines and we have begun the exploration of the incorporation of amine-terminated siloxanes into the GC resin system. Both low surface energy and amphiphilic coating systems are being explored and several approaches appear to be promising in laboratory assays.

Refereed Journal Articles

- Teluka Galhenage, Dylan Hoffman, Samantha Silbert, Shane Stafslien, Justin Daniels, Tatjana Miljkobic, John Finlay, Sofia Franco, Anthony Clare, Brian Nedved, Michael Hadfield, Dean Wendt, Grant Waltz, Lenora Brewer, Serena Teo, Chin-Sing Lim, Dean Webster, "Fouling-release performance of silicone oil-modified siloxane-polyurethane coatings," *ACS Applied Materials and Interfaces*, in press (2016). DOI: 10.1021/acsami.6b09484
- Teluka P. Galhenage, Dean C. Webster, Augusto M. S. Moreira, Ryan J. Burgett, Shane J. Stafslien, Lyndsi Vanderwal, John A. Finlay, Sofia C. Franco, Anthony S. Clare, "Poly (ethylene) glycol-modified, amphiphilic, siloxane polyurethane coatings and their performance as fouling-release surfaces," *J. Coat. Tech. Res.*, in press (2016).
- Shane J. Stafslien, Stacy Sommer, Dean C. Webster, Rajan Bodkhe, Robert Pieper, Justin Daniels, Lyndsi Vander Wal, Rhiannon David, Maureen C. Callow, James A Callow, Emily Ralston, Geoff Swain, Lenora Brewer, Dean Wendt, Gary H. Dickinson, Chin-Sing Lim, Serena Lay-Ming Teo, "Comparison of laboratory and field testing performance evaluations of siloxane-polyurethane fouling-release marine coatings," *Biofouling*, 32, 949-968 (2016). DOI: 10.1080/08927014.2016.1211269
- Chin-Sing Lim, Serena Lay-Ming Teo, Gary H. Dickinson, Stacy Sommer, Rajan B. Bodkhe, Dean C. Webster, Young Ying Loo, "A small-scale waterjet test method for screening novel foul-release coatings," *J. Coat. Tech. Res.*, 12, 533- 542 (2015). DOI: 10.1007/s11998-014-9648-x
- Rajan B. Bodkhe, Shane J. Stafslien, Justin Daniels, Nicholas Cilz, Andrew J. Muelhberg, Stephanie E. M. Thompson, Maureen E. Callow, James A. Callow, Dean C. Webster, "Zwitterionic siloxane-polyurethane fouling-release coatings," *Prog. Org. Coat.*, 78, 369-380 (2015). DOI: 10.1016/j.porgcoat.2014.07.011
- Rajan B. Bodkhe, Dean C. Webster, "Synthesis and characterization of novel polysiloxane based ABA-type triblock copolymers using ATRP," *e-Polymers*, 13, 124-134 (2014).
- Shane Stafslien, Justin Daniels, James Bahr, Bret Chisholm, Abdullah Ekin, Dean Webster, Beatriz Orihuela, Daniel Rittschof, "An improved laboratory reattachment method for the rapid assessment of adult barnacle adhesion strength to fouling-release marine coatings," *J. Coat. Tech. Res.*, 9, 651-665 (2012).

- Rajan B. Bodkhe, Shane J. Stafslien, Nicholas Cilz, Justin Daniels, Stephanie E. M. Thompson, Maureen E. Callow, James A. Callow, Dean C. Webster, "Polyurethanes with amphiphilic surfaces made using telechelic functional PDMS having orthogonal acid functional groups," *Prog. Org. Coat.*, 75, 28-38 (2012). DOI: 10.1016/j.porgcoat.2012.03.006
- Rajan B. Bodkhe, Stephanie E.M. Thompson, Carolyn Yehle, Nicholas Cilz, Justin Daniels, Shane J. Stafslien, Maureen E. Callow, James A. Callow, and Dean C. Webster, "The effect of formulation variables on fouling-release performance or stratified siloxane-polyurethane coatings," *J. Coat. Tech. Res.*, 9, 235-249 (2012).

Books And Chapters

- None

Technical Reports

- None

Contributed Presentations

- Dean C. Webster, "Tough and durable amphiphilic fouling-release coatings," 18th International Congress on Marine Corrosion and Fouling, Toulon, France, June 19-24, 2016.
- Madhura Pade, Jackson Benda, Dean Webster, Shane Stafslien, Lyndsi Vanderwal, "Non-toxic isocyanate-free fouling-release coatings," 12th National Graduate Research Polymer Conference, Akron, Ohio, June 19-22, 2016. Oral.
- Madhura Pade, Jackson Benda, Dean C. Webster, "Novel non-isocyanate siloxane-polyurethane coatings," American Coatings Conference, Indianapolis, Indiana, April 11-13, 2016. Oral.
- Teluka Galhenage, Dean C. Webster, Augusto Moreira, Ryan J. Burgett, Shane J. Stafslien, Lyndsi Vanderwal, John A. Finlay, Sofia C. Franco, Anthony S. Clare, "Poly(ethylene glycol) modified amphiphilic siloxane polyurethane coatings and their performance," American Coatings Conference, Indianapolis, Indiana, April 11-13, 2016. Oral. Winner of the 1st Place Roon Award.
- Madhura Pade, Jackson Benda, Dean Webster, Shane Stafslien, Lyndsi VanderWal, Non-isocyanate approach for the synthesis of polyurethane fouling-release coatings," ACS National Meeting, San Diego, Ca., March 13-17, 2016. Poster.
- Teluka Galhenage, Dean Webster, Augusto Moreira, Shane Stafslien, Lyndsi VanderWal, John Finlay, Sofia Franco, Tony Clare, "Poly(ethylene glycol) modified amphiphilic siloxane polyurethane coatings and their performance as effective fouling release surfaces," ACS National Meeting, San Diego, Ca., March 13-17, 2016.
- Dean C. Webster, "Approaches to tough coatings that resist adhesion by marine fouling organisms," Keynote lecture, 39th Annual Meeting, The Adhesion Society, San Antonio, Texas, February 21-24, 2016. Invited.
- Dean C. Webster, "Tough and cleanable fouling-release marine coatings via self-stratification," Pacific Polymer Conference 14, Kawai, Hawaii, December 9 – 13, 2015. Invited.
- Madhura Pade, Dean C. Webster, "Water dispersible glycidyl carbamate coatings for fouling-release applications," Pacific Polymer Conference 14, Kawai, Hawaii, December 9-13, 2015.

- Teluka Galhenage, Dean C. Webster, Shane Stafslien, Justin Daniels, John Finlay, "Fouling-release performance of silicone oil modified siloxane-polyurethane coatings," ACS National Meeting, Boston, MA, August 16-20, 2015.
- Teluka Galhenage, Dean Webster, Dylan Hoffman, Samantha Silbert, Shane Stafslien, Lyndsi Vanderwal, John Finlay, Sofia Franco, "Fouling-release performance of siloxane-polyurethane marine coatings: Comparison of laboratory biological assays and field immersion studies in the marine environment," ACS National Meeting, Boston, MA, August 16-20, 2015.
- Dean C. Webster, "Marine Coatings," "Self-stratified Polyurethanes," "Non-isocyanate polyurethanes," Weg Paints, Brazil, February 24, 2015.
- Teluka Galhenage, Dean C. Webster, Dylan Hoffman, Kunyu Zheng, Shane J. Stafslien, Justin Daniels, John A. Finlay, Maureen E. Callow, James, E. Callow, "Amphiphilic Acid Functional Siloxane Polyurethane Coatings," International Congress on Marine Corrosion and Fouling, Singapore, July 6 – 10, 2014.
- Madhura Pade, Dean C. Webster, James Bahr, Shane Stafslien, Justin Daniels, "PU-PDMS fouling release coatings: Effect of surface damage," ACS National Meeting, Dallas, Texas, March 16-20, 2014.
- Dean C. Webster, "Fouling-release marine coatings via self-stratification," ANZPAC Workshop, Melbourne, Australia, May 6-9, 2013.
- Dean C. Webster, "Towards tough fouling-release coatings with tailorable surface composition," Plenary Lecture, International Congress on Marine Corrosion and Fouling, Seattle, Wa., June 24-28, 2012.
- Dean C. Webster, "Marine Coatings," Tutorial Lecture, American Coatings Conference, Indianapolis, In, May 7-9, 2012.

Patents

- Dean C. Webster, Teluka Galhenage, "Amphiphilic siloxane-polyurethane fouling-release coating and uses thereof," U. S. Provisional Patent Application No. 62/169,514, Filed June 17, 2015.
- Dean C. Webster, Madhura Pade, "Novel non-isocyanate siloxane-polyurethane coatings," U. S. Provisional Patent Application No. 62/301,065, filed February 29, 2016.

Honors

- Dean Webster was named Fellow of the American Chemical Society in 2016.
- Oral paper/presentation by Teluka Galhenage won the first place Roon Foundation Award at the American Coatings Show, 2016
- Dean Webster awarded the Fred Waldron Research Award in 2015 by the North Dakota State University Alumni Foundation.

Related Sponsored Work

- None

ONR Statistics

Grad Students(total):	2
PI/Co-PI Women:	0

PI/Co-PI Minority:	0
Grad Students Women:	2
Grad Students Minority:	0
Post Docs Students:	0
Post Doc Women:	0
Post Doc Minority:	0
Under Grad Students(total):	7
Under Grad Students Women:	1
Under Grad Students Minority:	0
Degrees Granted:	1
Invention disclosures citing ONR support:	2
Other funding sources:	0

Appendix A

Effects of solvent content on fouling release performance of siloxane polyurethane formulations; X-ray photoelectron spectroscopy with ion milling study

Background:

In previous studies and in recent field tests it was evident that the A4 formulation was out performed by the C4 formulation in terms of fouling release performance in a fresh water environment. However this behavior is opposite in a seawater environment (see Appendix E below). Although both A4 and C4 formulations contain similar siloxane content, the C4 formulation contain slightly more solvent compared to the A4 formulation. Coupling XPS with argon ion milling can provide information on the composition as a function of depth into the coating and provide insight to the observed fouling release performance difference. Any significance in morphological variation due extra solvent can potentially be understood. In order to determine the appropriate etch rate, a calibration experiment was performed. Here the etch rate for both pure polyurethane and silicone elastomer was determined. Then appropriate etch rate was used to etch A4 and C4 coatings while observing the compositional change in C, Si, O and N atoms.

Progress

Calibration Experiment

To calibrate the Ar ion etching rate, pure polyurethane and Dow corning T2 silicone elastomer coatings were prepared by spin coating to achieve nanometer thick films on silicon wafer. The formulation and coating preparation procedure is explained below.

Formulations

The polyurethane formulation was prepared by reacting Desmodur 4470 BA (IPDI trimer, 70% Wt. in butyl acetate) with Acrylic Polyol (80:20 BA: HEA, 50% Wt. in toluene) at 1.1:1 NCO: OH ratio. Acetylacetone was used as the pot life extender (5% based on total solids). Dibutyltin diacetate (DBTDA) (0.05% based on total solids) was used as the catalyst. Additionally toluene was added to dilute the formulation to be 10% solids. Final solids were confirmed by percent solids test. Dow Corning T2 silicone elastomer formulation was prepared according to the manufacturer's specifications and further diluted with Sherwin Williams Reducer 15 to obtain the optimum formulation with 24% solids.

Spin Coating

Laurell WS-400A-6NPP spin coater was used to prepare thin films needed for the experiment. The program that conducts spinning at 6000rpm for 35 seconds were used for all the spin coated samples. Liquid mixture was placed on a silicon wafer and allowed to flow while spinning. Following spin coating the samples were carefully transferred into dust free cabinet and allowed to cure under ambient conditions. The next day the polyurethane was cured in the oven at 80°C for 45 minutes to ensure complete curing.

Film Thickness Measurements

Film thickness measurements were performed to accurately determine the thickness of polyurethane and silicone elastomer thin films. First, and Optec Micro Master Excimer laser was used to ablate and remove a thin strip of coating from each sample. Then a KLA-Tencor profilometer was used to measure step height from the top of the coating to the wafer substrate. Results from the test is summarized in Table A1.

Table A1: Thickness measurements of polyurethane and silicone elastomer thin films

Sample #	Formulation	Coating method	Average film thickness (nm)	STdV (±)
1	Pure - Polyurethane	Spin Coated	208.2	0.089
2	Silicone Elastomer T2	Spin Coated	287.3	0.0253

Etch rate determination

For each sample, area of 100µm×100µm was etched using an Ar ion source using the highest power while recording the etch time. The point at which complete penetration of the coating film was determined as an abrupt increase in Si concentration due to reaching the silicon wafer. Then time to etch through the film was divided by film thickness to obtain the etch rate for the two samples. Etch rates for polyurethane and silicone elastomer is shown in Table A2. Figure A1 shows the concentration changes with etching through each film.

Table A2: Etch rate for silicone elastomer and polyurethane

Sample	Thickness (nm)	Etch Time (s)	Etch Rate (nm/s)
Silicone Elastomer T2	287.3	42500	0.006753
Polyurethane	208.2	12000	0.01733

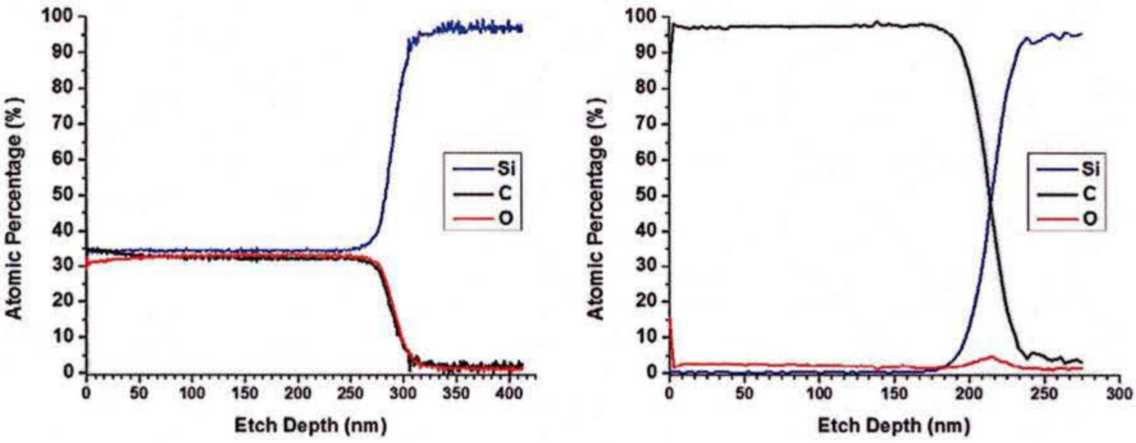

Figure A1: C, Si, O, and N atom concentration changes with depth of silicone elastomer (left) and polyurethane (right) films

Atomic concentration of C, Si, O, and N abruptly change around 287 nm for silicone elastomer and around 208 nm for polyurethane. This suggest that the coatings thicknesses are accurate. The silicone elastomer took a much longer etch time compared to polyurethane while using the same power of the XPS, which leads to significantly different etch rates for the two materials. Therefore the silicone elastomer has a slower etch rate compared to the polyurethane.

A4-20 and C4-20 depth profiling

For the purpose of fouling release performance, we are interested in the first few nanometers of the coatings. Since the siloxane polyurethane system consists of PDMS that self-stratifies and remains at a higher concentration on the surface, the silicone elastomer etch rate was used for depth profiling of A4 and C4. A4 and C4 coatings prepared on aluminum disks were used for the depth profiling experiment. An etch rate of 0.006753nm/s was used while obtaining scans every 10 seconds. Figure A2 shows the atomic concentration plots of A4 and C4 coatings with depth.

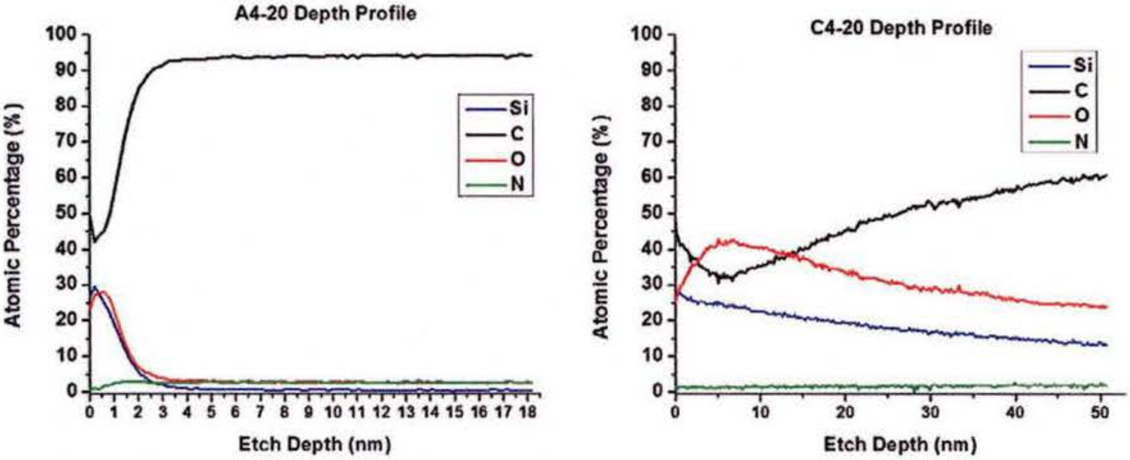

Figure A2: Depth profile of A4-20 (left) and C4-20 (right) coatings

For the A4 coating, the Si and O atomic concentration starts off at around 30% and rapidly decreases to 5% about 2.5 nm from the surface. Counter to this the C concentration increases from 45% to 90% for the same thickness suggesting that the A4 coating contains a higher concentration of PDMS in first few nanometers of the surface. Surprisingly the depth profile of the C4 coating is quite different from A4. Although C4 shows similar Si concentration on the surface, Si atomic concentration gradually decreases into the coating up to 40-50nm. Therefore it is valid to say that the C4 formulation have a gradual decrease in PDMS concentration from the surface to 50 nm deep into the coating. Additional solvent in C4 has allowed a more gradual self-stratification rather than a sharp surface segregation of PDMS.

Summary

Two siloxane-polyurethane formulations were studied using XPS to understand the cross sectional morphology of the coatings with intentions to possibly understand the underlying causes for the differences observed in fouling release performance. First a calibration experiment was conducted to determine the etch rate for silicone elastomer and polyurethane. A significant difference in etch rate was observed for the two material types. Since PDMS predominates on the surface, the silicone elastomer etch rate was used for depth profiling A4 and C4 coatings. Depth profiling of A4 and C4 coatings revealed that these two coatings show significantly different coating morphologies. The observed difference in morphology can be related to the additional solvent playing a key role in self-stratification.

Appendix B

Siloxane-Polyurethane Fouling Release Coatings: Effect of Surface Damage

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Abstract

In order to combat biofouling, self-stratified siloxane (PDMS)-polyurethane (PU) coatings have been developed as potential fouling release coatings. To understand the effect of surface damage on the fouling release performance of the coatings, the coatings were abraded using two different Scotch Brite pads with varying roughness, under varying loads. The contact angle and surface energy data showed that the coatings retained their hydrophobicity even after abrasion. The FR performance against microfoulants deteriorated, but the performance of the abraded coatings improved towards barnacles. Based on the results obtained, it was hypothesized that the FR behavior was dependent on the size of the features formed after abrasion, relative to the size of the fouling organism. Analysis of the surface features further supported this hypothesis.

Keywords Siloxane, Polyurethane, Biofouling, Abrasion, Surface damage, Roughness

Introduction

Marine biofouling is the unwanted accumulation, attachment and growth of microorganisms, plants and animals on surfaces submerged in natural bodies of water.[1] In general, there are four stages of biofouling: accumulation of a layer of organic molecules (called conditioning layer) like proteins and polysaccharides,[1] accumulation of microorganisms like diatoms and bacteria, settlement of algal species and finally attachment of macrofoulants like barnacles and mussels.[2] Biofouling results in approximately 2% reduction in the speed of the ship, up to 45% increase in fuel consumption[2] and combating biofouling can cost as high as one billion dollars annually.[3] Traditionally, antifouling coatings containing tin, copper or organic biocides have been used to combat biofouling.[2] The biocides from the anti-fouling coatings leach out to prevent the accumulation of the marine organisms on the ship hulls.[4] The potential hazards associated with the toxic leachates have necessitated the need to replace these anti-fouling coatings.[3] Fouling release (FR) coatings have been developed as alternate environment-friendly marine coatings.[4] FR coatings allow weak attachment of the organism on the surface, which can be easily broken by the hydrodynamic forces, experienced during the movement of the ship.[5] Commercial FR coatings are based exclusively on silicone elastomers. Lack of mechanical strength, poor adhesion to metal substrates and low durability of the commercial coatings make them less viable for marine applications.[4] In one such attempt, the siloxane (PDMS)-polyurethane (PU) FR coating system has been developed as a potential substitute to the anti-fouling and the commercial FR coatings. The polyurethane matrix provides the necessary adhesion and mechanical strength. The siloxane self-stratifies due to surface energy minimization, forming the outer low surface energy layer of the coating.[4, 6] In general, low surface energy materials have been shown to disallow attachment of organisms to the surface, out of which PDMS is the most preferred material.

Chemical composition of the surface determines the extent of "wetting". Wettability is also a function of the surface topography, which can be tailored as per requirement.[7] Water contact angle greater than 90° indicates a hydrophobic surface, while values lower than 90° indicate a hydrophilic surface. Abrading a hydrophobic (hydrophilic) surface increases the surface area, thereby increasing the hydrophobicity (hydrophilicity) of the surface.[7] But the different attachment mechanisms of the different marine organisms make it difficult to base the FR properties of the coatings on hydrophobicity or hydrophilicity alone.

Another approach to improve the FR performance of the coatings involves tailoring the surface topography by the formation of nano- and micro-gradients on the surface. Biomimetic approaches have shown great potential as novel and futuristic FR systems. One such biomimetic surface, based on the Lotus leaf, exhibits an inherent tendency to repel water because of its waxy nature with nanoscopic surface gradients, rendering the surface superhydrophobic (water contact angle greater than 150°).[7] But the biggest challenge with the synthetic Lotus leaf- like surfaces is maintaining the characteristic superhydrophobicity of the surface for longer duration. Similar to the Lotus leaf, another interesting approach is mimicking the shark skin on synthetic surfaces. Sharklet AF coatings, the surfaces with shark skin topography, have shown significant improvement in FR performance of coatings as compared to regular smooth coatings. Further analysis of the biomimetic Sharklet AF coating indicated the dependence of the FR performance on the size and shape of the surface features. For example, a Sharklet AF coating with 3 μm feature height reduced the algal settlement by 63%. Similarly, a feature height of 40 μm showed 97% reduction in barnacle attachment on barnacle specific Sharklet AF coatings.[8] Marine organisms adhere to ship hulls by secreting proteinaceous adhesives.[9] But proteins conform irreversibly onto hydrophobic surfaces.[7] Factors such as "wetting" of the surface and interlocking of the organism adhesive play an important role in determining the strength of attachment between the organism and the surface.[10] The surface features provide contact points, which support growth and metamorphosis of the organism, with higher number of contact points resulting in higher attachment of the organism. Marine organisms show less tendency to attach onto surfaces with features less than the size of the organism.[10, 11] To further understand the attachment behavior of the organism, engineering models have been devised to study the surfaces with distinct localized textures that provide insights into techniques to deter the marine foulants.[12] Generation of stresses in the bulk of the organism due to variations in the size and shape of the features renders the surface less conducive to the growth and metamorphosis of the organism.[13] Attachment point theory deals with the creation of such non-equilibrium in the organism.[13, 14] Later, Engineered Roughness Index (ERI) was developed to understand the effect of the feature size and geometry on the attachment behavior of the organism.[15] ERI is a dimensionless quantity that correlates Wenzel's roughness factor with the degrees of freedom of movement and the amount of depressed surface.[9] According to ERI theory, continuous recessed grooves show greater tendency of settlement than isolated ones, since degree of freedom is comparatively higher in case of a continuous network.[15] ERI theory also predicts critical sizes of the features for optimum performance of the surface to be 2 μm for algal spores and 20 μm for barnacle cyprids. For instance, cyprids did not settle on PDMS with gradient size 256 μm, because the groove hampers metamorphosis and interferes with the growth of the cyprids.[10] Furthermore, the surface energetic attachment (SEA) model, which serves as a combination of both the attachment point theory and the ERI, predicts the settlement of the organisms with respect to the number, the size and the geometry of the surface topography.[16] In spite of theoretical development of an optimized surface to deter most of the organisms, it is difficult to accurately predict the practical performance of the textured coatings because of the variations in the different attachment behavior of the target organisms.[7, 9, 16]

Although the self-stratified PU-PDMS coatings exhibit FR performance on par with commercial silicone elastomer coatings, one question that remains unanswered is the performance of the coatings upon damage. To explore the same, the PU-PDMS coatings were abraded using two different Scotch Brite pads. The numbers of abrasions were varied. The smooth and the abraded coatings were analyzed for their contact angles and surface energies. The coatings were further analyzed using SEM and XPS to observe the surface topography and the surface composition of the smooth and the abraded coatings. The FR performance of the coatings with respect to micro- and macro-foulants was determined. The results obtained led to the hypothesis that the FR performance of the coatings is a function of the size of the features formed after abrasions and the size of the organism. Detailed analysis of the surface features further supported this hypothesis.

Experimental

Coating formulation and application

Hydroxy terminated acrylic polyol was synthesized using butyl acetate and hydroxylethyl acetate by free radical polymerization, according to the procedure explained elsewhere.[5] Aminopropyl terminated PDMS was synthesized using D4 siloxane monomer and bis(3-aminopropyl)-tetramethyldisiloxane (BAPTMDS).[3] Based on the results obtained from the previous studies, "A4" coating formulation was selected for the abrasion study.[5] To briefly explain the formulation, the acrylic polyol resin was mixed 50% by weight with toluene. 20% by weight PDMS was mixed with the polyol solution and stirred overnight to compatibilize PDMS with the polyol.[5] Isocyanate was added to the formulation the next day in 1.1:1 isocyanate to polyol ratio. Prior to the application of the formulation, the aluminum substrates were coated with Intergard 264 epoxy primer. The final formulation was stirred for 45-60 min and applied using Meyer wire rod (RDS 80) on primed (Intergard 264 epoxy primer) aluminum panels. The coatings were allowed to cure under ambient conditions overnight. Next day, the coatings were oven-cured at 80°C for 45 min to remove any residual solvent. The same coating formulation was used for all the coatings.

Abrasion experiment

The abrasion set up was made up of a long plastic plank, with a handle on one end and sponge attached to it on the opposite side (Figure 1). Abrasion pads were attached to the sponge with the help of Velcro. The level of the plank was maintained parallel to the ground at all times by an adjustable screw attached below the handle. The coating panels, one at a time, were taped to the bottom of a plastic tray to prevent slipping. Distilled water was poured onto the panels before abrasions. Additional weights were applied as and when required. The plank was moved back and forth manually, with the abrasion pad in contact with the coating. One forward movement of the plank was counted as one abrasion.

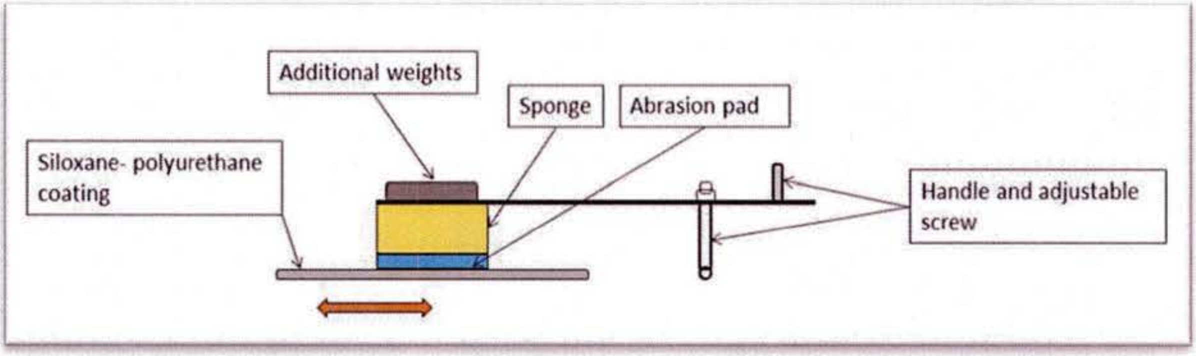


Fig. 1- Schematic representation of the experimental set up for abrading the FR coatings.

Two different Scotch Brite pads, namely the scouring pad (SP) and the general purpose pad (GP), were used to abrade the surface. The roughness of SP is significantly lower than that of GP. Therefore, 5 lb and 7 lb additional weights were applied while using SP. GP was used without (0 lb) any additional weight and 1 lb additional load. Combinations of the different Scotch Brite pads, additional weights and the number of abrasions are tabulated in Table 1. In this paper, the coatings have been labelled as type of abrasion pad_additional weight applied_number of abrasions. For example, SP_5lb_300 stands for the coating abraded with SP under 5 lb additional weight and 300 abrasions.

Table 1- Combinations of abrasion pad, load and number of abrasions.

Abrasion pad	Additional load (lb)	Number of abrasions
Scouring pad (SP)	5, 7	0, 20, 60, 100, 150, 200, 250, 300
General purpose pad (GP)	0, 1	0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220

Contact angles and surface energies

Symyx Coating Surface Energy Measurement System was used to measure the water contact angles (WCA) and methylene iodide contact angles (MICA) of the coatings by sessile drop method. For each coating, three WCA and MICA at three different spots were measured and analyzed using FTA software. The average WCA and MICA values obtained for the coatings were used to calculate the SE values by Owens-Wendt method.[17] WCA, MICA and SE of the coatings were measured once every week for a period of four weeks for every coating.

Statistical analysis

Statistical analysis was conducted using Minitab 17 software. One-way ANOVA was used to determine statistically significant variations in WCA values with changing surface abrasion treatments. Tukey-Kramer test was used to compare individual values with constant 95% confidence limit. In this paper, select coatings were compared to the smooth coating. The selection of the coatings, the smooth coating, GP_0lb_200, GP_0lb_220, GP_1lb_100, GP_1lb_120, GP_1lb_160, GP_1lb_180, GP_1lb_200 and GP_1lb_220, was based on the fouling release performance of the coatings against barnacles.

SEM

JEOL JSM-6490LV High-performance Variable Pressure SEM was used to analyze the surface of the smooth and select abraded coatings. Samples of the smooth coating, SP_5lb_300, SP_7lb-300, GP_0lb_220 and GP_1lb_160 coating were coated with a thin layer of gold before imaging. The gold coated samples were then observed under 250, 1000 and 3000 magnifications. The scans obtained for the abraded coatings were compared to the scans for the smooth PU-PDMS coating.

XPS

In order to determine the surface composition of the coatings after abrasions, select coatings were analyzed using KAlpha X-ray photoelectron spectroscopy (XPS) with aluminum (Al) source from Thermo Scientific. 3 scans were taken from a 400 μm area on the surfaces of the smooth PU-PDMS coating, SP_7lb_300 and GP_1lb_160 coatings. The results obtained showed a survey scan for the area as well as high resolution scans for the individual surface components, C, O and Si.

Analysis of surface features

In this study, features represent the valleys or the recessed zones formed on the surface after abrasions. The surfaces of the smooth and abraded coatings were analyzed using a Wyko NT Series Optical Profiler from Veeco. Magnification was maintained at 10X for all the coatings. Feature depth was considered to be the maximum distance between the highest point and the lowest valley of the feature. For each of the coatings, R_z is the average of five deepest features on the area under observation. In this study, an average of five such R_z values for each of the coatings was recorded. Further, Fourier Transform analysis from ImageJ software (Java- based program developed at National Institute of Health) was used to determine the width of the features (peak to peak distance) formed on the surface of select abraded coatings. The coatings that were selected included the smooth PU-PDMS coating, SP_5lb_300, SP_7lb_300, GP_0lb_220 and GP_1lb_160. The results shown are an average of five widths for the select coatings.

Laboratory Biofouling Assays

Preleaching and leachate toxicity analysis

In order to remove toxic leachates, impurities and catalyst from all the coatings before performance analysis with biological organisms, the coatings were placed in a recirculating water tank for four weeks.[5] The coatings were then tested for leachate toxicity by introducing algae in artificial sea water (ASW) with nutrients. The growth of algae on the coatings was observed by obtaining extracts from each coating after 48 hours using fluorescence. The growth of the organisms on the coatings was reported as a fluorescence ratio to a positive growth control. A negative growth control (medium+ bacteria+ triclosan) was also included in the experiment. The coatings were compared to the negative control to confirm the absence of toxic leachates.[4]

Biofilm Cellulophaga lytica (C.lytica) adhesion

Earlier, bacterial biofilm retention has been described in detail.[4, 18, 19, 20] Briefly, crystal violet colorimetry was used to determine *C.lytica* retention on the smooth and abraded coatings. Circular discs were carefully punched from the smooth and abraded coating panels. The discs were then glued to 24-well plates using a silicone adhesive from Dow Corning, such that the glue covered the circular basal area completely. 5% suspension of *C.lytica* in ASW (10^7 cells/ml) with nutrients was prepared. 1 ml suspension was added to each well of the 24-well plates. The well plates were incubated for 24 hours at 28°C to allow colonization of the biofilm on the coating surfaces. The plates were rinsed three times with deionized water to remove any unattached biofilm. Crystal violet was used to stain the samples. Extractions of crystal violet in acetic acid (33%) were observed under 600 nm absorbance, to determine amount of biofilm retained on the coatings. To determine the fouling release performance of the coatings, the plates were subjected to water jets at 10 psi and 20 psi, after 24 hours of the biofilm growth.[21] The first column in each 24-well plates served as bacterial growth before water jetting and was not exposed to the water jet. The second and the third columns were exposed to 10 psi and 20 psi water jet respectively for 5 seconds. Finally, the biofilm adhesion was reported as the percent removal from the coating surface at the above mentioned water pressures. In this paper, only biofilm adhesion after exposure to 20 psi water pressure has been shown.

Diatom Navicula incerta (N.incerta) attachment and adhesion

N.incerta adhesion was carried out in a fashion similar to *C.lytica* adhesion explained earlier.[4, 22, 23, 24, 25] Briefly, 24-well plates were prepared by carefully punching out discs from the smooth control and abraded coatings. The plates with the glued discs were treated with 1 ml solution of algae in ASW. The plates were incubated for 2 hours to allow diatom adhesion. Fluorescence was used to quantify the algal settlement on the coatings. Fouling release performance of the coatings was determined by exposing the well plates to water jet after 2 hours of cell settlement. The first column was used as a reference for the initial cell settlement and was not treated with the water jet. The second and the third columns were exposed to water jet at 10 psi and 20 psi for 10 seconds. The final results obtained were reported as percent removal at 20 psi water pressure. In this study, only the results obtained after 20 psi water pressure have been discussed. Water pressure of 10 psi could not facilitate sufficient removal of the diatoms from the commercial controls.

Microalgae Ulva linza (U.linza) release assay

Similar to diatoms, 24-well assay plates were prepared by carefully punching out and gluing discs from the smooth and select preleached abraded coatings. The coatings chosen for this experiment are the smooth PU-PDMS coating, SP_5lb_300, SP_7lb_300, GP_0lb_220 and GP_1lb_160. The plates were then shipped to Newcastle University to determine the FR performance of the coatings toward microalgae *U.linza*. Before the bioassay experiment, the assay plates were equilibrated in 0.22 µm seawater for 2 h. Then, 1 ml *U.linza* sporelings suspension (3.3×10^5 spores/ml) in enriched sea water was dispensed into each of the wells. The spores were grown in an illuminated incubator at 18°C for 6 days. After 6 days, the biomass from a single row of wells (6 wells) was assessed by extracting chlorophyll. Chlorophyll was extracted in 1 ml DMSO. Fluorescence was then determined using excitation of 360 nm and wavelength of 670 nm. To determine the release performance of the coatings, single rows of wells from each plate was sprayed using the spinjet apparatus at 18, 67, 111 kPa water pressure. Chlorophyll was again extracted, as explained earlier. The removal at each pressure was determined by comparing the sprayed and the unsprayed wells. The results were reported as the percent removal of the sporelings after spraying the wells.

Adult barnacle Amphibalanus amphitrite (A.amphitrite) reattachment assay

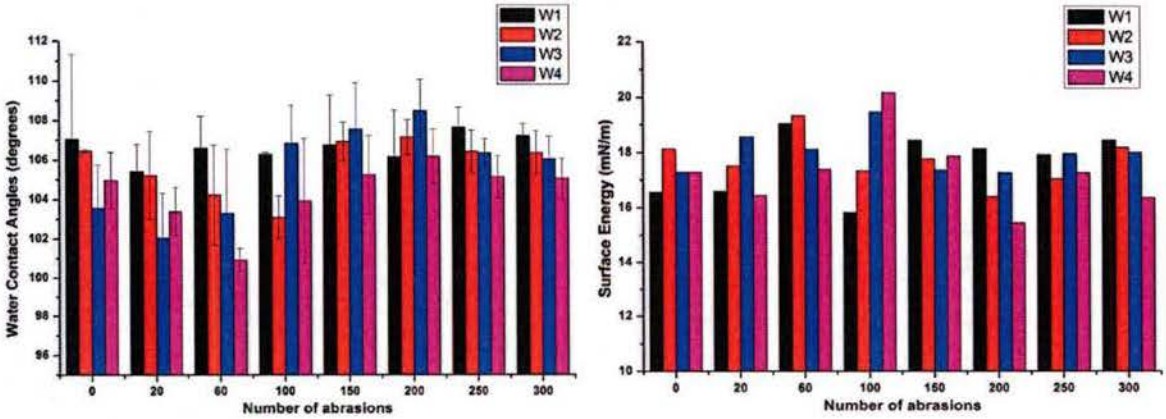
Adult barnacle adhesion experiment was conducted to determine the fouling release performance of the smooth and the abraded coatings against hard foulants.[4, 26, 27] Adult *A.amphitrite* barnacles, with basal diameter of approximately 5 mm, were allowed to grow and attach to the coating panels in ASW for 2 weeks with daily supply of brine shrimp nauplii. After 2 weeks, a hand held digital gauge was used to measure the force required to detach the barnacles from the coatings. Adhesion strength (MPa) of the barnacles was then calculated as the shear force required for barnacle removal to the basal area of the barnacle.

Not just barnacles, the smooth and abraded coatings were also evaluated for marine mussels *Geukensia demissa* adhesion according to a previously published procedure.[28, 29, 30] But, during the course of the experiment, none of the mussels attached to the smooth or the abraded coatings (all abrasion treatments). Therefore, experimental measurement of mussel adhesion was not possible. Qualitatively, all the coatings successfully deterred attachment of mussels.

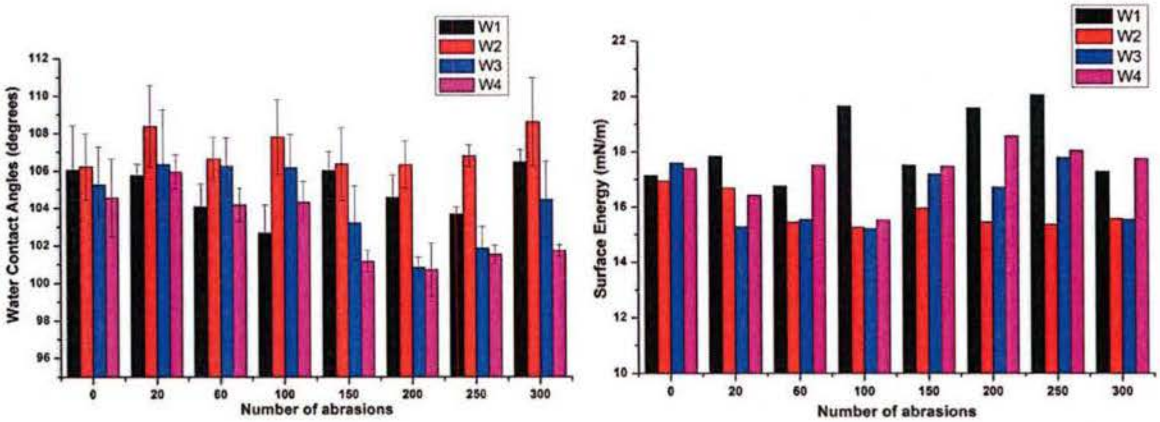
Results and discussion

Self-stratified PU-PDMS FR coatings were synthesized using isocyanate, acrylic polyol and aminopropyl terminated-PDMS. The surface energy of PDMS is significantly lower than PU. Due to the lower surface energy of PDMS and incompatibility between the two phases in the coating system, PDMS stratified to form the outer layer of the coating.[31] The coatings were abraded using two different Scotch Brite pads under varying number of abrasions, under varying load, using the set up shown in Figure 1.

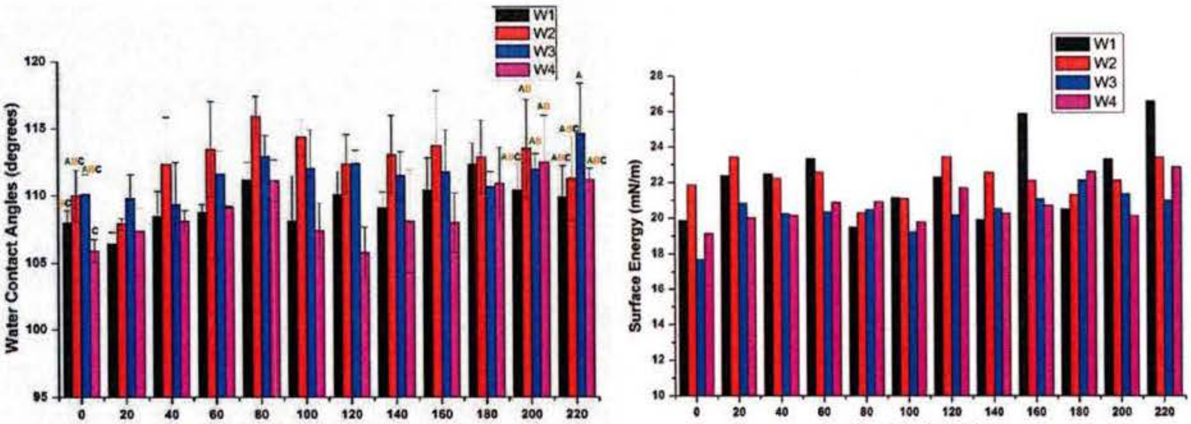
Figure 2 shows data for WCA and SE for the smooth and the abraded PU-PDMS coatings. The WCA values for the smooth and all the abraded coatings, were greater than 90°, with minor variations possibly due to the rearrangement of PDMS on the surface of the coatings.[5, 32] The highest WCA value obtained was 116° for GP_0lb_80 (Figure 2(c)). The coatings, thus, retained their hydrophobicity, even after abrasions. The SE of the coatings ranged from 15 mN/m to 25 mN/m.


W1
W2
W3
W4
Water Contact Angles (degrees)
96
98
100
102
104
106
108
110
112
0
20
60
100
150
200
250
300
Number of abrasions
Surface Energy (mN/m)
10
12
14
16
18
20
22

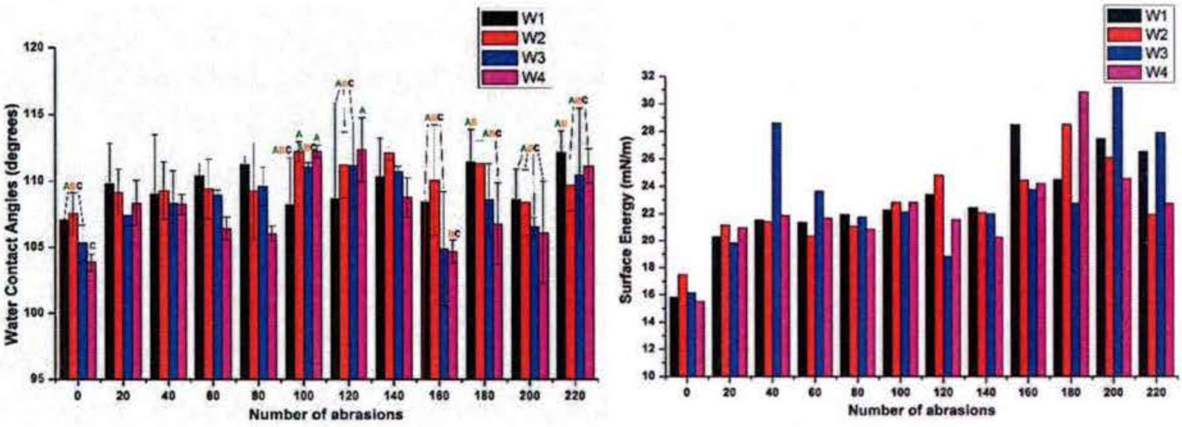
(a)


W1
W2
W3
W4
Water Contact Angles (degrees)
96
98
100
102
104
106
108
110
112
0
20
60
100
150
200
250
300
Number of abrasions
Surface Energy (mN/m)
10
12
14
16
18
20
22

(b)


W1
W2
W3
W4
Water Contact Angles (degrees)
95
100
105
110
115
120
0
20
40
60
80
100
120
140
160
180
200
220
Number of abrasions
ABC
AB
A
C
Surface Energy (mN/m)
10
12
14
16
18
20
22
24
26
28

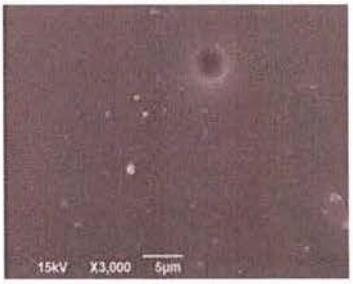
(c)



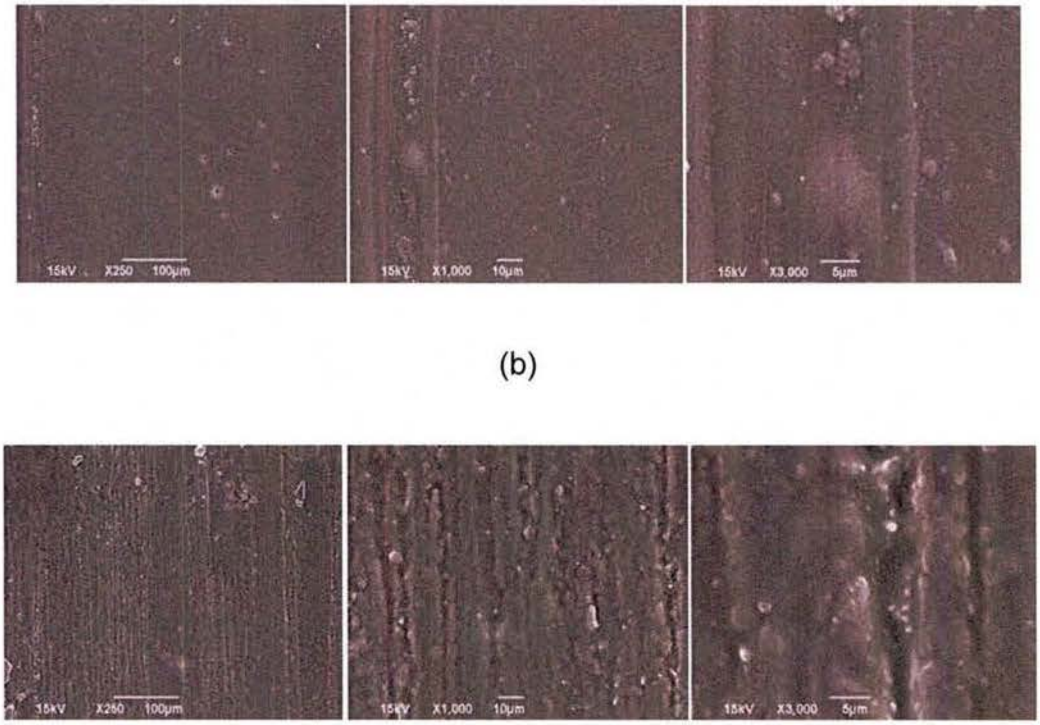
(d)

Fig. 2- WCA and SE values for coatings abraded with (a) SP under 5lb additional load, (b) SP under 7lb additional load, (c) GP under no additional load and (d) GP under 1lb additional load. The legends W1 to W4 indicate the weeks over which WCA values were measured. Error bars represent standard deviation. Same alphabets on select data points in (c) and (d) indicate values that are not statistically different from one another ($p < 0.001$ for both (c) and (d)).

As expected, the smooth PU-PDMS coating observed under SEM was devoid of any surface features in Figure 3(a). Minor defects maybe have been present on the smooth surface. Coatings abraded using SP (Figure 3(b)) showed small randomly distributed "scratches" formed on the coating surface. More "scratches" were formed after abrading the smooth coatings with GP, a pad with higher roughness (Figure 3(c)).



(a)



(b)

(c)

Fig. 3- SEM scans of (a) smooth PU-PDMS coatings and coatings abraded with (b) SP and (c) GP. Surface of the coatings abraded with SP or GP look similar to other treatments with the same abrasion pad.

Table 2 shows the results obtained from XPS for the smooth and two of the abraded coatings. The results show that the percentage of the individual atomic elements Si, C and O detected on the surface were approximately 25%, 50% and 25% respectively. The ratio of the elements Si: C: O, therefore, was 1:2:1. The binding energies from Figure 4, combined with the ratio of the individual elements, indicated the presence of PDMS on the surface even after abrasions.

Table 2- Data obtained from XPS.

Abrasion treatments	Atom percent		
	Si	C	O
Smooth PU-PDMS coatings	25.19	48.93	25.88
SP_7lb_300	25.00	50.33	24.68
GP_1lb_160	24.59	50.66	24.76

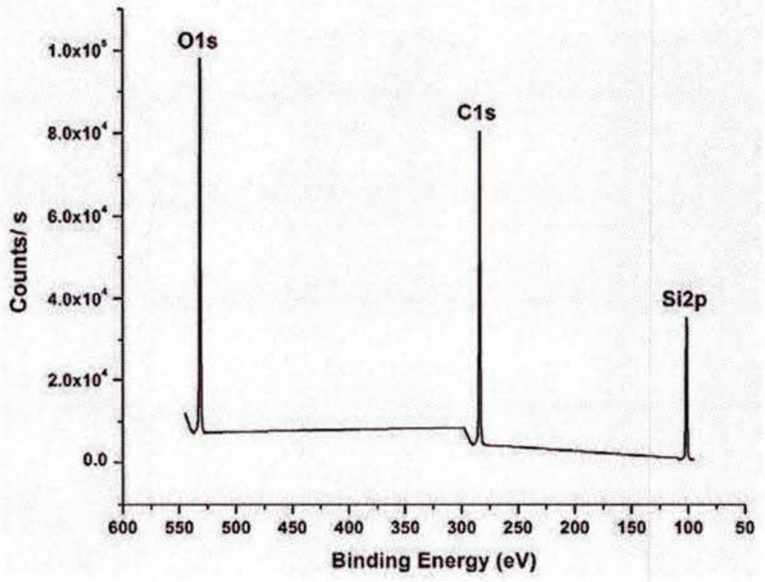


Fig. 4- Binding energy data from high resolution scan using XPS.

The coatings- all or select few- were analyzed for their fouling release behavior against micro- and macro-foulants. The criterion for "selection" of the coatings was the FR performance of the coatings toward barnacles. The smooth PU-PDMS coating was used as the control, SP_5lb_300 and SP_7lb_300 were two coatings on the worse end of the performance spectrum and GP_0lb_220 and GP_1lb_160 were two coatings from the better end of the spectrum. The fouling release performances of the smooth and the abraded PU-PDMS coatings were compared to the performance of the commercial FR coatings like Silastic T2, Intersleek 700, Intersleek 900 and a regular polyurethane coating (no siloxane).

Figure 5 shows the attachment and the removal of the biofilm after exposure to water jet. In general, the amount of biofilm attached to the coating increased with the roughness of the coatings. Most of the abraded coatings showed lower biofilm attachment as compared to the commercial coatings. The amount of biofilm removed (difference between the heights of the data points) from the abraded PU-PDMS coatings was almost similar to or higher than the commercial coatings. Almost 100% removal was obtained for some abrasion treatments at 20 psi water jet pressure. Therefore, the smooth and the abraded PU-PDMS coatings performed better in terms of the amount of biofilm removed from the surface. Abrading the coatings led to an increase in the number of contact points between the organism and the surface. Therefore, the amount of biofilm that attached to the abraded coatings was higher than the smooth coatings. But the size of the features formed on the surface may be lesser than the size of the biofilm. The suspended biofilm could be easily cleaned from the surface upon exposure to water pressure of 20 psi.

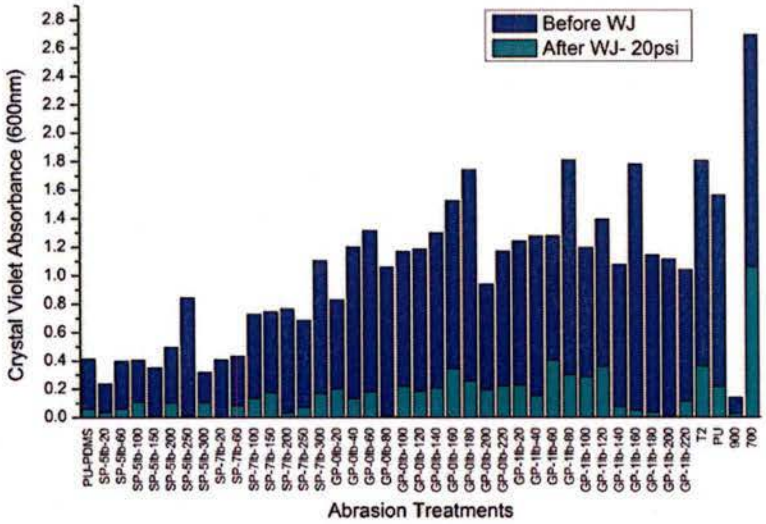


Fig. 5– *C.lytica* biofilm retention on the smooth and abraded coatings and the commercial coatings after 20 psi water jet pressure.

Figure 6 shows data from diatom removal from the smooth and the abraded coatings. The amount of diatoms removed from all the coatings was lower than the commercial FR coatings. The percent removal decreased with increasing roughness of the coatings. Lowest removal was obtained after 160 abrasions with GP under 1 lb additional weight (GP_1lb_160). In general, diatoms exhibit higher attachment on PDMS surfaces.[33] Presence of PDMS on the surface even after abrasions and the increase in the number of contact points may have resulted in higher attachment of the diatoms on rough surfaces.

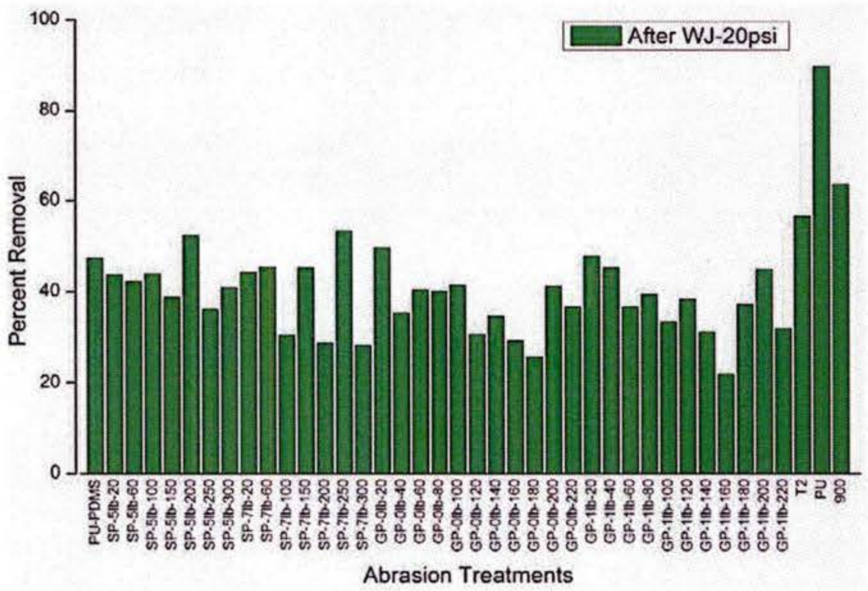


Fig. 6– Percent removal of diatoms *N.incerta* from the smooth and abraded coatings after exposure to 20 psi water jet pressure.

Figure 7 shows the microalgae removal data after exposure to water jets at 18, 67, 111 kPa for the smooth coatings and the select coatings. The amount of algae attached to the coatings (not shown here) was the same for the five coatings. In general, the algae removal decreased as the roughness of the coatings increased. Abrading the surface may have resulted in the formation of features that provided a secure environment to the growth of the microalgae. The sporelings were, therefore, able to withstand the impact from the water jet. Polystyrene substrate, used as a standard, showed lowest removal of the microalgae, due to the absence of a coating layer on the surface of polystyrene.

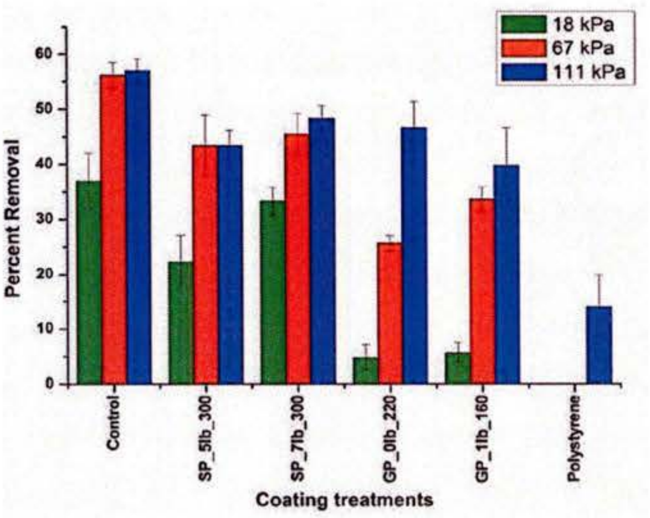
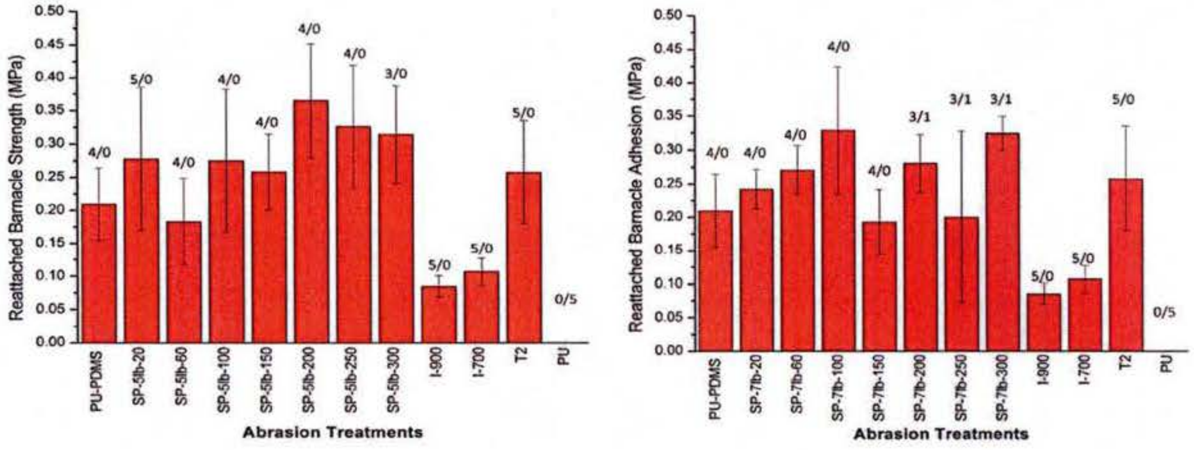


Fig. 7- Percent removal of microalgae *U.linza* from the smooth and the select abraded coatings after exposure to 18, 67 and 111 kPa water pressure. Control indicates the smooth PU-PDMS coating. Polystyrene has been used as the standard for this experiment.

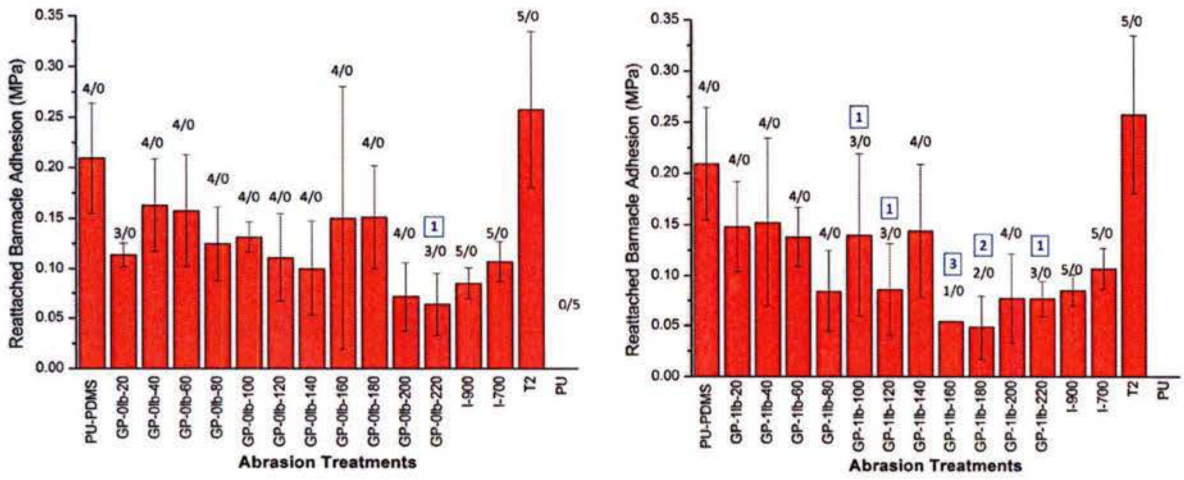
The abraded coatings showed an unusual yet interesting FR performance with respect to barnacles. Figure 8 shows the barnacle adhesion data for the smooth and the abraded coatings. The results showed that barnacle removal from the abraded coatings reduced for abrasion treatments with SP, while the removal was facilitated upon abrading with GP. The barnacles adhered strongly to the coatings abraded with SP, like SP_5lb_300, as seen in Figure 8(a). The removal force required to detach the barnacle from the coating was significantly higher than the force required for the commercial FR standards. Under 7lb additional weight (Figure 8(b)), the barnacle bases broke due to the possible mechanical interlocking of the barnacle adhesive with the abraded coatings.

Unlike SP, abrading the coatings with GP resulted in a decrease in the attachment of the barnacles onto the coating surface. The number of barnacles that adhered to the coatings reduced significantly with the roughness of the coatings (Figure 9(b)). For example, for GP_1lb_160, 3 out of 4 barnacles did not attach to the coating during the course of the experiment. The force of removal required to detach the only barnacle that attached to GP_1lb_160 was lower than 0.10 MPa, which is significantly lower than the commercial standards. The unusual results obtained above necessitated the need to analyze the dependence of the FR performance of the coatings on the surface topography of the abraded coatings.



(a) (b)

Fig. 8– Barnacle removal for coatings abraded using SP under (a) 5 lb and (b) 7 lb additional weights. Ratios above individual data points indicate the number of barnacles that were successfully removed from the coating to the number of barnacle bases that broke during the experiment.



(a) (b)

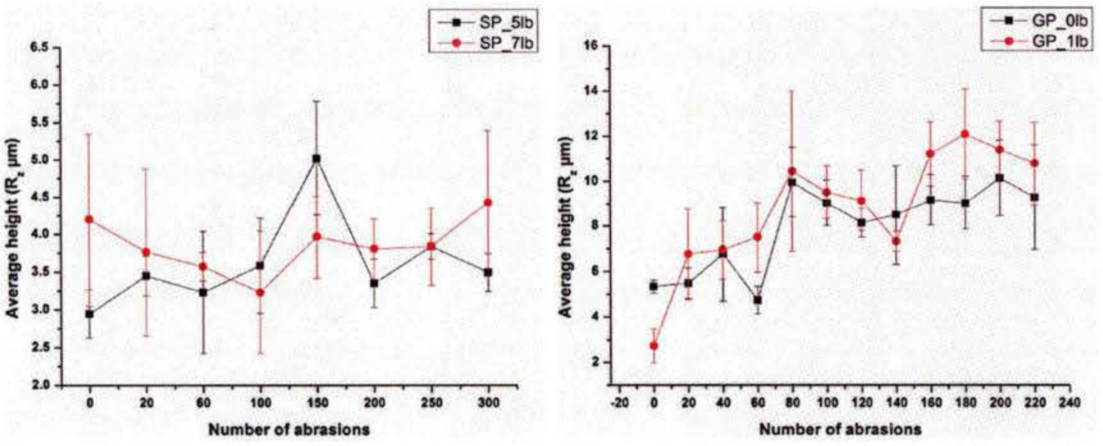
Fig. 9– Barnacle removal for coatings abraded with GP (a) without addiitonal weigth and (b) under 1 lb additional weights. Ratios above individual data points indicate the number of barnacles that were successfully removed from the coating to the number of barnacle bases that broke during the experiment. The number above select data points indicates the number of barnacles that did not attach to the coatings during the course of the experiment.

To understand the interesting behavior of the abraded coatings, the smooth and the select abraded coatings were analyzed for surface roughness. Roughness analysis showed that the roughness average (R_a) (not shown here) and R_z of the coatings increased with the number of abrasions and the roughness of the Scotch Brite pad. In this study, R_z, the height of the peaks protruding from the surface, indicates the depth of the features. From the values shown in Figure 4, abrading with SP resulted in shallower features, with depth ranging from 3.5 to 4.5 µm. The depth increased to between 9 to 12 µm upon abrading the coatings with GP.

The values obtained for the width of the features are tabulated in Table 2. Abrading the coatings with SP resulted in non-uniform wider surface features. The smooth surface and the SP-abraded surfaces possessed similar surface topography. On the other hand, the width significantly reduced upon abrading with GP. The standard deviation values indicated uniformity in the width of the surface features. The data points at 0 abrasions indicate R_z for the smooth PU-PDMS coatings. The variations in the R_z values for the smooth coatings may be due to rearrangement of PDMS on the surface or the presence of surface defects. Complexity and non-uniformity of the shape of the protruding peaks made the analysis of the width of the individual peaks extremely difficult.

Table 2- Height and distance between the features for different abrasion treatments.

Coating treatment	Depth (avg. R_z) (microns)	Width (microns)
Smooth PU-PDMS	4 ± 2	46.49 ± 8.63
SP_5lb_300	3.5 ± 0.25	40.70 ± 13.38
SP_7lb_300	4.42 ± 0.96	57.02 ± 11.99
GP_0lb_220	9.28 ± 2.32	12.27 ± 1.54
GP_1lb_160	11.21 ± 1.43	10.69 ± 1.00



(a) (b)

Fig. 10- Average height of the surface features (R_z) in microns after abrasions with (a) SP and (b) GP. All values are in microns. Error bars represent standard deviation.

Not only the dimensions of the surface features, but also the size of the organism determines the FR performance of the coating surface. For microalgae (5 to 7 µm), the percent removal from GP-abraded coatings decreased (Figure 7). The width of the features formed using GP was significantly higher than the size of the microalgae (Table 2). Also, the deeper "grooves" provided a "cozy" environment for the growth of the microalgae. The algae were, therefore, protected from the impact force of the water jet. On the other hand, SP-abraded surfaces resulted in higher exposure of the algae to the water jet due to the formation of wider surface features.

As against that, macrofoulants like barnacles (200 to 500 µm) were successfully deterred from the GP-abraded surfaces (Figure 9). The narrow features made it difficult for the barnacles to attach to the coatings, leading to "balancing" of the barnacles on the protruded peaks on the surface. The deeper features did not allow the barnacle to attach strongly to the surface. The resulting strain developed in the organism may have made the GP-abraded surfaces less suitable for attachment.[13] On surfaces abraded with SP, the shallower and wider grooves increased the mechanical interlocking between the barnacle adhesive by increasing the number of contact points available for attachment.

Conclusions

Self-stratified FR coatings were successfully synthesized using PDMS and PU. The coatings were abraded using two different Scotch Brite pads. The roughness of the coatings increased with the number of abrasions and the roughness of the Scotch Brite pad. The coatings maintained their hydrophobicity even after abrasions. Percent removal of *C.lytica* biofilm from the abraded coatings was greater than with the commercial FR coatings, almost 100% for some abrasion treatments at 20 psi water jet pressure. Diatom *N.incerta* removal was lower from the abraded coatings than from the commercial FR coatings. Microalgae *U.linza* removal decreased as the roughness of the coatings increased. The abraded coatings exhibited an unusual FR performance toward macrofoulants like barnacles and mussels. None of the mussels attached to the smooth or the abraded coatings. At higher roughness, the number of barnacles that attached to the coatings reduced significantly. The coating GP_1lb_160 showed the best performance against barnacles with 3 out of 4 barnacles not attaching to the coating at all. The above results indicated the dependence of the size of the surface features and the size of the organism on the FR performance of the coatings.

R_z and the analysis of the width of the features obtained from the roughness data showed that shallower and wider features were formed on the surfaces abraded with SP; abrading the surfaces with GP resulted in the formation of deeper and narrower features. The coatings abraded using GP may have provided a secure environment for the growth of microalgae. On the other hand, abrading with GP resulted in reduction in the number of barnacles that attached to the coatings. The narrow and deep features using GP may have caused "instability" to the bases of the barnacles. Therefore, although suitable to microalgae, the surfaces abraded with GP successfully deterred the barnacles. The results obtained from this study can be corroborated with the past research done with the engineered surfaces. The study also indicates the possibility of forming textured surfaces to deter macrofoulants for practical applications like marine coatings using regular Scotch Brite pads.

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Appendix C

Fouling-release performance of silicone oil-modified siloxane-polyurethane coatings

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Keywords: siloxane-polyurethane coatings, phenylmethyl silicone oil, fouling release coatings, field immersion assessments

Abstract

The effect of incorporation of silicone oils into a siloxane-polyurethane fouling-release coatings system was explored. Incorporation of phenylmethyl silicone oil has been shown to improve the fouling-release performance of silicone-based fouling-release coatings through increased interfacial slippage. The extent of improvement is highly dependent upon the type and composition of silicone oil used. The siloxane-polyurethane (SiPU) coating system is a tough fouling-release solution, which combines the mechanical durability of polyurethane while maintaining comparable fouling-release performance with regard to commercial standards. To further improve the fouling-release performance of the siloxane-PU coating system, the use of phenylmethyl silicones oils was studied. Coatings formulations were prepared incorporating phenylmethyl silicone oils having a range of compositions and viscosities. Contact angle and surface energy measurements were conducted to evaluate the surface wettability of the coatings. X-ray photoelectron spectroscopy (XPS) depth profiling experiments demonstrated self-stratification of silicone oil along with siloxane to the coating-air interface. Several coating formulations displayed improved or comparable fouling-release performance to commercial standards during laboratory biological assay tests for microalgae (*Navicula incerta*), macroalgae (*Ulva linza*), adult barnacles (*Balanus amphitrite* syn. *Amphibalanus amphitrite*) and mussels (*Geukensia demissa*). Selected silicone oil-modified siloxane-PU coatings also demonstrated comparable fouling-release performance in field immersion trials. In general, modifying the siloxane-PU fouling-release coatings with a small amount (1-5% wt basis) of phenylmethyl silicone oil resulted in improved performance in several laboratory biological assays and in long-term field immersion assessments.

Introduction

Marine biofouling is the unwanted growth and accumulation of biological organisms on materials submerged in seawater.[1] The process of marine biofouling is a complex phenomenon that can involve more than 4000 marine organisms in multiple stages (Figure 1).[1] Marine biofouling processes begin as soon as a structure is immersed in seawater. First a conditioning film is formed due to the adsorption of organic molecules present in the marine environment. The fouling process is highly dynamic and marine bacteria colonize the surface quickly (min) forming a bacterial biofilm.[2] Slime forming algae (diatoms) also colonize the surface and contribute to the microfouling community. Macro-foulers such as barnacles and mussels tend to settle within a few days of immersion. However, fouling organisms may settle even without colonization or the presence of other marine organisms.[2-3]

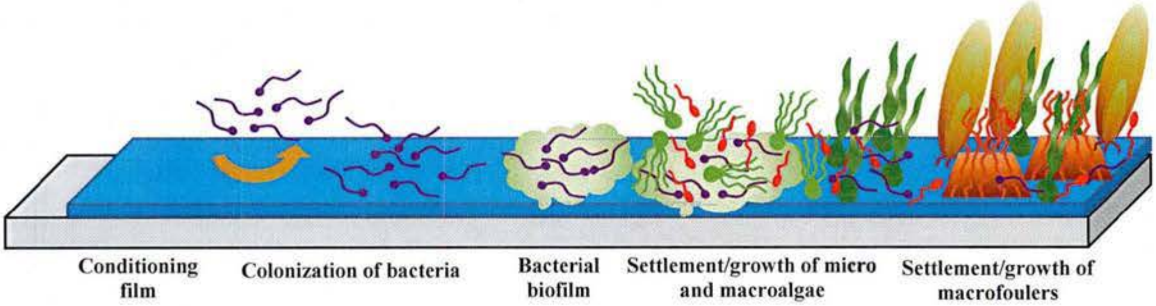

Figure 1: Fouling development on a structure submerged in seawater

Marine biofouling has caused significant economic and environmental penalties to the marine industry for centuries.[4] It has been estimated that biofouling costs $1 billion per year to the United States Navy alone.[5] Continuous accumulation of microfouling and macrofouling biomass on ships' hulls creates frictional drag, which in turn contributes to reduction in ship speed and maneuverability. Estimates have shown that even a marginal (2%) reduction in ship speed can reduce fuel efficiency significantly, especially for larger vessels.[4] Fouling of ships' hulls can also lead to increased frequency of dry docking, causing severe economic penalties to ship owners. On the other hand, given the extensive and global nature of shipping routes, biofouling also poses an environmental threat through the introduction of non-native species.[6]

Historically, ships' hulls made from copper alloys and lead sheaths were used to contend with biofouling.[4, 7] Even though they were very effective antifouling strategies, issues with corrosion of iron hulls and declining availability of resources limited their use in the post medieval era. Thus, antifouling paints with active biocides were investigated as a possible solution in the 1900s.[7] Biofouling was managed well with the introduction of tributyl tin (TBT) based self-polishing copolymer coatings in the 1970s until their toxicity to non-targeted marine organisms was discovered several decades later resulting in restrictions of their use in France.[3, 8] In 2003, the use of TBT in antifouling coatings was largely banned by an International Maritime Organization (IMO) treaty due to the harmful effects of TBT to aquatic ecosystems.[3]

Today antifouling coatings using copper oxide and other organic biocides contribute to the majority of ship hull paints used. These antifouling coatings with active biocides function by the release of toxic substances, which are able to kill or deter settlement of organisms that come in contact with or near the surface. These coatings allow ships to maintain clean hulls for as long as 5-10 years.[3] Fouling-release coatings were introduced in 1961 as a non-toxic alternative to biocide-based antifouling coatings, although they became a more widely mentioned topic between 1990 to 2000.[1, 3] Fouling-release coatings have no harmful chemical interactions and do not necessarily inhibit fouling, rather they provide a surface with significantly reduced adhesion strength to organisms.[1, 3, 4] Ideally, fouling-release surfaces achieve 'self-cleaning' due to the hydrodynamic forces of the vessel moving through the water.

Although antifouling coatings with biocides are largely used to contend with biofouling, fouling-release coatings have remained of special interest due to the ever-increasing desire to eliminate the use of biocide-containing paints. Polydimethyl siloxane (PDMS) elastomers are a commonly used system in most fouling-release coatings and contribute to fouling-release properties due to their low surface energy and high elasticity.[1, 7] However, PDMS has poor mechanical durability and low adhesion to substrates and primers making it difficult to use in marine coatings.[9, 10] Siloxane-polyurethane (SiPU) coatings invented in the Webster research group, on the other hand, have combined the mechanical and adhesion properties of polyurethanes and the fouling-release performance of siloxane.[11, 12] Siloxane-polyurethane coatings are a viable approach to combat biofouling with comparable performance to commercial fouling-release coatings.[13, 14]

Non-reactive silicone oils are known to be used in PDMS-based fouling-release coatings.[15] The earliest reports of silicone oil additives in marine topcoats originated in 1977.[16, 17] Several studies suggest that the oil provides lubricity to the coating surface resulting in weaker adhesion of marine organisms.[18-20] Therefore polydimethylsiloxane (PDMS) based elastomers can benefit from silicone oil to obtain improved fouling release properties. Truby *et al.* reported a decrease in barnacle and oyster adhesion strength to PDMS coatings with the addition of small amounts of phenylmethyl silicone oil during immersion studies conducted in Hawaii.[15] However the observed differences in release properties are closely related to the chemical composition of the silicone oil and the degree of compatibility with the PDMS matrix.[21, 22] The amount of silicone oil used in coatings was varied from 1-10% based on the total solids of the formulation. Truby *et al.* also highlighted possible issues with the release of silicone oil into marine environments. The amount of silicone oil released by such coatings was, however, negligible and there is no direct threat to marine life given the extremely low toxicity of silicone.[15]

In this study, silicone oils with a range of phenylmethyl compositions were incorporated into a SiPU coating system at 1, 2 and 5 wt% based on PDMS with the intention of obtaining improved fouling-release performance relative to the 1st generation SiPU (A4-20) system without oil.[14] Fouling-release performance of these silicone oil-modified coatings was also compared against the commercial fouling-release systems Intersleek®700 and Intersleek®900. Surface characterization of the experimental coatings was conducted using XPS, contact angle and surface energy measurements. Fouling-release performance of these coatings was evaluated using laboratory biological assays and field immersion studies at multiple test sites.

Experimental

Materials

Phenylmethyl silicone oils (PMM-1025, PMM-1043, PMM-5021, PMM-6025, PMM-0021, and PMM-0025) were purchased from Gelest Inc. Polyisocyanate Desmodur Z 4470 BA was provided by Bayer MaterialScience (now Covestro LLC). Acetylacetone, toluene, methyl amyl ketone (MAK) and dibutyltin diacetate (DBTDAc) were purchased from Sigma Aldrich. All reagents were used as received. An acrylic polyol containing 80% butyl acrylate (BA) and 20% 2-hydroxyethyl acrylate (HEA) was selected for this study and synthesized as previously reported.[23] An aminopropyl terminated poly(dimethylsiloxane) (APT-PDMS) of 20,000 g/mol molecular weight was synthesized as reported previously.[14] Details of the synthesis of the acrylic polyol and siloxane are provided in the Supporting Information.

Experimental Design

The study was designed using 6 types of phenylmethyl silicone oils at three levels of oil (1%, 2% and 5% based on PDMS weight). Characteristics of the 6 silicone oils provided by the manufacturer are summarized in Table 1. The oils have phenylmethyl composition varying from 8% to 100%, with 100% being the homopolymer of phenylmethyl silicone oil. The representative chemical structures of the phenylmethyl silicone oils used are shown in Figure 2. The oils were selected to have a range of viscosities based on their molecular weight to later understand correlations with fouling release performances. The coatings were designed as a two-factor factorial study where type of oil and weight percent of oil were considered as factors. Factor 1 (type of oil) had 6 levels and factor 2 (wt % of oil) had 3 levels resulting in 18 different treatment combinations (Table 2).

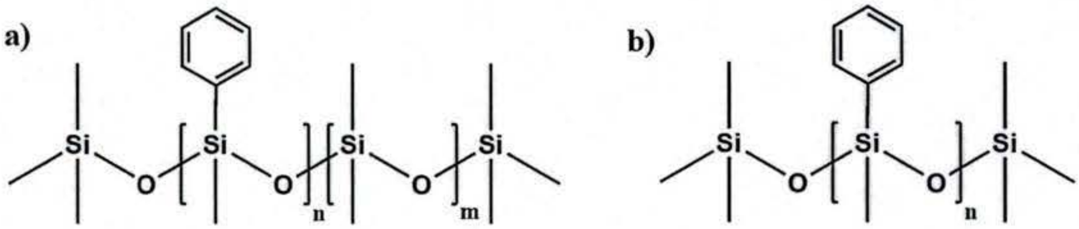

Figure 2: Chemical structure of silicone oils used for the experiment. **a)** phenylmethyl dimethyl siloxane copolymer oil and **b)** phenylmethyl siloxane homopolymer oil.

Table 1: Properties of the phenylmethyl silicone oils used in the study

Name of Oil	Type	% Phenylmethyl	Viscosity (cs)	Mw (g/mol) Reported	Surface Tension (mN/m)
PMM-1025	Copolymer Oil	8-12	500	9000-11000	24.4
PMM-1043	Copolymer Oil	8-12	30000	40000-50000	24.8
PMM-5021	Copolymer Oil	45-50	125	2000-2200	24.5
PMM-6025	Copolymer Oil	58-60	500	3500-4000	-
PMM-0021	Homopolymer Oil	100	100-200	700-1200	-
PMM-0025	Homopolymer Oil	100	500	2500-2700	28.5

Coating Formulation

A general formulation procedure described here was followed. The non-reactive components such as APT-PDMS (20% by wt. based on the total solids of the formulation), corresponding silicone oil (1, 2 and 5%

based on PDMS wt.), acrylic polyol, and pot life extender were combined in a glass vial and allowed to mix overnight. The next day, 1.1 equivalents (for 1 equivalent of hydroxyl and amine combined) of isocyanate (Desmodur Z4470 BA) and 0.05% of DBDTAc catalyst were added (using a diluted solution of 1% by wt in MAK). The formulations were allowed to mix for about an hour before coating preparation. Table 2 shows all the experimental coating formulations.

Table 2: Silicone oil-modified experimental coating compositions

	Amount oil based on solids of PDMS		
Silicone Oil	**1%**	**2%**	**5%**
PMM 1025	**1**	**7**	**13**
PMM 1043	**2**	**8**	**14**
PMM 5021	**3**	**9**	**15**
PMM 6025	**4**	**10**	**16**
PMM 0021	**5**	**11**	**17**
PMM 0025	**6**	**12**	**18**

Coating Application and Curing

Drawdowns were made using a wire wound drawdown bar to achieve 80 µm dry film thickness on 8"x 4" aluminum panels previously primed with Intergard 264 marine grade primer. The coatings were allowed to cure for 24 h under ambient conditions inside a dust free cabinet, followed by forced curing in the oven at 80 °C for 45 min. These panels were used for barnacle and mussel reattachment (1 panel per each test). Coatings for other biological assays (described later) were prepared by depositing 250 µL of formulation in to 24-well plates modified with primed aluminum discs.[24] These were also cured following the same procedure described above.

Control and Standard Coatings

As an internal control, the 1st generation SiPU formulation (A4-20) was prepared. This is the base coating formulation without the added silicone oil. A pure polyurethane formulation without APT-PDMS was also prepared to be included as a control. Commercial coating standards, Dow Corning T2 (silicone elastomer), Intersleek®700 and Intersleek®900 (AkzoNobel International Paint), were prepared according to manufacturer's specifications to serve as standards. All internal control coatings and commercial standards were prepared on both primed aluminum panels and in 24-well plates in order to be characterized in parallel with the experimental coatings.

Water Aging

All the coatings prepared on both panels and plates were pre-leached in running tap water for 28 days (45 days of pre-leaching in the case of samples for green algae *Ulva linza*) in tanks separated by the oil type. The water tanks were equipped to automatically fill and empty every 4 h. Water aging of the coatings is carried out for two purposes: To leach out any impurities that could interfere with the fouling-release assays and to determine if there are any significant surface rearrangements of the coatings after being on contact with water.[25] All biological laboratory assays were carried out after the pre-leaching process was complete.

Surface Characterization of Coatings

All experimental coatings were characterized for water and methylene iodide contact angles (WCA and MICA) using a Symyx®/First Ten Angstroms™ surface energy system. Three measurements the contact angle of each test liquid were obtained using a CCD camera and First Ten Angstroms™ software. Then the average WCA and MICA contact angles were used to calculate the SE for each coating by Owens-Wendt method.[26] Contact angle and SE analysis were performed both before and after water aging.

X-ray photoelectron spectroscopy (XPS) was utilized to investigate the effects of silicone oil incorporation on coating morphology. A Thermo Scientific™ K-Alpha™ XPS equipped with monochromatic Al K_α (1486.68 eV) X-ray source and Ar^+ ion source (up to 4000 eV) for depth profiling was used for the XPS experiments. Initially an etch rate calibration experiment was performed to determine the appropriate etch rate for depth profiling experiment using thin film of silicone elastomer of known thickness (287.3 nm). Dow Corning T2 silicone elastomer was spin coated on a silicon wafer at a speed of 6000 rpm for 35 s using a Laurell WS-400A-6NPP spin coater. Following spin coating, the sample was carefully transferred to a dust free cabinet and allowed to cure under ambient conditions. For accurate film thickness measurements, a First Optec Micro Master Excimer laser was used to ablate and remove a thin strip of coating from the spin coated sample and then a KLA-Tencor profilometer was used to measure step height from the top of the coating to the wafer substrate. The thickness of the silicone elastomer was determined to be 287.3±25.3 nm. Depth profiling of the silicone elastomer was performed using a 1000 eV Ar$^+$ source sputtering on a spot of 1 mm^2 in 30 s intervals for about 50 min (until complete penetration into the silicon wafer). Chamber pressure was maintained below 1.5×10^{-7} Torr. Photoemission lines for C 1s, N 1s, O 1s, and Si 2p were collected after each etch for an interval of 5s at constant analyzer pass energy 155 eV, and an energy increment of 0.167 eV. Silicone elastomer etch rate with Ar$^+$ ion etch power of 1000eV was determined to be 0.0384 nm s^{-1}.

Several experimental coatings prepared on aluminum substrates were analyzed through depth profiling using similar settings mentioned above. Ar$^+$ sputtering was performed on a spot of 1 mm^2 of experimental coating with an etch power of 1000eV in 10s intervals for 25-50 min. Following each etch photoemission lines for C 1s, N 1s, O 1s, and Si 2p were collected as described before. Atomic concentrations were determined using the integrated areas after subtracting the background and atomic sensitivity factors of 1.000, 1.676, 2.881, and 0.900 for C 1s, N 1s, O 1s, and Si 2p lines respectively. Previously determined etch rate was used to convert etch time to etch depth and atomic concentration with etch depth for each sample were plotted to observe composition variations.

Laboratory Biological Assays

Growth and Release of the Macroalga (*Ulva linza*)

A detailed description of the *Ulva linza* growth and removal assay using high-throughput screening methodologies can be found elsewhere.[27] A brief description of the procedure is provided here. All 24-well plates for the *U. linza* removal assay were aged in water for 45 days. The coatings were equilibrated with filtered artificial seawater (ASW; Tropic Marin) for 2 ~~hours~~ h before starting the experiment. Then 1 mL of *U. linza* spores in a single strength enriched ASW suspension (with 3.3×10^5 spores/mL, adjusted to 0.05 OD at absorbance 660 nm) was deposited into each coating well. Spores were allowed to settle and cultured for 6 days by incubating at 18 °C with a 16:8 light: dark cycle (photon flux density 15.39 Wm^{-2}) with nutrients renewed every 48 h. To evaluate ease of removal the ASW medium was removed and three of the rows of wells were subjected to water-jetting at 9 and 67 kPa using a spinning water-jet apparatus. One row of wells was not subjected to the water jet and was used as the measure of growth. [28] Biomass of sporelings in coated wells was determined using chlorophyll extraction. Chlorophyll was extracted by adding 1 mL of DMSO to each well and the fluorescence determined at excitation 360 nm and emission at 670 nm wavelengths. Fluorescence is directly proportional to the biomass present on each coating surface. The fluorescence from water-jetted vs. non-jetted wells was used to determine relative percent removal of sporelings.

Growth and Release of Microalgae (*Navicula incerta*)

The microalga (*Navicula incerta*) assay was conducted using methods described elsewhere.[29, 30] Briefly, coatings prepared in 24-well plates were used for assessments of diatom attachment and adhesion following 28 days of water immersion pre-conditioning in running tap water. A suspension with 4×10^5 cells/mL of *N. incerta* (adjusted to 0.03 OD at absorbance 660 nm) in Guillard's F/2 medium was deposited into each well (1 mL per well) and cell attachment was encouraged by static incubation for 2 h under ambient conditions in the dark. Coating surfaces were then subjected to water-jet treatments.[28] Three replicate wells did not receive the water-jet treatment so that initial cell attachment could be determined and three replicate wells were water-jetted at 138 kPa (20 psi) for 10 s. Microalgae biomass was quantified by extracting chlorophyll using 0.5 mL of DMSO and measuring fluorescence of the transferred extracts at an excitation wavelength of 360 nm and emission wavelength at 670 nm. Relative fluorescence (RFU) measured from the extracts was considered directly proportional to the biomass present or remaining on the coating surfaces after water-jetting. Percent removal of attached microalgae was determined using relative fluorescence of non-jetted and water-jetted wells.

Bacterial (*Cellulophaga lytica*) Biofilm Adhesion

A detailed description of the marine bacterial retention and adhesion assays for evaluating fouling-release coatings can be found elsewhere.[28, 30-31] Similar to the microalgal attachment and adhesion assay, 24-well plates were incubated statically at 28°C for 24 h with a 1 mL/well of suspension consisting of the marine bacterium *Cellulophaga lytica* at 10^7 cells/mL concentration in ASW containing 0.5 g/L peptone and 0.1g/L yeast extract. The ASW growth medium was then removed and the coatings were subjected to water-jet treatments. The first column of each coating (3 replicate wells) was not treated and served as the initial amount of bacterial biofilm growth. The second column (3 replicate wells) was subjected to water-jetting at 69 kPa (10 psi) for 5 s. Following water-jet treatments, the coating surfaces were stained with 0.5 mL of a crystal violet solution (0.3 wt. % in deionized water) for 15 minutes and then rinsed three times with deionized water. After 1 hour of drying at ambient laboratory conditions, the crystal violet dye was extracted from the coating surfaces by adding 0.5 mL of 33% acetic acid solution for 15 min. The resulting eluates were transferred to a 96-well plate (0.15 mL/coating replicate) and subjected to absorbance measurements at 600nm wavelength using a multi-well plate spectrophotometer. The absorbance values were considered to be directly proportional to the amount of bacterial biofilm present on coating surfaces before and after water-jetting treatments. Percent removal of bacterial biofilm was quantified by comparing the mean absorbance values of the non-jetted and water-jetted coating surfaces.[27]

Adult Barnacle (*Amphibalanus amphitrite*) Adhesion

An adult barnacle reattachment and adhesion assay was used to evaluate the fouling-release properties of the coatings towards macrofouling organisms.[32, 33] Barnacles were removed from silicone substrates sent from Duke University and placed on experimental coatings (5 barnacles per coating) using a custom-designed immobilization template. The immobilized barnacles were allowed to reattach and grow for 2 weeks via immersion in an ASW aquarium tank system with daily feedings of brine shrimp *Artemia* nauplii (Florida Aqua Farms). The number of non-attached barnacles was recorded and the attached barnacles were pushed off (in shear) using a hand-held force gauge mounted onto a semi-automated stage. Once the barnacles were dislodged, their basal plate areas were determined from scanned images using Sigma Scan Pro 5.0 software program. Barnacle adhesion strength (MPa) was calculated by dividing the peak force of removal by the basal plate area for each reattached barnacle. The average barnacle adhesion strength for each coating was reported as a function of the number of barnacles released with a measureable force and that exhibited no visible damage to the basis or shell plates.

Mussel (*Geukensia demissa*) Adhesion

The assessment of marine mussel adhesion to the coating surfaces was evaluated using a modified version of previously published protocols.[34-36] Marine ribbed mussels (*Geukensia demissa*; 3-5 cm length) were received from Duke University Marine Laboratory in Beaufort, North Carolina, USA. Prior to the attachment study, a 4 cm long acetal plastic rod (product# 98873A105, McMaster-Carr) was attached to each mussel perpendicular to the ventral edge, using a 3M® acrylic adhesive (product# 7467A135, McMaster-Carr). Six mussels were then immobilized on to each coating surface using a custom-designed template fabricated from PVC sheets. The coatings containing immobilized mussels were then placed in an ASW aquarium system and fed daily with live marine phytoplankton (DTs Premium Reef Blend Phytoplankton). The coatings were removed from the ASW aquarium tank system after three days of immersion and the total number of mussels exhibiting attachment of byssus threads was recorded for each coating. The plastic rod of each attached mussel was then affixed to individual 5 Newton load cells of a custom-built tensile force gauge where all mussels were pulled off simultaneously (1 mm s^{-1} pull rate). The total force (Newtons) required to completely detach all byssus threads for each mussel was recorded and the mean value of the total number of attached mussels for each coating was calculated.

Field Immersion Study

Select experimental coatings were sent to static ocean immersion field testing sites in Hawaii, California, and Singapore to evaluate their fouling-release performance. Coating formulations 5 and 6 along with controls, A4-20 and Intersleek®900 were included in the field study. At each test site, panels were immersed in the ocean about 1 m deep from the water line. Every month, visual inspections were performed before and after water-jet treatments (1.65 or 0.69 MPa).

Statistical Analysis

The analysis of variance for completely randomized design and a cell-means model were performed in SAS 9.4. The GLM Procedure with Least Squares Means (LS-Means) was used to compute the LS-Means of each treatment combination of coating and oil type for a given percent removal in case of *U. linza*, microalgae and bacteria. Similarly, the LS-Means of each treatment combination of coating and oil type was computed for adhesion strength of adult barnacles. Five replicates were considered in each treatment combination of coating and oil type. Barnacle release scores were assigned based on zero MPa strength corresponding to score 100 and 0.4 MPa strength corresponding to score zero following the equation

$$100 - \left(\left(\frac{F_r}{F_0}\right) \times 100\right)$$

where F_r is the adhesion strength of individual barnacle and F_0 is the maximum adhesion strength observed during the test.

Adhesion strength of non-attached barnacles was considered to be zero. This allows for non-attached or broken barnacles for which adhesion strength was not recorded to be included in the statistical analysis. Significant difference for pairwise comparisons between treatments and five controls was defined at $p < 0.05$ based on Tukey's test.

Results and Discussion

Biofouling can be a nuisance to marine organisms and plants which share the marine environment. Often, these marine organisms and plants have naturally evolved defensive anti-fouling and fouling-release strategies that are chemical, physical, mechanical or behavioral.[37] Release of oils and mucus to weaken the adhesion of fouling organisms is a commonly observed physical strategy in nature.[38] The oils provide slipperiness to the surface when needed allowing for the easy release of fouling. From early times scientists have attempted to employ this strategy in marine coatings for minimizing biofouling, although in 1970s it was investigated for fouling-release paint applications.[16-17, 39] Most commonly, a non-reactive silicone oil is incorporated into silicone elastomer paint formulations and the oil trapped in the matrix slowly exudes over time providing a similar effect as seen for some organisms. However, achieving continuous lubrication over a long period of time is quite challenging with a coating system.

Through this study, the question regarding whether a similar strategy would help to improve the fouling-release performance of highly crosslinked SiPU marine coatings was addressed. Phenylmethyl silicone oil was chosen for the study given its surface tension being close to PDMS yet slightly higher, a strategy to have some control over the oil exuding behavior. In this study, a total of 18 experimental formulations modified with phenylmethyl silicone oil (Table 2) were evaluated for fouling-release performance along with several internal control coatings and commercial standards.

Water and methylene iodide contact angles were measured for the as-made coatings as well as following 28 days of water immersion. Figure 3 a. shows the contact angles of the coatings plotted against the coating compositions. The experimental coating surfaces showed water contact angles (WCA) in the range of 90°-105° suggesting hydrophobic character. Water contact angles for the silicone oil-modified SiPU coatings remained mostly unchanged after 28 days of water immersion. The WCA for A4-20 (siloxane-PU without silicone oil) was ~102°, which is in the same range as silicone oil-modified siloxane-PU coatings signifying self-stratification of siloxane.

Methylene iodide contact angles (MICA) for silicone oil-modified coatings were in the range of 67-71° before water immersion. Although experimental coatings 1-14 did not show much change in MICA after water aging, coatings 15-18 showed an increase in MICA (75-85°) following water aging. Interestingly, the coatings which displayed increased WCA and MICA after water immersion were attributed to formulations modified with phenylmethyl content greater than 50% and oil amount 5%. Figure 3 a. shows the trends in surface energy (SE) changes before and after water immersion. SE values for phenylmethyl silicone oil-modified coatings were very similar to each other prior to water aging. However, after water aging, a slight decrease in SE was observed for silicone oil-modified coatings 3-6, and 11-13. Coatings 2, 9, and 15-18 showed a significant decrease in SE mainly attributed to the increase in MICA highlighted before. Internal control A4-20 also demonstrated lower surface energy after water immersion. However, in general all coatings surfaces remained hydrophobic after water aging suggesting that no significant surface rearrangement had occurred.

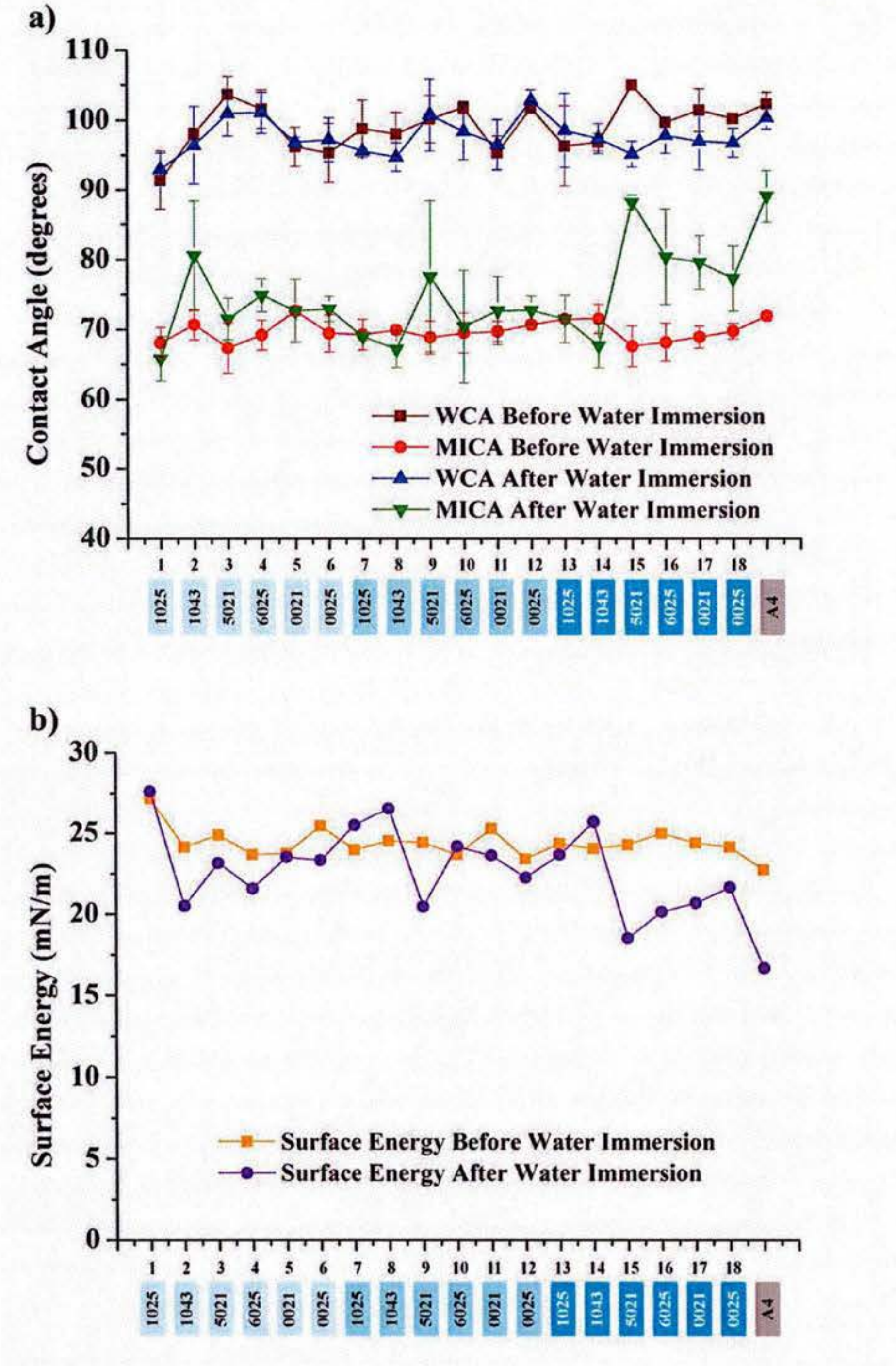

Figure 3: a) Water and methylene iodide contact angles before and after 28 days of water aging. Each data point represents the average and standard deviation of 3 measurements. **b)** Surface energy of coatings calculated by the Owens-Wendt method utilizing the average WCA and MICA measurements. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone

oil (ex: 1-6, 7-12, 13-18) while the darkening of blue shade indicate increasing oil content from 1, 2 to 5% and the controls and standards are shaded in gray.

Figure 4 (a, b, c) shows the atom concentration change determined using XPS of Si, C, O, and N as a function of etch depth from the coating surface (for coatings A4-20, silicone oil-modified formulation 5 and 17). The depth profiling graph (Figure 4 a.) for SiPU without silicone oil (A4-20) showed about 22% surface concentration of Si, which gradually decreased and leveled off to 5% after about 3.5 nm deep into the coating. For the A4-20 coating, the concentration of O followed a similar trend as that for Si, yet slightly higher atomic concentration than Si was observed. The results suggest that siloxane was concentrated near the first 3.5 nm of the surface for A4-20, which was very similar to previous surface characterization of siloxane-PU coatings conducted by Siripirom *et al.*[40] In that study it was reported that siloxane-PU formulation with difunctional APT-PDMS has a siloxane layer thickness of about 3.5 nm when characterized using Rutherford backscattering. The phenylmethyl silicone oil-modified SiPU formulation 5 (Figure 4 b.) showed a similar trend for atomic concentration profiles as A4-20 had a thicker layer of siloxane/silicone oil. For formulation 5, the Si concentration appears to plateau at around 6 nm from the surface, which was almost double for that of A4-20 without silicone oil. In addition, formulation 5 showed a Si surface concentration of 25-29%, which was slightly higher than that for A4-20. As the phenylmethyl silicone oil concentration was increased from 1% to 5%, siloxane/silicone oil was predominant up to about 20 nm deep into the coating (comparing Figure 4 b. and c.). The surface concentration of Si had increased up to 30% for formulation 17. The increase in thickness of the siloxane layer suggests that the added phenylmethyl silicone oil had segregated closer to the surface along with the siloxane component of the SiPU coating system.

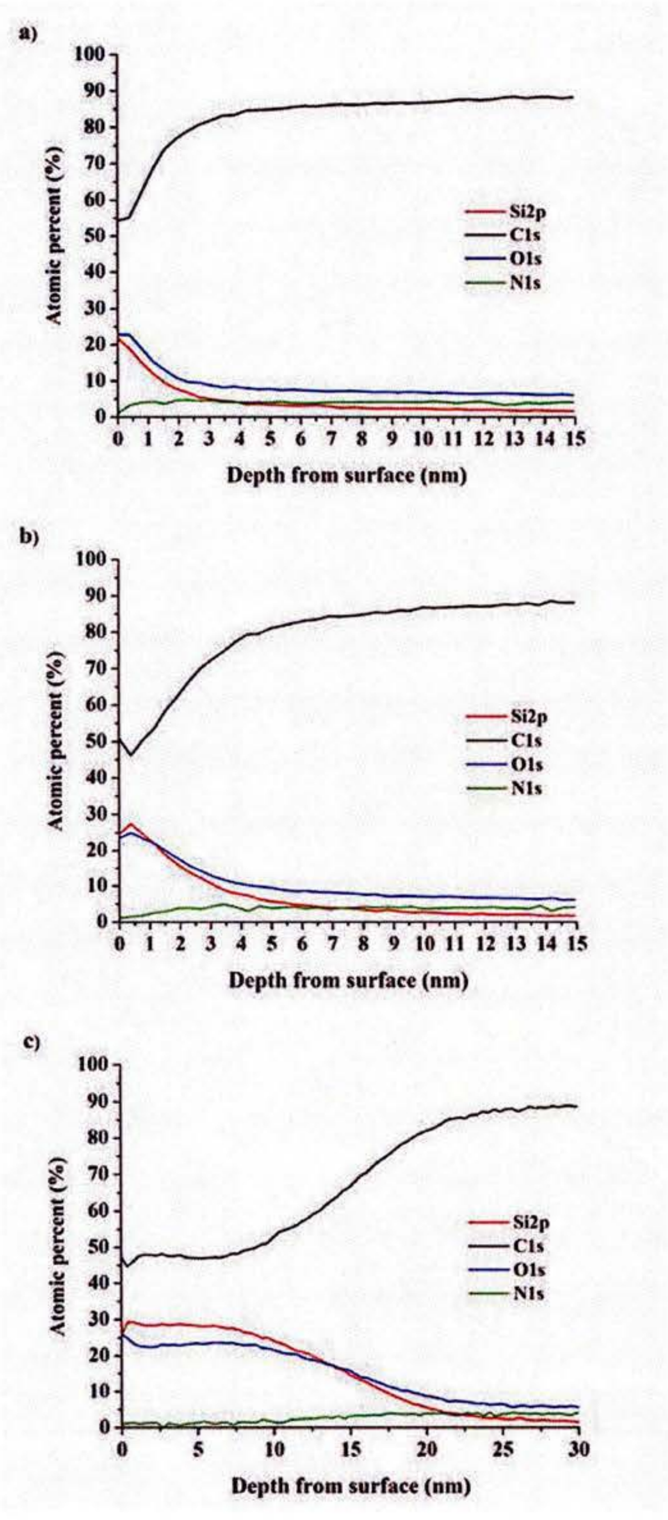

Figure 4: XPS atomic concentration depth profile of **a)** A4-20 siloxane-PU without oil; **b)** silicone oil-modified formulation 5; and **c)** silicone oil-modified formulation 17.

Laboratory biological assays using single model marine species provide an effective method to quickly screen a range of bench scale marine coating formulations. This method has enabled efficient identification of successful candidate marine coatings formulations without having to expend valuable resources at field testing sites which can be time- and cost-consuming. However, it is widely accepted that field immersion studies represent a more realistic environment in which new marine formulations need to perform in order to enter the marine paint market as a successful product. Therefore, select formulations which performed well during laboratory biological assays were subjected to field immersion studies. Formulation screening conducted using laboratory assays have shown good correlation with field immersion results, indicating the ability to forecast the fouling-release performance and downselect coating candidates before conducting field immersion studies.[41]

Following 28 days of water aging and prior to any biological characterization studies, all experimental, internal control coatings and commercial standards were subjected to leachate toxicity assessments. Leachates (extracts in growth mediums described above) from coatings were collected and measured for growth and compared to positive growth control (fresh nutrient medium). None of the silicone oil-modified coatings displayed toxicity compared to the positive growth control (data not provided).

Ulva linza is present in oceans around the world and it is one of the most common species of green macroalgae that contributes to biofouling on ships' hulls.[42] It is known that surface wettability plays a key role in both promoting settlement and adhesion strength of *U. linza*.[43-45] In particular hydrophobic surfaces tend to promote settlement of *U. linza*, whereas spores tend to adhere more strongly to hydrophilic surfaces. Figure 5 shows *U. linza* removal from the experimental, internal control and commercial standard coatings after water-jetting at 9 kPa and 67 kPa. ANOVA's conducted for the *U. linza* removal assay suggest that there are coatings within the set from which removal at both water jet pressures were significantly different (p-value<0.0001, Tables S2 and S5, included in Supporting Information). Several experimental coatings with silicone oil displayed significantly higher sporeling removal compared to all internal control and commercial standard coatings when subjected to 9kPa water jet treatment (Figure 5). In particular, a Tukey's comparison test (pairwise comparison) revealed that the phenylmethyl silicone oil-modified coatings, except formulations 11 and 17, showed significantly higher biomass removal compared to A4-20, silicone elastomer (Dow Corning T2), pure polyurethane (PU) and Intersleek® 900 (IS 900) (all p-values<0.05, Table S4). Water-jet treatments conducted at the higher pressure (67 kPa) resulted in more biomass removal from most coatings. Phenylmethyl silicone oil-modified coatings displayed slightly higher removal of sporelings compared to that of A4-20 without silicone oil, yet statistically most experimental coatings were similar in performance against sporeling removal at 67 kPa water-jet pressure (Table S7). However, all silicone oil-modified coatings showed significantly higher sporeling removal when compared to internal controls of T2 and PU and the commercial standard IS 900 (Table S7).

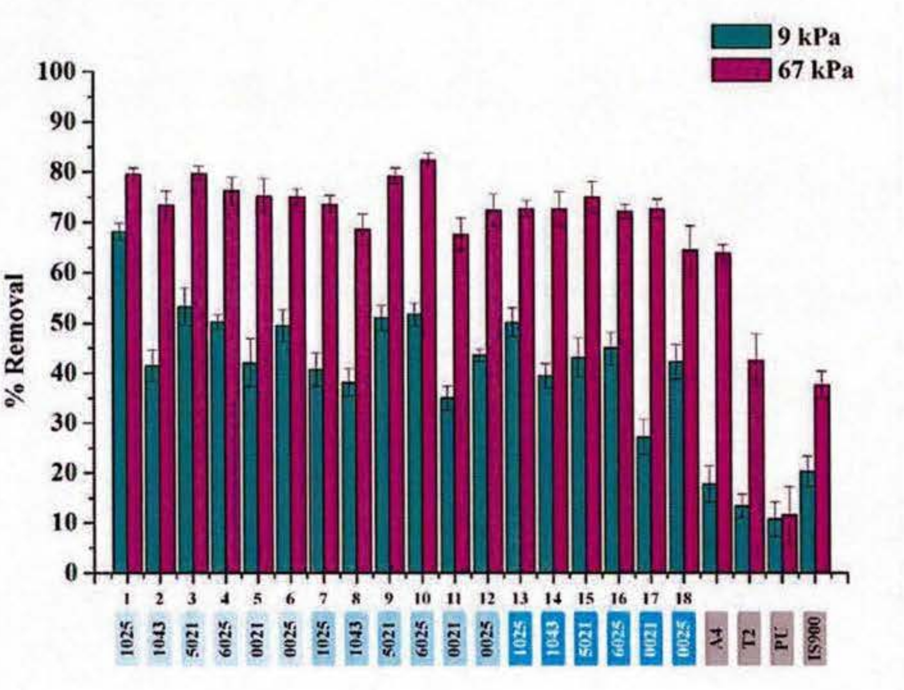

Figure 5: Macroalgae (*Ulva linza*) removal from experimental and control/standard coatings after water-jet treatment at 9kPa and 67kPa. Each data point represents the average percent removal value of 6 replicates. Error bars indicate one standard error of the mean. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1-6, 7-12, 13-18) while the darkening of blue shade indicates increasing oil content from 1, 2 to 5% and the controls and standards are shaded in gray.

In general, all of the phenylmethyl silicone oil-modified siloxane-PU coatings showed a high removal of sporelings of *U. linza* upon water-jet treatment (Figure 5). Interestingly, silicone oil-modified experimental coatings demonstrated higher removal of sporelings at low water jet pressures (9k Pa) compared to the internal control A4-20 without any oil, which suggests that incorporation of oil improved sporeling removal from the siloxane-PU system. At water-jet treatments of 9 kPa and 67kPa, all silicone oil-modified siloxane-PU coatings exceeded the amount of removal observed for the commercial fouling-release coating IS 900 (Figure 5, and Table S4,S7). Experimental coating formulations 1, 3, 9 and 10 exhibited good fouling-release performance towards sporelings of *U. linza* at both water jet pressures with percent removal values as high as ~75-80% (Figure 5). These coatings showed statistically higher removal of sporelings of *U. linza* than standard IS 900 and the internal controls, T2 and PU at 95% significance level (all p-values<0.05, Table S3 and S6). Therefore, silicone oil-incorporated coatings seem to impart good fouling-release properties towards *U. linza*. It is apparent that self-segregated silicone oil may lead to weaker attachment allowing higher biomass removal at low water jet pressure. Greater removal of *U.linza* has been observed with coating surfaces having low SE (ex. PDMS) while removal was extremely poor for those with high SE.[46] It is proposed that the adhesive secreted by the spores spreads more on hydrophilic surfaces covering a greater surface area compared to that on hydrophobic surfaces which leads to easy release when subjected to stress or shear force. The SE of the silicone oil-modified coatings indicates a hydrophobic surface (Figure 3 b.), thus fouling-release trends for *U.linza* are in agreement with well-accepted studies. Additionally, interfacial slippage introduced by the silicone oil enhanced the easy release of green algae, as fouling-release performance of experimental coatings were significantly superior at very low water-jet pressure (9 kPa) compared to all other coatings. Specifically, silicone oils with 40-60% phenylmethyl content provided the best sporeling release performance at 1-2% oil level (Table S3 and S6).

With respect to the diatom *N. incerta,* the pure polyurethane internal control (PU) and IS 900 standard displayed the highest amount of cell removal (Figure 6~~7~~). Pure polyurethane, which does not contain any PDMS, exhibited more than 90% *N. incerta* removal. However, all silicone oil-modified coatings displayed impaired removal of *N. incerta* when compared to the A4-20 internal control. The observed results can be explained when one considers the adhesion preference of this diatom strain, which typically adheres more strongly to hydrophobic surfaces than to hydrophilic surfaces (a behavior that is the exact opposite of green algae *U.linza*).[44, 47] Contact angle and SE measurements for silicone oil-modified SiPU coatings indicate hydrophobic surface characteristics (Figure 3 a. and b.). Therefore, diatom removal was negatively affected, which is not unexpected. Coatings which displayed good fouling-release performance towards *U. linza* (1, 3, 9 and 10) performed rather poorly towards *N. incerta* highlighting the complexity of attaining a fouling-release surface which performs well for a variety of organisms. The high amount of cell removal observed for IS 900 is attributed to its reported amphiphilic character. The 1st generation SiPU formulation showed *N. incerta* removal comparable to Intersleek ®700 and T2 silicone elastomer. Interestingly, however, the experimental coatings modified with phenylmethyl homopolymer oil (100% phenylmethyl) showed similar *N. incerta* removal at all oil levels (1, 2, and 5%).

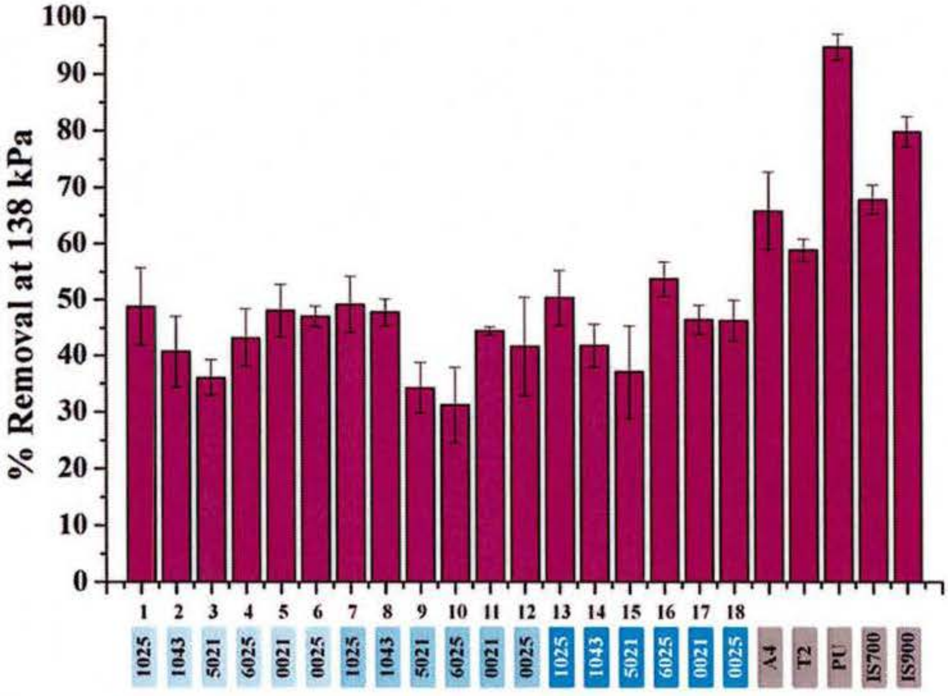

Figure 6: Diatom (*Navicula incerta*) removal from experimental and control/standard coatings after treatments with a 138 kPa (20 psi) water jet pressure for 10 s ~~seconds~~. Each percent removal value represents the average of 3 replicates samples. Error bars indicate one standard deviation of the mean. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1-6, 7-12, 13-18) while the darkening of blue shade indicates increasing oil content from 1, 2 to 5% and the controls and standards are shaded in gray.

Statistical analysis of silicone oil-modified experimental coatings revealed those with significantly different performance towards diatom removal at 138 kPa water jet treatment (p-value < 0.0001, Table S8). Tukey's comparison showed that SiPU without silicone oil (A4-20) has similar diatom removal performance to that of IS 700, IS 900 and silicone elastomer T2. Even though a few experimental coatings display impaired diatom removal, coatings 1, 7, 13, and 16 (best performers out of experimental coatings) are statistically similar in performance to the A4-20 formulation at $\alpha=0.05$ significance level (Table S9). On the other hand, they also showed comparable performance to Dow Corning T2 silicone elastomer in regard to *N. incerta* removal (Table S9). Coatings 16 and 13 also showed comparable *N. incerta* removal performance to IS 700 although most of the other experimental coatings showed slightly impaired performance compared to IS 700. In general, coatings with silicone oils, which contain low phenylmethyl compositions seemed to provide the best performance against slime forming diatoms.

Marine bacterium *Cellulophaga lytica* biofilm removal from coatings after exposure to 69 kPa (10 psi) water jet treatment is shown in Figure 7. Statistical analysis on biofilm removal data for experimental coatings showed that there are formulations with statistically different biofilm removal properties (p-value<0.0001, Table S11). The commercial fouling release-coating IS 900 outperformed all of the experimental coatings in terms of biofilm removal (97%), including the five best performing silicone oil-modified coatings (1, 5, 8, 16, and 17) observed in this particular assay (Table S12). However, several siloxane PU-coatings modified with phenylmethyl silicone oils showed a similar degree of biofilm removal as the IS 700 standard. Coating 1 with 1% of PMM1025 silicone oil showed the greatest removal (72%) of bacterial biofilm out of all the experimental coatings, and at $\alpha=0.05$ significance level, this formulation also outperformed IS 700 (p-value <0.05, Table S12 and S13). On the other hand, the five best experimental coatings displayed similar bacterial biofilm removal performance to A4-20, Dow Corning T2 and pure polyurethane control coatings (all p-values are >0.05, Table S12 and S13). In general, the incorporation of phenylmethyl silicone oil did not affect the bacterial biofilm removal properties of the siloxane-PU system since several experimental coatings showed similar performance to the A4-20 internal control. No significant trend was observed with regard to phenylmethyl composition of silicone oils in this assay.

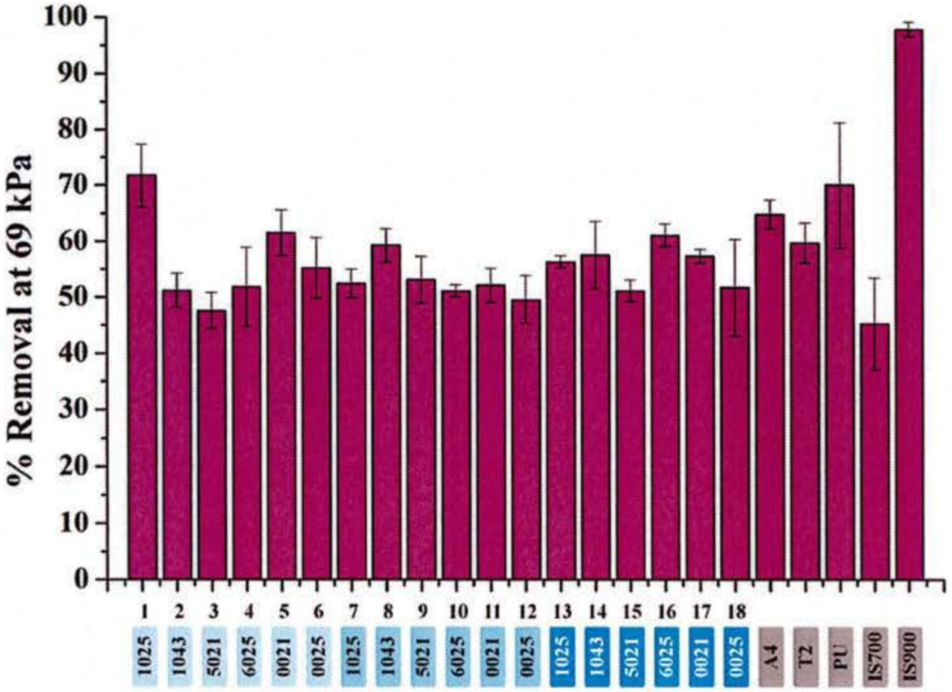

Figure 7: Bacterial (*Cellulophaga lytica*) biofilm removal from experimental and control/standard coatings after being exposed to a 69 kPa (10 psi) water-jet treatment for 5 s. The percent removal values represent the average of 3 replicate samples. Error bars indicate one standard deviation of the mean. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1-6, 7-12, 13-18) while the darkening of blue shade indicates increasing oil content from 1, 2 to 5% and the controls and standards are shaded in gray.

Macrofouling organisms are the main culprits of heavy calcareous fouling which leads to increased hull roughness and severe powering penalties.[48] Barnacle cyprids are known to conduct surface exploration before permanently cementing themselves (a process known as metamorphism).[49-50]Like other marine organisms, barnacles also display species specific adhesion preferences according to surface chemistry and wettability.[49] Therefore, barnacle adhesion strength to silicone oil-modified coatings reflect the surface properties of these coatings. Figure 8 shows the adhesion strength measurements of adult barnacles that were reattached to the experimental and control/standard coatings. During this test, reattached barnacles were pushed off in shear using a force gauge. If the barnacle is adhered weakly, the barnacle will release without any damage. Strongly adhered barnacles would break during the test indicating poor fouling-release. For a good fouling-release coating, the adhesion strength of barnacles should be minimal and have several non-attached barnacles. Poor fouling-release surfaces show high adhesion strength of barnacles and multiple broken barnacles.

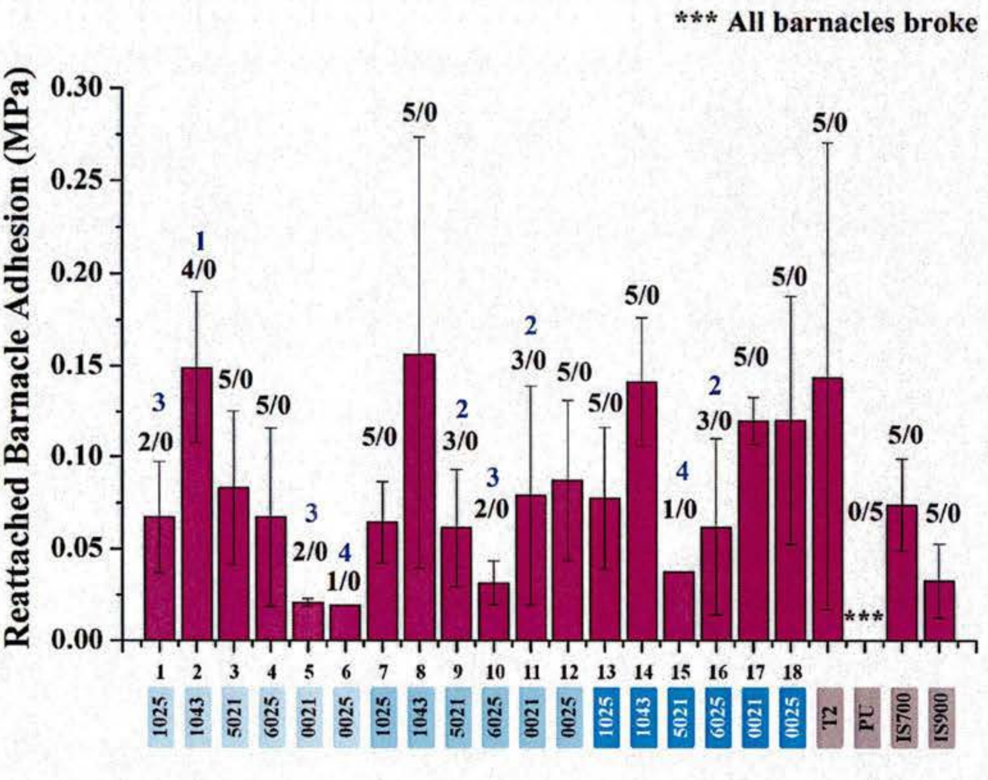

Figure 8: Adhesion of reattached barnacle (*Amphibalanus amphitrite*) experimental and control coatings. Five adult barnacle reattachments were attempted for each coating. Each adhesion strength value represents the average of total number of reattached barnacles released without damage. Error bars represent the standard deviation of average barnacle release stress. The ratio represents the number of measured barnacles over the number of broken/damaged barnacles. The blue digits represent the number of non-attached barnacles. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1-6, 7-12, 13-18) while the darkening of blue shade indicate increasing oil content from 1, 2 to 5% and the controls and standards are shaded in gray.

All five barnacles reattached onto the pure polyurethane surface exhibited base/shell plate damage during push off measurements, indicating its poor fouling-release properties. Adhesion strength values of approximately 0.10-0.15 MPa were observed for the 1st generation SiPU coating.[14] Several of the silicone oil-modified siloxane-PU coatings showed comparable or better fouling-release properties than IS 900 in this category. Several of the experimental coatings also had several non-attached barnacles suggesting excellent performance against barnacle adhesion.

In order to conduct statistical analysis of data obtained from barnacle adhesion assay, a scoring system was introduced as explained in statistical analysis section. According to this scoring system non-attached barnacles were regarded as 100 and the highest adhesion strength was regarded as score of 0. ANOVA of the adhesion data converted to scores indicated that the coatings display significantly different adhesion strengths of reattached barnacles (Table S14). Barnacle adhesion strengths of several experimental coatings (Table S15; coatings 1, 5, 6, 10, and 15) were similar to that of IS 900 and IS 700 although significantly better than Dow T2 silicone elastomer. Barnacles (*A.amphitrite*) adhered to low SE coatings have shown low critical removal stress; indicative of good fouling-release properties of low SE materials towards barnacles.[51] Coatings discussed here (silicone oil-modified SiPU coatings) have SE in the range of 20-25 mN/m, therefore providing low adhesion strength for barnacles. A decrease in barnacle adhesion and an increase in the number of non-attached barnacles were observed with a low amount (1wt %) of phenylmethyl homopolymer oil, whereas a similar effect was obtained with slightly higher amounts of phenylmethyl copolymer oil suggesting a correlation between phenylmethyl composition and barnacle adhesion. Overall, siloxane-PU coatings displayed comparable barnacle release performance to the commercial fouling-release coatings.

Mussels are fairly large fouling animals which tend to attach to substrate with the use of multiple byssal threads. Several studies have shown that amino acid 3,4-dihydroxyphenyl-L-alanine (DOPA) plays a key role in producing adhesive plaque during mussel attachment to a substrate.[52] Studies have also shown that mussel adhesive plaque spreads the least on low SE surfaces (such as PTFE) and requires more byssal threads to attach to the surface.[52] However, the exact opposite behavior is observed for hydrophilic surfaces. Figure 9 provides the results from the mussel adhesion experiment. Several siloxane-PU coatings had no mussel attachment during the 3-day attachment test. However, a few coatings with phenylmethyl silicone oil displayed minimal mussel attachment where the mussels were released with very low forces. This observation is in agreement with previous findings on the preference of mussel adhesion behavior, where significantly low mussel adhesion strengths were observed for low SE materials. Control coating A4-20 and the IS 900 standard did not enable any mussels to attach to their respective surfaces, which may imply that these coatings perform well against mussel settlement. The viscosity of the silicone oil additive seems to play an important role in the case of mussel adhesion. Interestingly, the experimental coatings which did not enable any mussels to attach contained phenylmethyl silicone oils with similar viscosities, regardless of phenylmethyl composition. It may be hypothesized that the silicone oils with similar viscosity have enough mobility to self-stratify to the surface. Statistical analysis was not performed due to numerous data points with no mussel attachment.

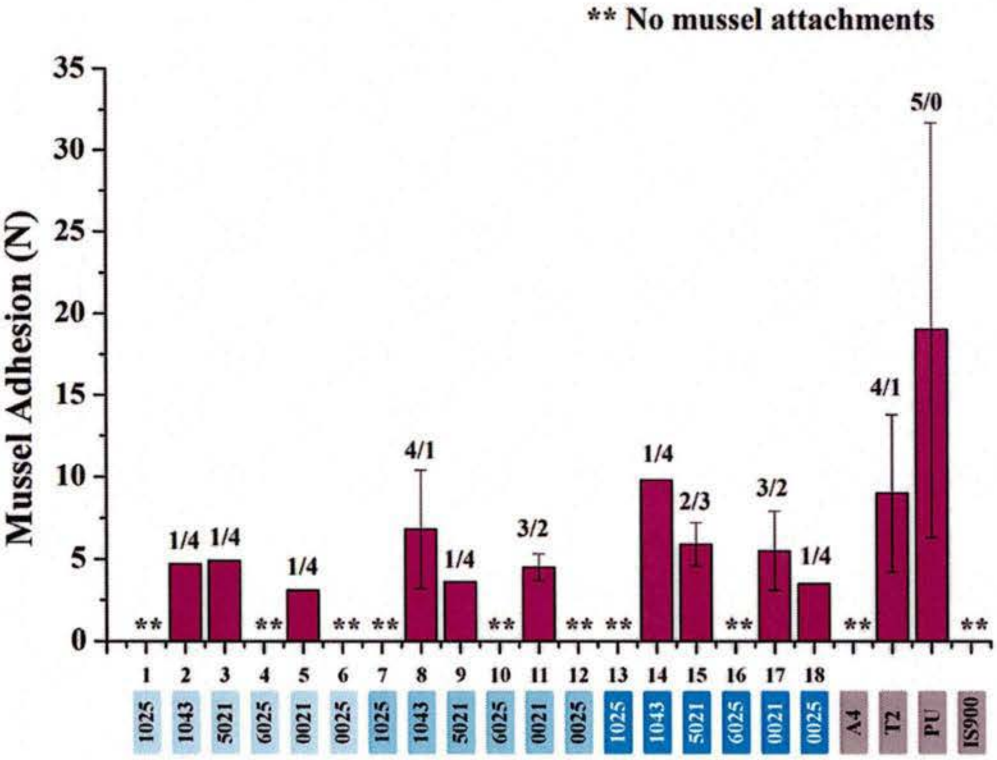

Figure 9: Adhesion of mussels (*Geukensia demissa*) to experimental and control coatings. Five mussels were introduced to each coating. Each adhesion strength value represents the average of total number of attached mussels released from the surface. Error bars represent the standard deviation of the average

adhesion force. The ratio represents the number of attached mussels over the number of non-attached mussels. ** indicate the coatings that did not have any attached mussels. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1-6, 7-12, 13-18) while the darkening of blue shade indicates increasing oil content from 1, 2 to 5% and the controls and standards are shaded in gray.

Coatings which demonstrated overall good fouling-release properties during laboratory biological assays were down selected for field immersion testing. Coating formulations 5 and 6 were selected since they had the lowest barnacle adhesion (with several barnacles not adhering at all), and good release properties for *Ulva* and *C. lytica*. Included in the field test were also control coatings A4-20 and IS 900. Figure 10 shows the visual appearance of the panels before and after water-jet cleaning at the indicated pressures (i.e., 0.69 and 1.65 MPa). After 3 months of field immersion in Hawaii, the two experimental coatings showed qualitatively similar fouling-release performances to the SiPU control and commercial standard. As the coatings were exposed for a longer duration, the effects of incorporating silicone oil can be observed. Specifically, after 11 months of exposure at the Morro Bay testing site in California, coating 5 (containing silicone oil PMM-0021) outperformed the internal control A4-20 and displayed similar fouling-release performance to the commercial standard IS 900. The oil in coating 5 has a lower molecular weight and viscosity than the one used in coating 6 and may contribute more effectively to interfacial slippage. After 11 months of exposure in Singapore, Formulation 5 showed comparable performance to A4-20 slightly edging over formulation 6. However, it is worth noting that a lower water-jet pressure was used at the Singapore test site. Variations in the marine environments in these different bodies of water could contribute to the observed trend in fouling-release properties of formulations 5 and 6. In the past, studies have shown that oceanic conditions vary quite a bit based on their location.[53-54] Although it is well recognized that different sea water parameters such as temperature, salinity, density, and pH have an influence over biofouling, little attention has been given to understand their exact effects.[1]

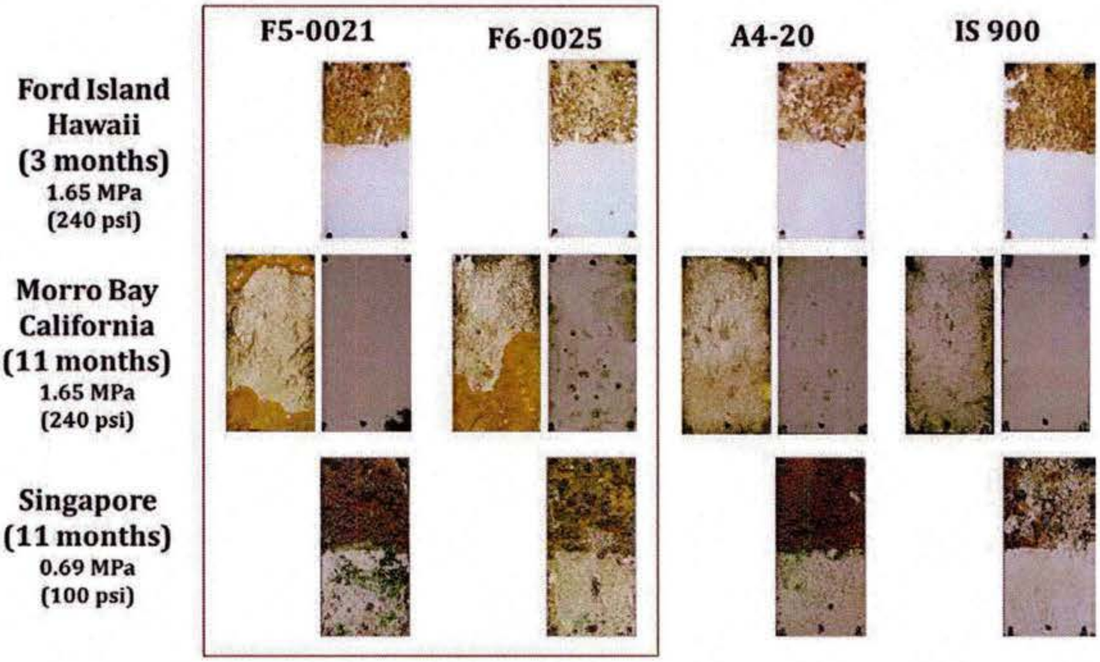

Figure 10: Visual appearance of coatings included in field immersion trials at California, Singapore and Hawaii test sites. In Hawaii and Singapore test sites, half of each panel was subjected to water jet cleaning while the other half represents the accumulated fouling. At the California test site, the entire panel was subjected to water jet treatment. Thus the picture on the left (2nd row) represent the accumulated fouling while picture on the right represent the coating after cleaning.

Incorporation of phenylmethyl silicone oil into siloxane-PU coatings has been shown to improve the fouling-release performance towards macrofouling organisms during laboratory biological assay tests; in particular, for macroalgae sporeling release, where coatings with silicone oils containing <60% phenylmethyl composition showed significantly better performance than the SiPU control and commercial standards. Coatings modified with 1 % of silicone oils PMM-0021 and PMM-0025 (phenylmethyl homopolymer) showed reduced barnacle adhesion. For phenylmethyl copolymer oils PMM-5021 and PMM-6025, low barnacle adhesion strength was observed with slightly higher oil amount (2%or 5% by wt.). Several silicone oil-modified coatings showed excellent fouling-release performance towards marine mussels where the SiPU coatings that did not allow any mussels to adhere to their surface contained phenylmethyl silicone oils with a viscosity of 500 cs. However, silicone oil incorporation did not seem to substantially affect the bacterial biofilm and microalgae removal properties compared to the SiPU formulation without silicone oil

(A4-20). The field immersion studies showed that incorporating small amounts of phenylmethyl silicone oil could enhance the fouling-release properties of SiPU coatings.

Conclusions

Previous studies had suggested that inclusion of phenylmethyl silicone oil in silicone elastomer-based fouling-release coatings led to improved fouling-release performance.[15-22] These improvements were reasoned by hypothesizing that the reduced adhesion strength of marine organisms was due to increased interfacial slippage induced by the exuding silicone oil. This study investigated the effects of incorporating phenylmethyl silicone oils in a SiPU fouling-release coating system. Contact angle and surface energy measurements suggested that the coating surfaces were hydrophobic and remained hydrophobic after 1 month of water immersion. XPS analysis was helpful to understand the effects of silicone oil on coating morphology and indicated that stratification of the silicone oil occurred along with siloxane and formed a thicker interfacial layer. Laboratory biological assays indicated that an improvement in release properties for several types of model fouling organisms might have reflected the silicone oil modification. Siloxane-PU coatings modified with silicone oils demonstrated excellent release properties against the macroalga *U. linza*; high removal was observed at low water-jet pressures. An improvement in lower adhesion strength of macrofouling organisms was also observed with incorporation of silicone oil. In particular, silicone oils with high phenylmethyl composition provided good fouling-release performance towards barnacles (*A. amphitrite*). Excellent fouling-release performance towards marine mussels (*G. demissa*) was observed for coatings containing phenylmethyl silicone oil with an approximate viscosity of 500 cs, regardless of oil type or composition. However, fouling-release performance towards diatoms (*N. incerta*) and bacteria (*C. lytica*) was largely unaffected by silicone oil modification into SiPU coating system. Selected phenylmethyl silicone oil-modified siloxane-PU coatings also displayed long-term fouling-release performance comparable to commercial IS 900 standard during field immersion tests at three different test sites.

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Supporting Information

Table S1 includes the film thickness of coatings used for XPS analysis. Tables S2 through S16 showing the statistical analysis of the laboratory fouling-release assays are provided as Supporting Information.

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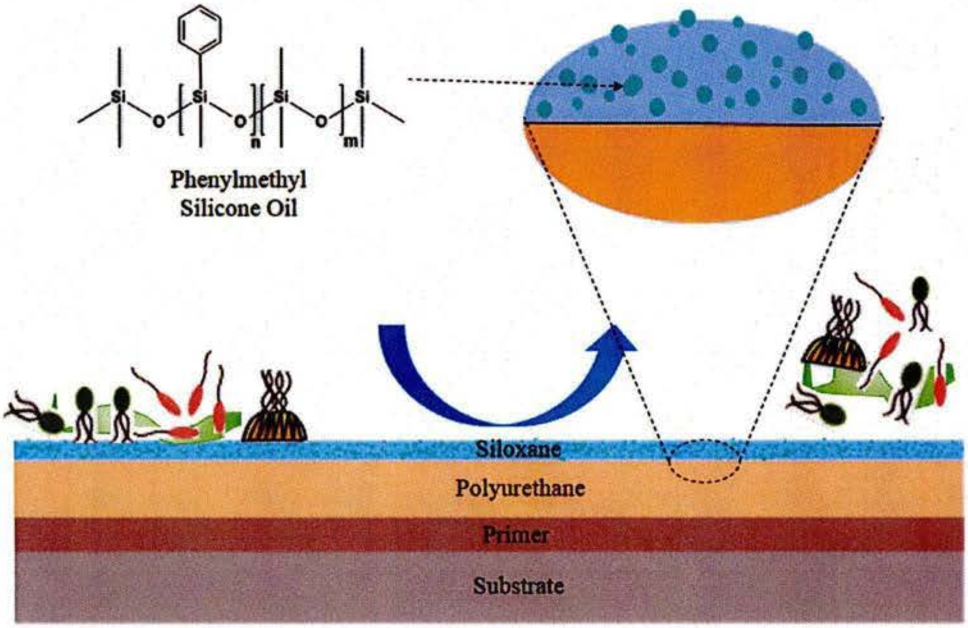
Graphical TOC



Silicone Oil Modified Siloxane-Polyurethane Fouling Release Coating System

Supporting Information

Fouling-release performance of silicone oil-modified siloxane-polyurethane coatings

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Acrylic Polyol Synthesis

Butyl acrylate (BA), 2-hydroxyethyl acrylate (HEA), toluene were purchased from Sigma Aldrich. Free radical source VAZO 67 (2',2'-Azobis(2-methylbutyronitrile)) was provided by DuPont. The acrylic polyol was synthesized using free radical polymerization. Briefly, toluene (320 g) was weighed into a 2 liter reaction flask equipped with an overhead mechanical stirrer, thermocouple, N_2 purge, and reflux condenser. The temperature of toluene was brought to 90 °C. Then the monomer mixture containing BA (400 g), 2-HEA (100 g), toluene (180 g), and VAZO 67 (20 g) was added drop-wise at a rate of 5.5 mL/min while maintaining the temperature of the reaction at 90 °C. Next the temperature was maintained for two hours following the monomer addition. Then 1.33 g of VAZO 67 dissolved in 12 g of toluene was added as the chaser. The temperature of the reaction was further maintained for 4 additional hours. Then the resin was transferred in to a container. The resin was characterized for percent solids and molecular weight was evaluated using GPC. The final acrylic polyol was 50% solids in toluene with number average molecular weight of 9613g/mol with a PDI of 1.74.

Synthesis of APT-PDMS (20000 g/mol)

Octamethylcyclotetrasiloxane (D_4), bis(3-aminopropyl)-tetramethyldisiloxane (BAPTMDS) were purchased from Gelest, Inc. Benzyltrimethylammonium hydroxide (in 40% methanol) was purchased from Sigma Aldrich. The cyclic siloxane monomer D_4 (1200 g) and benzyltrimethyl ammonium hydroxide (3.12 g) catalyst were combined in a one neck round bottom flask. The content was rotary evaporated to remove the methanol. The mixture was then transferred in to a 2 liter reaction flask equipped with a mechanical stirrer, N_2 inlet, reflux condenser and a thermo couple. BAPTMDS (15.09 g) was added to the reaction and heated up to 80 °C. Once the temperature was settled, the reaction was allowed equilibrate overnight. The next day the temperature was raised to 170°C for an hour to decompose the catalyst. Then the product was transferred to a container. The polymer was characterized for its molecular weight using GPC. Average molecular weight was determined to 19,760 g/mol with a PDI of 1.70.

Table S1: Film thickness measurements of coatings analyzed using XPS

Coating	Average Film Thickness (μm)	Standard Deviation (±)
Siloxane-PU no oil (A4-20)	45.63	0.81
F5-0021-1%	46.73	1.12
F17-0021-5%	47.50	0.95

Table S2: ANOVA results for *U. linza* removal at 9 kPa

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	21	21294.92	1014.04	18.61	<.0001
Error	110	5995.09	54.50		
Corrected Total	131	27290.01			

Table S3: *U. linza* removal: Top five performing experimental coatings at 9 kPa statistically compared against control coatings. The table shows t-values for pairwise comparison and the corresponding p-value. *Significant Difference at α=0.05.

Exp Coating→ Controls ↓	Coating 3 5021 (1%)	Coating 1 1025 (1%)	Coating 10 6025 (2%)	Coating 9 5021 (2%)	Coating 4 6025 (1%)
Coating 19 A4-20	-8.32185* <.0001	-7.95942* <.0001	-7.9465* <.0001	-7.8051* <.0001	-7.61259* <.0001
T2	-9.35732* <.0001	-8.99489* <.0001	-8.98197* <.0001	-8.84057* <.0001	-8.64806* <.0001
PU	-9.98242* <.0001	-9.61999* <.0001	-9.60706* <.0001	-9.46567* <.0001	-9.27316* <.0001
IS900	-7.73196* <.0001	-7.36953* <.0001	-7.3566* <.0001	-7.21521* <.0001	-7.0227* <.0001

Table S4: *U. linza* removal: Tukey's comparison for Least squares means of *U. linza* removal for coatings at 9 kPa. Least square means with the same letter indicates non-significance.

Tukey's grouping						***Ulva* Removal 9kPa LS mean**	**Coating #**
A						53.2515	3
A						51.7068	1
A						51.6517	10
A						51.049	9
A	B					50.2285	4
A	B					50.1641	13
A	B					49.4959	6
A	B					44.979	16
A	B					43.6018	12
A	B					43.1757	15
A	B	C				42.2589	18
A	B	C				42.1427	5
A	B	C				41.4689	2
A	B	C				40.7319	7
A	B	C				39.5418	14
A	B	C				38.1946	8
	B	C	D			35.0582	11
		C	D	E		27.1557	17
			D	E	F	20.2958	IS900
				E	F	17.7816	19 (A4-20)
				E	F	13.3681	T2
					F	10.7038	PU

Table S5: ANOVA results for *U. linza* removal at 67 kPa

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	21	34569.30	1646.16	30.09	<.0001
Error	110	6017.37	54.70		
Corrected Total	131	40586.67			

Table S6: *U. linza* removal: Top three performing experimental coatings at 67 kPa statistically compared against control coatings. The table shows t-values for each comparison and the corresponding p-value. *Significant Difference at α=0.05.

Exp Coating→ Controls ↓	Coating 10 6025 (2%)	Coating 3 5021 (1%)	Coating 1 1025 (1%)	Coating 9 5021 (2%)	Coating 4 6025 (1%)
Coating 19 A4-20	-4.33452* 0.0058	-3.71018* 0.0463	-3.65439 0.0546	-3.57717 0.0683	-2.91376 0.3346
T2	-9.33078* <.0001	-8.70644* <.0001	-8.65065* <.0001	-8.57342* <.0001	-7.91002* <.0001
PU	-16.5807* <.0001	-15.9564* <.0001	-15.9006* <.0001	-15.8233* <.0001	-15.1599* <.0001
IS900	-10.4598* <.0001	-9.83546* <.0001	-9.77967* <.0001	-9.70245* <.0001	-9.03904* <.0001

Table S7: *U. linza* removal: Tukey's comparison for Least squares means of *U. linza* removal for coatings at 67 kPa. Least square means with the same letter indicates non-significance.

Tukey's grouping					***Ulva* Removal 67kPa LS mean**	**Coating #**
A					82.39338	10
A	B				79.72733	3
A	B	C			79.4891	1
A	B	C			79.15933	9
A	B	C			76.32648	4
A	B	C			75.2338	5
A	B	C			75.11485	6
A	B	C			75.01478	15
A	B	C			73.666	7
A	B	C			73.4351	2
A	B	C			72.74301	13
A	B	C			72.67015	17
A	B	C			72.63992	14
A	B	C			72.42177	12
A	B	C			72.20804	16
A	B	C			68.67201	8
A	B	C			67.63361	11
	B	C			64.41499	18
		C			63.88418	19 (A4-20)
			D		42.54926	T2
			D		37.72811	IS900
				E	11.59077	PU

Table S8: ANOVA results for *N. incerta* (diatom) removal at 20 psi.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	22	14629.22	664.96	22.18	<.0001
Error	46	1379.14	29.98		
Corrected Total	68	16008.35			

Table S9: *N. incerta* (diatom) removal: Top five performing experimental coatings at 20 psi statistically compared against control coatings. The table shows t-values for each comparison and the corresponding p-value. *Significant Difference at α=0.05, No symbol means the two coatings are similar in performance.

Exp Coating→ Controls ↓	Coating 16 6025 (5%)	Coating 13 1025 (5%)	Coating 7 1025 (2%)	Coating 1 1025 (1%)	Coating 5 0021 (1%)
Coating 19 A4-20	2.769187 0.4652	3.423688 0.137	3.747879 0.0631	3.77471 0.059	3.959984* 0.0363
T2	1.224217 0.9998	1.878719 0.9545	2.202909 0.8347	2.22974 0.8206	2.415015 0.709
PU	9.255145* <.0001	9.909647* <.0001	10.23384* <.0001	10.26067* <.0001	10.44594* <.0001
IS700	3.173087 0.2324	3.827589 0.0515	4.151779* 0.0215	4.17861* 0.0199	4.363885* 0.0117
IS900	5.928335* <.0001	6.582837* <.0001	6.907027* <.0001	6.933858* <.0001	7.119133* <.0001

Table S10: Tukey's comparison for Least squares means of diatom removal for coatings at 20 psi. Least square means with the same letter indicates non-significance.

Tukey's grouping								Diatom Removal 20psi LS mean	Coating #
A								94.7754	PU
A	B							79.9021	IS900
	B	C						67.5841	IS700
	B	C	D					65.7784	19
		C	D	E				58.8713	T2
		C	D	E	F			53.3981	16
		C	D	E	F	G		50.472	13
			D	E	F	G		49.0226	7
			D	E	F	G		48.9027	1
				E	F	G	H	48.0744	5
				E	F	G	H	47.5733	8
				E	F	G	H	46.9634	6
				E	F	G	H	46.5285	17
				E	F	G	H	46.263	18
				E	F	G	H	44.3305	11
				E	F	G	H	43.2351	4
				E	F	G	H	41.7553	12
					F	G	H	41.2634	14
					F	G	H	40.7551	2
					F	G	H	37.2877	15
						G	H	36.0557	3
						G	H	33.9785	9
							H	30.9737	10

Table S11: ANOVA results for *C. lytica* (bacteria) removal at 10 psi.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	17	1625.2287	95.60169	3.09	0.0022
Error	36	1115.2995	30.980541		
Corrected Total	53	2740.5282			

Table S12: *C. lytica* (bacteria) removal: Top five performing experimental coatings at 10 psi statistically compared against control coatings. The table shows t-values for each comparison and the corresponding p-value in the parentheses. *Significant Difference at α=0.05, No symbol means the two coatings are similar in performance.

Exp Coating→ Controls ↓	Coating 1 1025 (1%)	Coating 5 0021 (1%)	Coating 16 6025 (5%)	Coating 8 1043 (2%)	Coating 17 0021 (5%)
Coating 19 A4-20	-1.39419 0.9985	0.572544 1	0.660138 1	1.001329 1	1.408036 0.9983
T2	-2.38345 0.7295	-0.41672 1	-0.32912 1	0.012066 1	0.418773 1
PU	-0.29663 1	1.670102 0.9863	1.757696 0.9764	2.098886 0.8835	2.505594 0.648
IS700	-5.27972* 0.0007	-3.31299 0.1744	-3.2254 0.2093	-2.88421 0.3902	-2.4775 0.6672
IS900	5.358331* 0.0005	7.32506* <.0001	7.412654* <.0001	7.753844* <.0001	8.160551* <.0001

Table S13: Tukey's comparison for Least squares means of *C. lytica* (bacteria) removal for coatings at 10 psi. Least square means with the same letter indicates non-significance.

Tukey's grouping					Bacteria Removal 10psi LS mean	Coating #
A					97.7557	IS900
	B				71.1918	1
	B	C			69.7212	PU
	B	C	D		64.2801	19
	B	C	D	E	61.4417	5
	B	C	D	E	61.0075	16
	B	C	D	E	59.3758	T2
	B	C	D	E	59.316	8
	B	C	D	E	57.2997	17
	B	C	D	E	56.9545	14
	B	C	D	E	55.246	6
	B	C	D	E	55.1763	13
	B	C	D	E	53.1342	9
	B	C	D	E	52.4481	7
		C	D	E	51.9789	11
		C	D	E	51.8543	4
		C	D	E	51.4172	18
		C	D	E	51.1585	2
		C	D	E	51.056	15
		C	D	E	51.0008	10
			D	E	49.4418	12
			D	E	47.5703	3
				E	45.0175	IS700

Table S14: ANOVA results for barnacle (*A. amphitrite*) adhesion.

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	21	15220.26	724.77	4.05	<.0001
Error	88	15767.52	179.18		
Corrected Total	109	30987.79			

Table S15: barnacle *(A. amphitrite)* adhesion: Top three performing experimental coatings statistically compared against control coatings. The table shows t-values for each comparison and the corresponding p-value. *Significant Difference at α=0.05, No symbol means the two coatings are similar in performance.

Exp Coating→ Controls ↓	Coating 6 0025 (1%)	Coating 15 5021 (5%)	Coating 5 0021 (1%)	Coating 10 6025 (2%)	Coating 1 1025 (1%)
Coating 19 A4-20	-3.09042 0.2383	-2.98098 0.2979	-2.95907 0.3108	-2.83132 0.3923	-2.40886 0.6976
T2	-4.12634* 0.0136	-4.0169* 0.0194	-3.99499* 0.0208	-3.86724* 0.031	-3.44478 0.103
IS700	-2.06707 0.893	-1.95763 0.9324	-1.93572 0.9389	-1.80797 0.9683	-1.38551 0.9987
IS900	-0.84953 1	-0.74009 1	-0.71818 1	-0.59043 1	-0.16797 1

Table S16: Tukey's comparison for Least squares means of barnacle *(A. amphitrite)* adhesion for coatings. Least square means with the same letter indicates non-significance.

Tukey's grouping			**Release Score LS mean**	**Coating #**
A			99.0465	6
A			98.12	15
A			97.9345	5
A			96.853	10
A	B		93.2765	1
A	B	C	91.8545	IS900
A	B	C	90.797	9
A	B	C	90.7285	16
A	B	C	88.111	11
A	B	C	83.8675	7
A	B	C	83.219	4
A	B	C	81.547	IS700
A	B	C	80.5785	13
A	B	C	79.175	3
A	B	C	78.151	12
A	B	C	72.8835	19
A	B	C	70.2235	2
A	B	C	70.0345	17
A	B	C	69.976	18
	B	C	64.7345	14
	B	C	64.1135	T2
		C	60.8685	8

Appendix D

Poly (ethylene) glycol-modified, amphiphilic, siloxane polyurethane coatings and their performance as fouling-release surfaces

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Abstract

Amphiphilic siloxane polyurethane (AmSiPU) coatings were prepared using a series of polyisocyanate pre-polymers modified with polydimethyl siloxane (PDMS) and poly (ethylene glycol) (PEG). Fouling-release performance of the AmSiPU coatings was evaluated through laboratory biological assays using several representative marine organisms. First, polyisocyanate pre-polymers with compositional variation in PDMS and PEG were synthesized and characterized using Fourier Transform Infrared Spectroscopy (FTIR) and isocyanate titrations. Then, the pre-polymers were incorporated into coatings. Surface wettability of the coatings was evaluated using contact angle and surface energy (SE) measurements. Coatings' surfaces were also characterized using Attenuated Total Reflectance Fourier Transformed Infrared Spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and Atomic Force Microscopy (AFM). ATR-FTIR and XPS experiments revealed that both PDMS and PEG moieties were present on the surface suggesting amphiphilic character. AFM phase images show microphase separation. AmSiPU coatings show excellent fouling-release performance towards bacteria (*Cellulophaga lytica*), the diatoms (*Navicula incerta*) and the green algae (*Ulva linza*), demonstrating comparable or superior performance to many commercial amphiphilic fouling-release coatings. Despite the incorporation of hydrophilic PEG, AmSiPU coatings showed good macrofouling release which is often challenging with amphiphilic coating systems. AmSiPU coatings are a non-toxic and tough fouling release solution with comparable performance to benchmarks in the fouling release coatings market.

Key Words

Amphiphilic, siloxane polyurethane, fouling release coatings, poly (ethylene glycol), polyisocyanate pre-polymers

Introduction

Biofouling is created by the buildup of micro- and macro-organisms on materials that are immersed in natural bodies of water.[1] Biofouling is a complex process which is often fast and dynamic. It may also involve more than 4000 marine organisms which span a range of sizes and several adhesion mechanisms.[1] [2] [3] Biofouling begins with formation of a conditioning film.[4] A conditioning film is formed as soon as a material is immersed in seawater due to the absorption of proteins and organic molecules. Once the surface is conditioned, colonization of organisms is rather dynamic attributing to available nutrients, types of marine organisms available, surface exploration and their adhesion preferences.[5] Although a successional model of biofouling is frequently advanced,[3] a dynamic model, reflecting a more complex interplay between fouling species, is gaining acceptance.[5] Marine bacteria; unicellular microorganisms colonize the surface first reversibly by electrostatic forces then irreversibly by covalent interactions. Slime forming diatoms and algae spores settle on the substrate contributing to form complex biofilms. Larvae of macrofouling organisms such as barnacles, mussels and tubeworms are often attracted to microfouling yet they can settle on freshly conditioned surfaces illustrating the highly dynamic nature of biofouling.[5]

Contending with biofouling has been a challenging problem since the beginning of navigation.[2] Extensive and rapid buildup of fouling on a ship hull causes reduction in ship speed and maneuverability which in turn increases operating costs and environmental penalties.[6] [7] [8] Environmental concerns include the spreading of non-native species around the world and increased emissions due to decreased fuel efficiency. It is estimated that marine biofouling costs the United States Navy approximately 56 million dollars per year (for their mid-sized vessels) and it could add up to 1 billion dollars for 15 years.[7] [8] Historically, copper and lead sheathing covering the ship hulls were used as the primary method of controlling biofouling.[2] Advancements in polymer and resin technology in the 1960 - 1970s led to the use of self-polishing copolymers with controlled release of biocides such as tributyl tin (TBT).[1] [2] However, by the late 1970s the deleterious effects of TBT towards non-targeted aquatic life was recognized. This issue was addressed by introducing new regulations to reduce the use of TBT which later culminated in a complete ban of tin based antifouling paints by the International Maritime Organization (IMO) in 2003.[1] Antifouling technologies using copper oxide (CuO) as biocides have predominated in recent decades.[9] More recently, a considerable amount of research has been conducted towards using non-toxic anti-fouling (AF)/fouling release (FR) technologies that are environmentally friendly.[3]

Paints containing CuO and/or organic biocides are still the main AF coatings used on ship hulls. However, they are considered to be a less sustainable and more an environmentally costly solution to marine biofouling control. Commercial FR coatings primarily consist of silicone elastomers which only allow weak attachment of fouling organisms that can be removed later by hydrodynamic forces or light cleaning.[3] However these silicone based FR coatings have some drawbacks such as deterioration of FR properties over time and poor mechanical durability compared to anti-fouling coatings with controlled release of biocides.[1] [3] Siloxane polyurethane (SiPU) FR coatings have been able to address the issues with durability by incorporating polydimethyl siloxane (PDMS) into a polyurethane matrix.[10] [11] [12] Self-stratification of PDMS to the coating surface provides the FR properties on par with commercial FR coatings and the polyurethane bulk provides mechanical performance that is several orders of magnitude higher than silicone elastomers.[13] [14] [15] Unlike silicone elastomer-based FR coatings, siloxane polyurethane coatings have excellent adhesion to primers which eliminates the need for a tie-coat.[14]

Adhesion of marine organisms to surfaces is a complex phenomenon that is often not completely understood.[1] [2] However, the primary method of adhesion involves spreading of an adhesive consisting of a complex protein or glycoprotein.[16] Surfaces modified with polyethylene glycol

(PEG) are of great interest mainly due to their ability to resist protein adhesion.[17] PEG-based materials tend to prevent biofoulant settlement and adhesion via hydrophilic interaction.[4] Although there is no well-established reasoning for biofouling resistance of PEG, several theories have been proposed to explain this complex phenomenon. One reasoning considers the extremely low interfacial tension attributed to PEG (5 mN m^{-1}) when in contact with water allowing minimal absorption of organic material due to surface energy minimization.[18] PEG chains can hydrogen bond with neighboring water molecules and bind water tightly to the surface. Some argue that the protein-resistant properties of PEG arise from a high degree of organization in this PEG-water complex, which is unfavorable to be disrupted due to considerations of thermodynamics and kinetics.[19, 20] Although the exact method is still controversial, PEG is very efficient in biofouling prevention.[4] Self-assembled mono-layers (SAM) containing PEG are commonly used as protein-resistant materials.[17] [21] However, SAMs are not practical as marine coatings.[22] Polyurethanes modified with PEG on the other hand have demonstrated their versatility in biomedical applications. A number of different parameters are commonly discussed in the literature to tune protein resistant properties of PEG-based coatings; the MW weight of PEG and chain density of PEG are most commonly considered.[4]

The complexity and diversity in the adhesion mechanisms of marine organisms has led to the investigation of amphiphilic surfaces with mixed hydrophobic and hydrophilic character.[3] [4] However, achieving the right balance between hydrophilicity and hydrophobicity is still a significant challenge. Several studies of amphiphilic coatings have shown promise as effective fouling release surfaces. [23] [24] [25] [26] [27] [28] Lately, state-of-the-art commercial FR coatings have also incorporated amphiphilic character. In previous attempts to modify SiPU with polyethylene glycol, amino propyl terminated siloxane with pendent PEG chains provided amphiphilic coatings with improved algae removal compared to the first generation siloxane polyurethane coatings.[29] However, the synthesis of polydimethyl siloxane with pendent PEG chains involves multiple steps.

Although the use of PDMS with PEG side chains in the siloxane-polyurethane coating system helped to improve microfouling release performance, macrofouling release performance was impaired.[29]

In this study, a new approach to generating polyurethanes having amphiphilic surface character is explored. A series of isophorone diisocyanate-based polyisocyanate pre-polymers was prepared by reacting with PDMS and PEG. The pre-polymers were then used to formulate amphiphilic siloxane-polyurethane (AmSiPU) FR coatings. The polyisocyanate pre-polymers were prepared by reacting an isophorone diisocyanate (IPDI) trimer with monocarbinol terminated PDMS and polyethylene glycol methyl ether (PEG). The ratio of isocyanate: hydroxyl groups was maintained at 3:2 for the pre-polymer synthesis. Several variations of the pre-polymers were obtained by varying the molecular weight of PDMS and PEG. The pre-polymers were characterized using FTIR and isocyanate titrations. Later these pre-polymers were mixed with an acrylic polyol and additional polyisocyanate to form the siloxane polyurethane coatings. Overall, the formulations were adjusted so that the PDMS and PEG content was maintained at 5 and 10 weight % based on solids of the coating formulation. Water contact angle (WCA) and methylene iodide contact angle (MICA) were evaluated before and after water immersion for 28 days and SE was also determined. Water aged coatings were characterized using ATR-FTIR, XPS and AFM to understand the coating surface morphology. The FR properties of the AmSiPU coatings were assessed using biological laboratory assays for bacteria (*Cellulophaga lytica*), microalgae (*Navicula incerta*), macroalgae (*Ulva linza*), barnacles (*Amphibalanus amphitrite*) and marine mussel (*Geukensia demissa*).

Experimental

Materials

Monocarbinol terminated polydimethyl siloxane (PDMS) with three molecular weights (MCR-C12:1000, MCR-C18:5000, MCR-C22:10000 g/mole) were purchased from Gelest, Inc. Polyisocyanate Desmodur Z 4470 BA was provided by Bayer MaterialScience (now Covestro LLC). Acetylacetone, methyl amyl ketone (MAK), ethyl-3-ethoxypropionate (EEP), polyethylene glycol methyl ether (PEG 550 and 750 g/mole), and dibutyltin diacetate (DBTDAc) were purchased from Sigma Aldrich. An acrylic polyol composed of 80% butyl acrylate and 20% 2-hydroxylethyl acrylate was synthesized via conventional free radical polymerization and diluted to 50% in toluene. Aminopropyl terminated polydimethyl siloxane (APT-PDMS) with molecular weight 20000g/mole was also synthesized through a ring-opening equilibration reaction. Detailed descriptions of the synthesis procedures for the acrylic polyol and APT-PDMS can be found elsewhere.[14] Both the acrylic polyol and APT-PDMS were used for the internal control (A4-20).

Intersleek® 700 (IS 700), Intersleek® 900 (IS 900), Intersleek® 1100 SR (IS 1100SR) commercial FR coatings and Intergard 264 marine primer were provided by AkzoNobel International Paint. Hempasil® X3 commercial FR coating was provided by Hempel. Silicone elastomer, Silastic® T2 (T2) was provided by Dow Corning. Aluminum panels (4 x 8 in., 0.6 mm thick, type A, alloy 3003 H14) purchased from Q-lab were sand blasted and primed with Intergard 264 using air-assisted spray application. Multi-well plates were modified using circular disks (1 inch diameter) of primed aluminum.

Synthesis of pre-polymers

A commercially available IPDI trimer (Desmodur Z4470 BA) polyisocyanate was modified with PDMS and polyethylene glycol to prepare pre-polymers with several different compositions (Table 1). A general formulation procedure for pre-polymer IPDI-10-5kPDMS-550PEG (formulation 8) modified with PDMS (MW=5000) and PEG (MW=550) is described here (for the pre-polymer described here, amount of PDMS and PEG are 10% each by wt. based on the total weight of final SiPU formulation). First PEG (1.6000g) was diluted with EEP (1.6000g) in a 40 mL glass vial with a magnetic stir bar. Next, PDMS (1.6000g) was added to the vial and mixed using a vortex mixer for 5 mins. Isocyanate (2.4567g) and DBTDAc catalyst solution (1% by wt. in MAK) (0.3200g) were added into the vial. The contents were mixed using a vortex mixer for 5-10 min followed by further stirring for 24 hrs using a magnetic stir bar. The isocyanate to total hydroxyl equivalents ratio was maintained at 3:2 for all pre-polymers. Detailed formulations can be found in Supplemental Information Table S1.

A general structure depicted in Figure 1 is proposed for the pre-polymers synthesized. In the proposed structure, X can be either an unreacted isocyanate group, PDMS chain linked through urethane or PEG chain linked through urethane. Several pre-polymer compositions were explored in this study and their compositional variations can be found in Supplemental Information Table S2. Pre-polymer compositions investigated in this study contain isocyanate equivalents (X_1) 0.000573-0.00225, PDMS equivalents (X_2) 0.00008-0.0016, and PEG equivalents (X_3) 0.00107-0.00291.

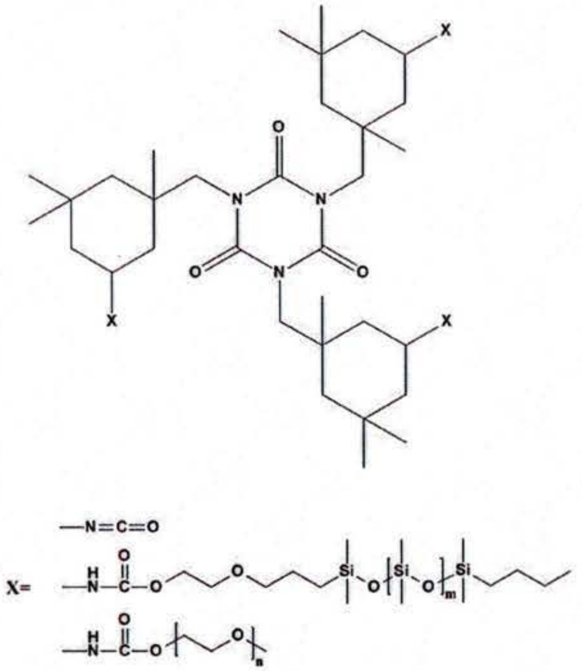

Figure 1: General structure of the IPDI-PDMS-PEG pre-polymers

Isocyanate titrations

Isocyanate titration was used to confirm the presence of NCO groups after the pre-polymer synthesis. In general, a sample of pre-polymer (0.3-0.5g) was placed in Erlenmeyer flask and diluted with isopropanol. Then 25mL of 0.1N dibutyl amine solution was added to the flask followed by additional isopropanol (25 mL). Next the solution was mixed for 15 mins. A few drops of bromophenyl blue indicator were added and titrated using a standardized 0.1N hydrochloric acid solution until the end point blue to yellow. A blank prepared only with 25 mL of dibutyl amine solution was also titrated using the same acid solution and then the % NCO of the pre-polymer was determined.

Instrumentation

Fourier Transform Infrared (FTIR) spectroscopy was used to characterize the pre-polymers prepared using a Thermo Scientific Nicolet 8700 FTIR. The liquid pre-polymer was spread on a potassium bromide (KBr) plate as a thin film prior to obtaining the spectrum.

Coating Formulation and Curing

Formulation of coatings containing the pre-polymers described before is provided here. Coating formulation was carried out as follows: additional polyisocyanate (5.5314g), acrylic polyol (14.4166g, BA: HEA 80:20 in 50% toluene) and pot life extender acetylacetone (0.3200g) were added into the vial containing the pre-polymer. The overall isocyanate to total hydroxyl equivalents was maintained at 1.1:1 for the final formulation. The contents were thoroughly mixed using a vortex mixer followed by magnetic stirring for 1 hr. Coating formulations were deposited into multi-well plates and drawdowns were prepared on primed aluminum panels. Coating formulations (250 μL) were deposited using an automatic repeat pipette to each well in multi-well plates. Drawdowns were made using a wire-wound drawdown bar with a wet film thickness of 80μm on 8"×4" primed aluminum panels. All coatings were allowed to cure under ambient conditions for 24 hrs followed by oven curing at 80 °C for 45 mins. All other consequent formulations were also prepared following a similar procedure. In this study, PDMS and PEG levels of 5% and 10% were considered based on the overall coating formulation. Table 1 summarizes the compositional details of 12 experimental coating included in this study.

Table 1: Coating compositions

Formulation #	Type of pre-polymer used	Type of PDMS	Overall Wt.% PDMS	Type of PEG	Overall Wt.% PEG
1	IPDI-5-1kPDMS-550PEG	PDMS-1k	5	PEG-550	5
2	IPDI-5-5kPDMS-550PEG	PDMS-5k	5	PEG-550	5
3	IPDI-5-10kPDMS-550PEG	PDMS-10k	5	PEG-550	5
4	IPDI-5-1kPDMS-750PEG	PDMS-1k	5	PEG-750	5
5	IPDI-5-5kPDMS-750PEG	PDMS-5k	5	PEG-750	5
6	IPDI-5-10kPDMS-750PEG	PDMS-10k	5	PEG-750	5
7	IPDI-10-1kPDMS-550PEG	PDMS-1k	10	PEG-550	10
8	IPDI-10-5kPDMS-550PEG	PDMS-5k	10	PEG-550	10
9	IPDI-10-10kPDMS-550PEG	PDMS-10k	10	PEG-550	10
10	IPDI-10-1kPDMS-750PEG	PDMS-1k	10	PEG-750	10
11	IPDI-10-5kPDMS-750PEG	PDMS-5k	10	PEG-750	10
12	IPDI-10-10kPDMS-750PEG	PDMS-10k	10	PEG-750	10

Control and Standard Coatings

All commercially available coatings were prepared following the technical data sheets provided by the suppliers. The procedure to prepare internal control SiPU FR coating (A4-20) is described in a previous publication.[14] All control and standard formulations were also coated/deposited on 8" x 4" primed aluminum panels and multi-well plates following a similar method as for experimental coatings. The SiPU control coatings were cured similar to the experimental coatings, while all other control coatings were cured following manufacturers' guidelines. Table 2 contains detailed descriptions of the control and standard coatings used for this study.

Table 2: List of control and standard coatings used in the study

Coating	Name	Description
13	A4-20%	Internal Siloxane-PU FR Control
14	Hempasil X3	Silicone Hydrogel based Commercial FR
15	NDSU-PU	Pure Polyurethane Standard
16	Dow T2	Silicone Elastomer Standard
17	IS 700	Intersleek Commercial FR Control
18	IS 900	Intersleek Commercial FR Control
19	IS 1100SR	Intersleek Commercial FR (Slime Release)

Water Aging

All the coatings were subjected to a pre-leaching process for 28 days in running tap water. Coated multi-well plates and panels were placed in a tap-water tank system equipped with automated filling/emptying capability where the tank water was emptied and refilled every 4 hours.

Biological Laboratory Assays

Growth and Release of Macroalgae (*Ulva linza)*

A set of multi-well plates was sent to Newcastle University, following pre-leaching, to conduct fouling release assay for the microalga *U.linza*. More detailed descriptions of the algae (*U.linza*) growth and removal assay using high throughput screening can be found elsewhere.[30] All multi-well plates were equilibrated in 0.22μm-filtered artificial seawater (FSW) for 2 hrs at Newcastle (after leachate collection) before the start of the experiment. To each well, 1 mL spores of *U.linza* suspension adjusted to 3.3×10^5 spores mL^{-1} (0.05 OD at absorbance 660 nm) in single strength enriched seawater medium was added. Spores settled on the plates were grown for 7 days inside an illuminated incubator at 18 °C with a 16:8 light: dark cycle (photon flux density 30 $\mu mol.m^{-2}.s^{-1}$) with renewal of nutrients every 48 hrs (there was no washing performed to remove unsettled spores after settlement). After 7 d, the biomass generated was assessed from a single row of wells (6) from each plate. Single rows of wells on each plate were sprayed using the spinjet apparatus at 18 and 36 kPa impact pressure. Chlorophyll was extracted by adding 1 mL of DMSO to each well followed by determining fluorescence at excitation at 360 nm and emission at 670 nm wavelengths. Fluorescence is directly proportional to the biomass present on each coating surface. The removal of sporelings at each pressure was compared with the unsprayed wells (that were used to assess sporeling growth above).

Growth and Release of Microalgae (*Navicula incerta)*

Pre-leached coatings prepared in multi-well plates were used for the microalgae (*N.incerta*) assay at NDSU using methods described previously.[31] [32] To each coating well, 1 mL of diatom (*N.incerta*) suspension with 4 x 10^5 cells/mL (adjusted to 0.03 OD at absorbance 660 nm) in Guillard's F2 medium was deposited. The plates were incubated for 2 hrs under ambient conditions to allow for cell attachment and then the suspension was removed. Coating wells were then subjected to water jet treatments, where 3 replicate wells (1st column) were kept untreated while other columns of wells were treated with water jet pressure 20 psi (138k Pa) for 10 seconds. Biomass was quantified through chlorophyll extraction using 0.5 mL of DMSO and measuring fluorescence of the extracts (excitation wavelength at 360 nm; emission wavelength at 670 nm). The relative fluorescence from the extract is directly proportional to the algae biomass present on the coating surface before and after water jet treatment. Percent removal of diatoms was determined using relative fluorescence of non-jetted and water-jetted wells.

Bacterial (*Cellulophaga lytica*) Biofilm Adhesion

Evaluating fouling release performance of coatings towards marine bacteria (*C.lytica*) has been outlined by Stafslien *et al.*[32] [33] Multi-well plates containing coatings were inoculated by dispensing a 1 mL suspension of marine bacteria (*C.lytica*; 10^7 cells/mL) in FSW supplemented with 0.5 g/L of peptone and 0.1 g/L of yeast extract. The plates were incubated statically for 24 hrs at 37°C. The plates were carefully rinsed 3 times with DI water to remove any unattached bacteria cells. The first column (3 wells) was saved as the initial bacterial biofilm growth while the next columns

(3 wells) were subjected to water jet treatment at 20 psi (138 kPa) for 5 seconds. The coating surfaces were then stained with crystal violet (0.3% solution in deionized water). The crystal violet was extracted using 33% acetic acid solution and 0.15 mL aliquots of the resulting eluates were measured for absorbance at 600nm wavelength. The absorbance values were directly proportional to the amount of bacterial biofilm present on coatings. Biofilm removal from the coatings was quantified by comparing the relative absorbance values obtained for the non-jetted and water-jetted wells.

Re-attached Adult Barnacle (*Amphibalanus amphitrite*) Adhesion

An adult barnacle reattachment assay described by Stafslien *et al* was used to evaluate the fouling release performance of the coatings towards macrofouling organisms.[34] [35] Coatings were prepared on 8 x 4" panels and evaluated following 28 days of pre-leaching. Adult barnacles (~5 mm in diameter) supplied by Duke University attached to silicone substrates were dislodged (n = 6) and immobilized onto the surface of experimental coatings using a custom template. The barnacles were allowed to reattach and grow while they were immersed in an artificial sea water aquarium tank system with daily feedings of Artemia nauplii (Florida Aqua Farms). After two weeks, the barnacles were pushed off in shear using a hand-held force gauge mounted to a semi-automated device and the peak force of removal for each barnacle was recorded. Image analysis (Sigma Scan Pro 5.0) was used to quantify the base plate area for each barnacle after it was dislodged. Barnacle adhesion strength (MPa) was calculated by taking the ratio of force for removal to basal plate area. The average barnacle adhesion strength for each coating was reported as the total number of barnacles removed with a measureable force. Barnacles that were adhered strongly resulted in broken barnacles implying poor FR. In some cases, barnacles were unable to reattach to the coating surfaces, in which case the lack of attachment was considered to be an advantage for fouling release coatings.

Mussel (*Geukensia demissa*) Adhesion

Coatings prepared on 4" x 8" panels were also utilized for the mussel adhesion assay. Marine mussels (*G.demissa*) were provided by Duke University Marine Laboratory in Beaufort, North Carolina, USA. Each mussel was modified by attaching a 4 cm long acetal plastic rod (product# 98873A105, McMaster-Carr) perpendicular to the ventral edge, using a 3M® acrylic adhesive (product# 7467A135, McMaster-Carr) prior to attachment assay. Six mussels were immobilized on to each coating surface followed by placing PVC sheets (custom-designed template) firmly against the plastic rods so that the mussels were in contact with the coating surface. The coatings with immobilized mussels were placed in the ASW aquarium system and fed daily with live marine phytoplankton (DTs Premium Reef Blend Phytoplankton) for three days. The coatings were removed from the ASW aquarium tank system and the total number of mussels showing attachment of byssus threads was recorded for each surface. The plastic rod from each mussel was attached to individual 5 N load cell of a custom built tensile force gauge where mussels were pulled off (1 mm/s pull rate) simultaneously. The force required for detachment of all byssus threads was averaged and the pull-off value for each coating was recorded. As in the barnacle assay, the presence of non-attached mussels during the 3 day attachment period indicated good mussel deterrence properties.

Surface Characterization

A Symyx®/First Ten Angstroms surface energy system was used to evaluate wettability of experimental coatings. Water/methylene iodide contact angles measurements were performed before and after 28 days of water immersion. Three measurements of each water and methylene iodide contact angle were obtained using First Ten Angstroms™ software. The average WCA and MICA were used to calculate the SE for each coating by Owens-Wendt method.[36]

Attenuated Total Reflectance Fourier Transformed Infrared spectroscopy (ATR-FTIR) was utilized to characterize the coating surfaces after water aging. A Bruker Vertex 70 with Harrick's ATR™ accessory using a hemispherical Ge crystal was used to obtain ATR-FTIR spectra of the coatings.

X-ray photoelectron spectroscopy was utilized to investigate the surface composition of the experimental coatings. A Thermo Scientific™ K-Alpha™ XPS equipped with monochromatic Al K_α (1486.68 eV) X-ray source and Ar^+ ion source (up to 4000 eV) was utilized for the XPS experiments. All the samples were cleaned to remove trace contaminants. A 2 mm × 2 mm area of the sample was sputtered with a large Ar^+ ion cluster with a power of 4000 eV using the MAGCIS® cluster gun before analysis. Survey spectra were collected at low resolution with a constant analyzer pass energy of 200 eV. Three scans were collected with an energy increment of 1.000 eV/step for a total of 10 ms. High resolution spectra was collected with a constant analyzer pass energy of 50 eV. Ten scans were collected using an energy increment of 0.100 eV/step for a total of 50 ms. For each run, photoemission lines for C 1s, N 1s, O 1s, and Si 2p were observed and the spectrum consists of the average of 10 cycles. Spectra were collected at an angle normal to the surface (90°) of a circular analysis area with a 400 μm diameter. Throughout the experiments chamber pressure was maintained below 1.5×10^{-7} Torr and samples were analyzed at ambient temperature. Atomic concentrations were determined utilizing the integrated areas after subtracting Smart background and corresponding atomic sensitivity factors of 1.000, 1.676, 2.881, and 0.900 for C 1s, N 1s, O 1s, and Si 2p lines respectively.

Atomic Force Microscopy (AFM) was used to observe the topography of experimental coatings. A Dimension 3100 microscope with Nanoscope controller was used to scan the surface of water-leached experimental coatings. A sample area of 100 μm x 100 μm was scanned in tapping mode, in air, under ambient conditions, using a silicon probe with a spring constant (0.1-0.6N/m) and resonant frequency (15-30 kHz).

Results and Discussion

Opposing preferences for surface wettability by marine organisms makes it challenging to formulate anti-fouling/fouling release (FR) coatings that have good performance towards a broad spectrum of organisms. Therefore, the amphiphilic strategy appears to be a viable approach to combat biofouling. However achieving a suitable hydrophobic vs. hydrophilic balance is challenging. This study investigated the FR performance of AmSiPU coatings formulation containing a hydrophobic component of PDMS and hydrophilic component of PEG. During this study, a series of isophorone diisocyanate (IPDI) based pre-polymers modified with PDMS and PEG were synthesized. These pre-polymers were used to prepare amphiphilic siloxane polyurethane FR coatings (AmSiPU). IPDI trimer (Desmodur Z4470 BA) was reacted with polyethyleneglycol methyl ether (PEG) and a monocarbinol terminated polydimethyl siloxane (PDMS) at different equivalent ratios to obtain pre-polymers with compositional variation. PDMS with three different molecular weights (1000, 5000 and 10000 g/mol) and PEG with two molecular weight variations (550, 750 g/mol) were used for pre-polymer synthesis.

The successful synthesis of the isocyanate pre-polymers was confirmed by isocyanate titrations and FTIR characterization. Table 3 summarizes the results of isocyanate titrations for some selected pre-polymers used in this study. The % NCO values obtained for pre-polymers from titration method match closely with the theoretical % NCO, suggesting successful synthesis of the pre-polymers.

Table 3: Average percent isocyanate (% NCO) for some pre-polymers determined through isocyanate titrations.

Pre-polymer	Theoretical % NCO	Average % NCO ± StdDev
IPDI-5-5kPDMS-550PEG	2.2521	2.181±0.006
IPDI-5-5kPDMS-750PEG	1.9446	1.639±0.001
IPDI-10-5kPDMS-750PEG	1.9089	1.785±0.001

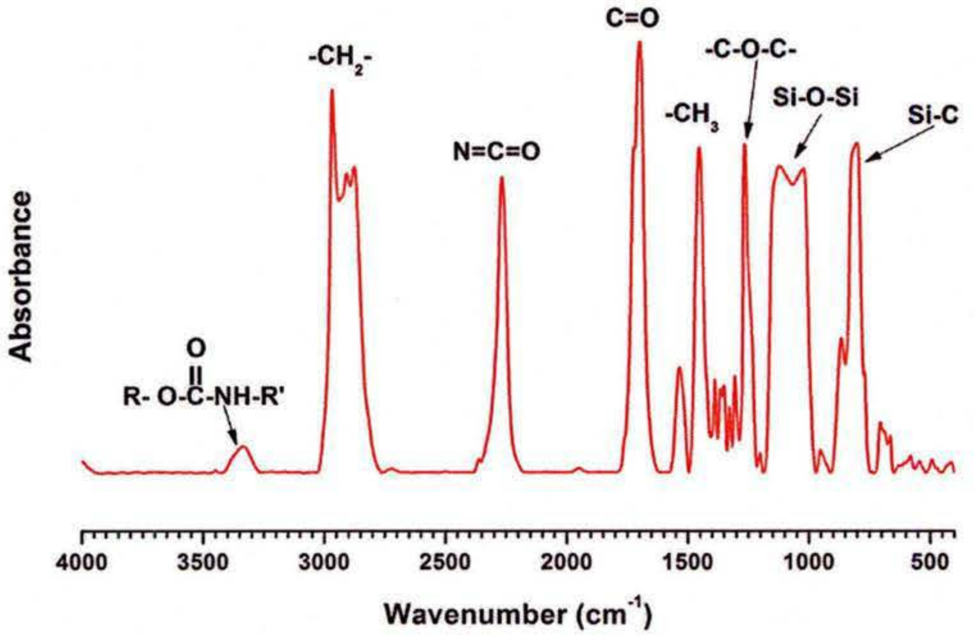

Figure 2: FTIR spectrum for IPDI-10-5kPDMS-550PEG pre-polymer

Figure 2 shows the FTIR spectrum of the pre-polymer IPDI-10%-5kPDMS-550PEG. The peak at approximately 2250cm^{-1} indicated the presence of remaining isocyanate which was used later for crosslinking with an acrylic polyol. The peak at 3300-3400 cm^{-1} due to N-H stretching showed successful reaction of isocyanate with hydroxyl end groups on monofunctional PDMS and PEG. The presence of a carbamate carbonyl (C=O) peak at 1690 cm^{-1} also supported the successful reaction of monofunctional components with the IPDI trimer. The ether stretching (–C-O-C-) due to ethylene glycol was observed in the FTIR spectrum at 1210 cm^{-1} and the presence of siloxane (-Si-O-Si-) stretching was apparent at 1000-1100 cm^{-1}.

During the coating formulation step, the isocyanate pre-polymers were mixed with acrylic polyol and additional IPDI trimer (Desmodur Z4470 BA) so that the final content of PDMS and PEG would be either 5 or 10 % by wt on a resin solids basis. This way the compositional variations in isocyanate pre-polymers were translated into the coating formulations. Surface characteristics and morphology of the experimental coatings were studied using contact angle measurements, ATR-FTIR, XPS, and AFM. Coatings obtained from this experiment displayed amphiphilic character indicating the presence of both hydrophobic PDMS and hydrophilic PEG moieties on the coatings' surfaces.

Figure 3 shows the water and methylene iodide contact angles for coatings before and after water immersion. Water contact angles 95° or above were observed for all coatings. Coatings made using a longer chain length of monocarbinol terminated PDMS (higher MW of PDMS) provided slightly higher WCA. Water contact angles of the 12 experimental coatings remained essentially unchanged after 28 days of water immersion. A marginal increase in methylene iodide contact angle (MICA) for most of the AmSiPU coatings was observed following 28 days of water aging. Change in PDMS composition of pre-polymer also showed an apparent trend in MICA for AmSiPU coatings. The lowest MICAs were observed for coatings containing pre-polymers modified with 1000MW PDMS. The second highest MICAs were observed for those modified with 10000MW and the highest MICAs were observed for coatings with 5000 MW PDMS chain pre-polymers. Changing the PEG component in the pre-polymer compositions did not seem to result in a significant effect on WCAs and MICAs of AmSiPU coatings. WCA for the A4-20 SiPU internal control was observed to be higher than 100° and slightly increased following water immersion. MICA for A4-20 was greater than 67° which did not change significantly after water aging.

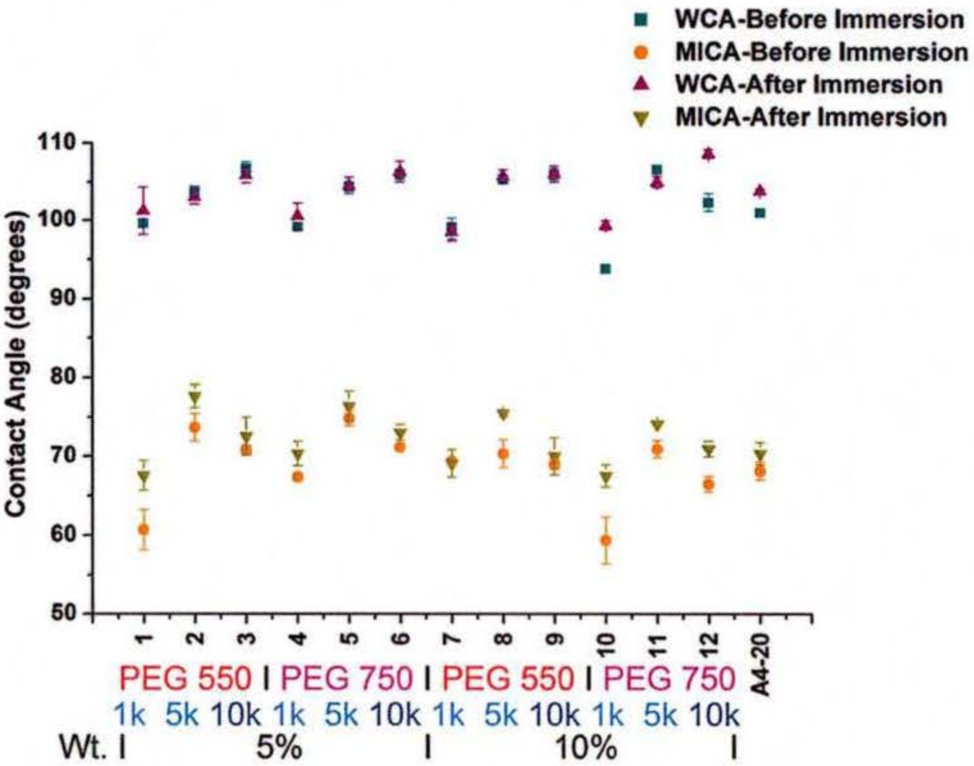

Figure 3: Water (WCA) and methylene iodide (MICA) contact angles for 12 experimental coatings and SiPU internal control before and after 28 days water immersion. Each data point represents the average and standard deviation of 3 measurements. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively.

Figure 4 shows the SE for experimental coatings and A4-20 calculated using the average WCA and MICA measurements using the Owens-Wendt method. It is often considered that minimal adhesion strength of marine organisms tends to be observed for materials with surface energy between 21-25 mN/m (Baier curve).[37] Most of the coatings displayed SE in the range of 22-25 mN/m, although coatings 1 and 10 showed significantly higher SE after water immersion. In general, all coatings except 7 and 12 showed a decrease in SE after 28 days of pre-leaching. The changes in SE may be attributed to changes in MICA following water aging.

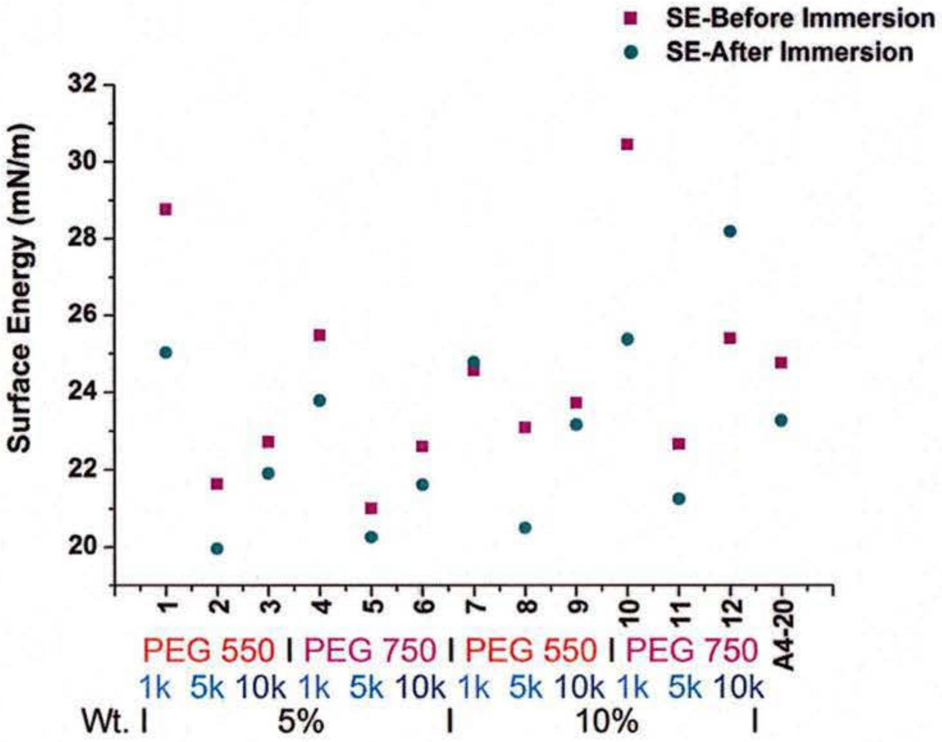

Figure 4: Surface energy of coatings calculated by Owens-Wendt method utilizing the average WCA and MICA measurements. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively.

ATR-FTIR provides information about chemical functional groups present on the top surface of solid materials. The penetration depth of ATR-FTIR varies from 0.5 to 2μm depending on the angle of incidence, wavelength of light and the refractive indices of ATR crystal and the material of interest. Figure 5 shows the ATR-FTIR spectra for coatings 7, 8 and 9 (Table 1). These coatings had 10% PDMS and PEG content (based on the total solids) with PEG 550 being used in all three. Data for PDMS molecular weights 1000, 5000 to 10000 are provided. The FTIR spectra show the presence of -C-O-C- (1180 cm^{-1}) and -Si-O-Si- (1020-1100 cm^{-1}) functionalities suggesting the presence of both PEG and PDMS. However -Si-O-Si- (1020-1100 cm^{-1}) and Si-CH_3 (790 cm^{-1}) peaks were less prominent in coatings 8 and 9 compared to coating 7. In addition, the peaks corresponding to PEG were slightly lower in intensity for coating 7 compared to the other two coatings. Therefore, coating 7 had a significant amount of siloxane closer to the surface compared to the other two coatings. The spectra showed the presence of two types of carbonyl groups C=O" (1750 cm^{-1}) and C=O* (1690 cm^{-1}). The C=O" corresponds to the carbonyl on the acrylic polyol and the C=O* corresponds to the carbamate group. The peak for R-CO-NH-R' was weak but visible at 3350-3450cm^{-1} suggesting a very low concentration closer to the coating surface.

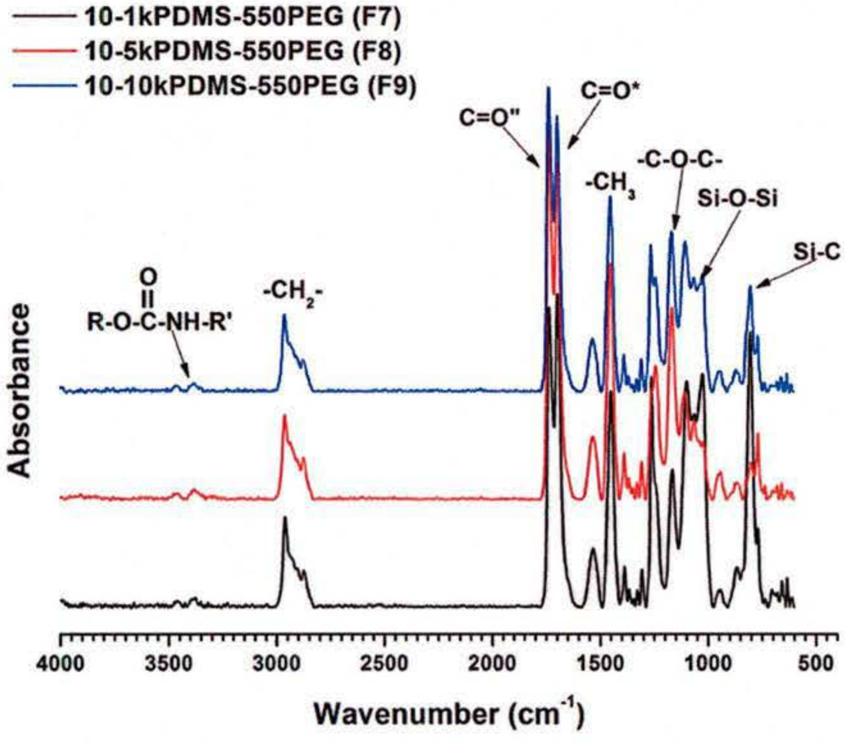

Figure 5: ATR-FTIR spectrum for water aged coatings (7, 8, and 9) containing pre-polymers IPDI-10-1kPDMS-550PEG, IPDI-10-5kPDMS-550PEG, IPDI-10-10kPDMS-550PEG.

XPS spectra of AmSiPU coatings 10, 11 and 12 were obtained to analyze the surface chemical compositions and to observe changes due to variation in PEG and PDMS components. Spectra were obtained at an angle normal (90°) to the surface. Photoemission lines for C 1s, O 1s, N 1s and Si 2p were observed for each sample. Curve fitting was performed based on the possible chemical composition of AmSiPU formulations. Table 4 shows the estimates of atom % based on peak fitting for each coating and Figure 6 shows the spectra for C 1s and O 1s for totals and the fit. Si 2p peak at around 101.87 eV is indicative of siloxane.[38] A small amount of nitrogen from urethane links was also present on the surface as indicated by N 1s peak at 400.08 eV.[39] However, the C 1s peak was indicative of several chemical states as there was C from several functional groups (carbonyl, ester, either and carbon attached to N in isocyanate). Therefore, C 1s peak was fitted with three distinctive sub peaks for C=O at 288.89 eV (from urethane and acrylate groups), C-C-O/C-C-N at 286.19 eV (from ether, and carbon next to isocyanate nitrogen), and all other C-C/C-H at 284.45 eV.[40] Similarly O 1s was fitted with corresponding peaks for C=O at 533.7 eV (from urethane and acrylate groups), C-O-C at 531.48 eV (ether from PEG) and Si-O-Si at 532.05 eV (from siloxane).

Table 4: Estimated surface atomic compositions based on peak fitting.

		Atomic %		
Chemical state	Peak Binding Energy (eV)	Coating 10	Coating 11	Coating 12
Si2p Total	101.87	10.75	10.90	18.20
N1s Total	400.08	3.60	2.05	0.89
C1s C-C/C-H	284.45	45.63	35.04	38.13
C1s C-C-O/C-C-N	286.19	12.75	6.99	2.81
C1s C=O	288.89	4.86	3.02	0.66
O1s C=O	533.27	3.68	3.43	0.97
O1s C-O-C	531.48	8.01	3.49	1.26
O1s Si-O-Si	532.05	10.72	10.69	17.94

XPS spectra for AmSiPU coatings showed the presence of both PEG and PDMS moieties. The main difference between the coatings comprised of IPDI-PDMS-PEG pre-polymers arise from the length of the PDMS chain. Pre-polymers in coatings 10, 11, and 12 were prepared with PDMS MWs 1000, 5000, and 10000 respectively. The surface atom percent of Si shows a significant increase with 10000 MW PDMS compared to the coatings with PDMS MWs 1000 and 5000.

Simultaneously the atom % of N decreased indicating that the increase in PDMS MW had affected the surface morphology of AmSiPU coatings. Graphs of C 1s for coatings indicated a very distinctive decrease in peaks for C1s C-C-O/C-C-N (≈ 286 eV) and C1s C=O (≈289 eV) with increase in PDMS MW of the pre-polymer. The peaks C1s C-C-O/C-C-N (≈ 286 eV) and C1s C=O (≈289 eV) resulted mainly due to the presence of PEG and urethane linkages, therefore the gradual decline of these peaks is indicative of changes in surface morphology of the coatings. This analogy is further supported by spectra of O1s peaks for coatings 10, 11 and 12. Going from coatings 10 to 12, peaks for O1s C-O-C (531.5 eV) and O1s C=O (533.3 eV) show a steady decrease whereas a steady increase is observed for O1s Si-O-Si (532 eV). XPS surface analysis indicates that compositional variations in isocyanate pre-polymers had a significant effect on the surface composition of the AmSiPU coatings. Therefore, tuning the pre-polymers may help to optimize the properties of AmSiPU coatings.

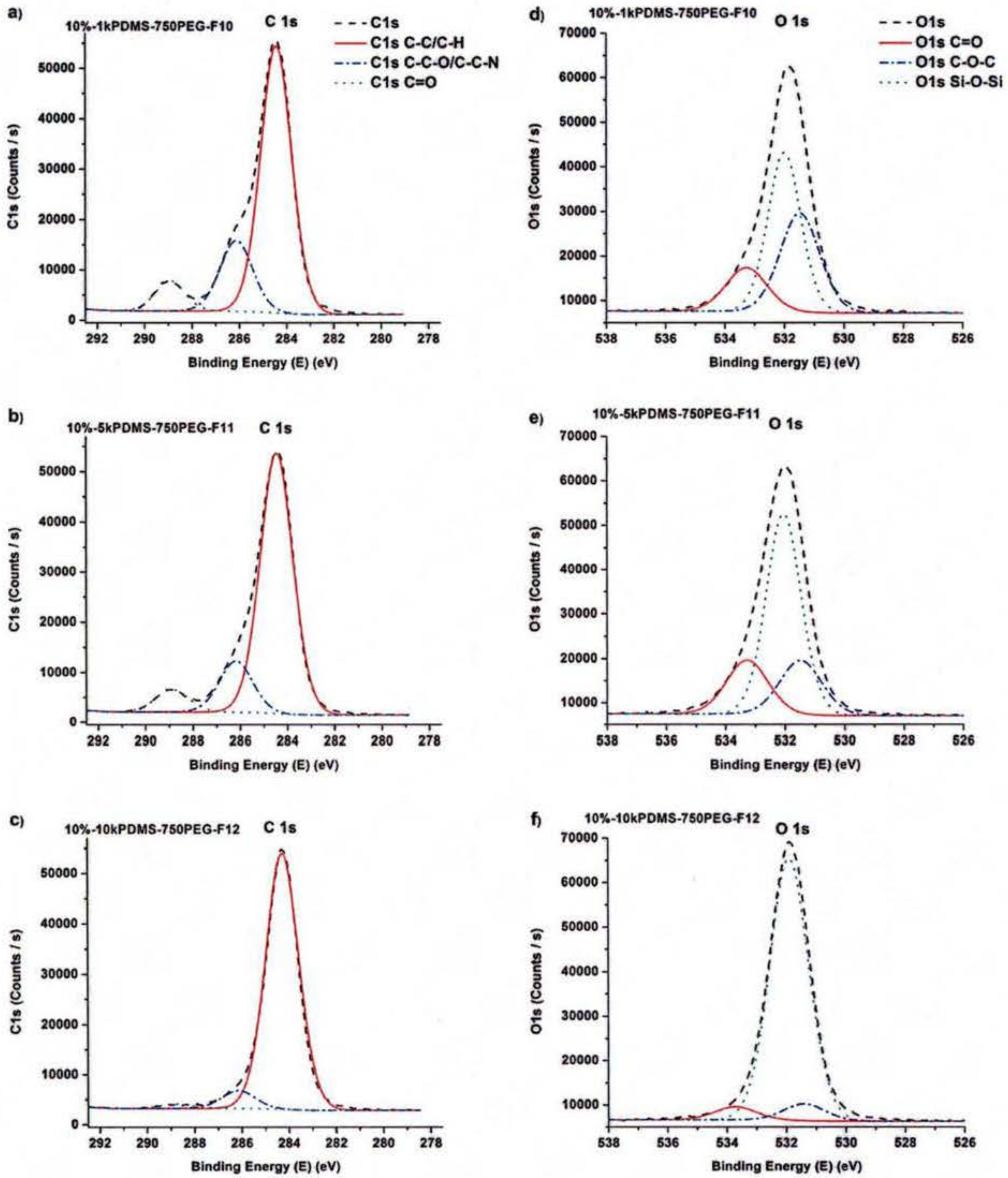

Figure 6: XPS spectra of AmSiPU coatings 10, 11 and 12. The plots represent C 1s and O 1s spectrum for each coating with peak fittings corresponding to chemical composition. Spectra a) and b) are for coatings 10, spectra c) and d) are for coating 11, and e) and f) are for coating 12.

All AmSiPU coatings were analyzed using AFM and Figure 7 shows the phase images for the coatings. During AFM scanning, smaller phase angles (0°) indicate harder or more rigid materials whereas high phase angles indicate the presence of softer material such as PDMS. Very prominent surface features were observed for several AmSiPU coatings. These surface features were more distinctive for coatings 7-12 with 10% concentration of PDMS and PEG compared to 5%. Also significant phase separation was observed for coatings with PDMS MW 10000 compared to those with 1000 and 5000. Coatings 1, 2, 5 and 8 do not show much surface heterogeneity compared to the other coatings although a few spots with low phase angle are observed. A clear trend was observed for coatings with pre-polymer containing PDMS MW of 1000 and varying PEG composition (coatings 1, 4, 7 and 10), where increasing the PEG content from 5% to 10% and increasing the PEG MW from 550 to 750 may have allowed the formation of slightly larger yet uniformly distributed hard segments on the surface. For coatings modified with PDMS MW of 10000, AFM showed an enlargement of domains with low phase angle when the PEG composition was varied. However, these coatings show domains with a range of sizes. Coatings 10, 11 and 12 showed very distinctive phase separation when PDMS MW was varied from 1000 to 10000. In general, AFM images indicated the presence of surface heterogeneity for several AmSiPU coatings which is distinctive of many amphiphilic coating systems.

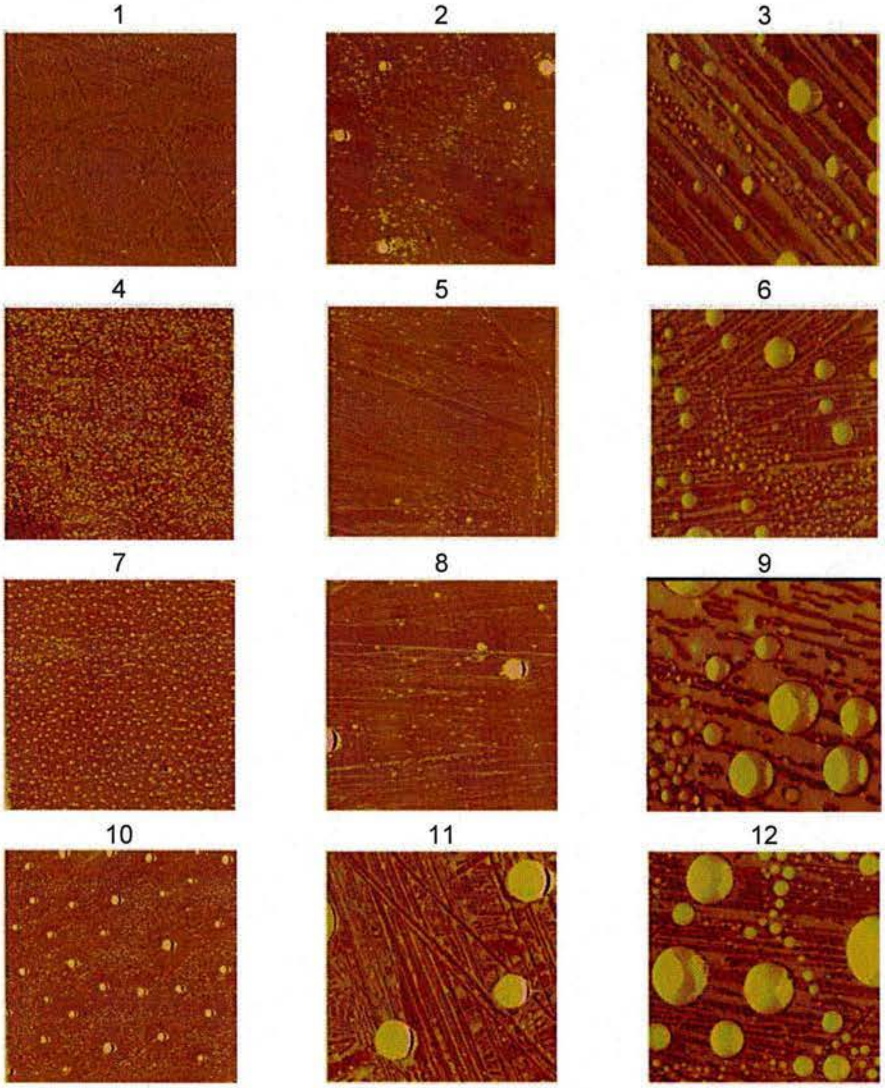

Figure 7: AFM phase images of AmSiPU coatings for a scan area of 100µm x 100µm.

All biological laboratory assays were conducted following 28 days of water immersion and assessments of leachate toxicity (using *C.lytica* and *N.incerta*) as described previously.[41] Briefly, overnight extracts of the coatings were collected and inoculated with algae and bacterial. Growth of algae was quantified by fluorescence of chlorophyll after 48 hrs and growth of bacteria was quantified via crystal violet absorbance. Fluorescence and absorbance measurements of the coating extracts were then compared to positive and negative growth controls. Leachates from all experimental coatings did not show toxicity (data not reported), thus biological laboratory assays were carried out to evaluate their fouling release properties.

U.linza is one of the main type of macroalgae which contribute to marine biofouling.[42] Multi-well plates modified with coating formulations were evaluated for their fouling removal performance of towards *U.linza* sporelings (young plants). Previous studies have suggested that the settlement of spores of *U.linza* and adhesion strength of sporelings can be influenced by the substrate wettability.[43] [44] [45] Low settlement of spores of *U.linza* has been observed on some surfaces with hydrophilic moieties, yet the adhesion strength of spores tend to be stronger for hydrophilic surfaces. The opposite behavior has been observed on some hydrophobic surfaces. As a result of this, it has been suggested that surfaces with amphiphilic character would be effective at combating fouling by organisms like *U.linza*. Figure 8 shows the percent removal of sporelings after water jet treatment. Several AmSiPU coatings showed similar or better removal compared to the state-of-the-art commercial standard Intersleek® 1100SR. On the other hand, all the experimental coatings were significantly better in performance compared to Dow Corning® T2 and pure polyurethane controls. It is interesting to observe that the AmSiPU coatings with pre-polymers modified with 10% of PDMS and PEG performed better than those with 5% at low water jet pressure (18 kPa). However at 36 kPa water jet pressure the coatings modified with 10 wt. % of PEG 750 outperformed all coatings reaching close to 75-80% removal of sporelings. PDMS MW did not seem to play a role in determining FR performance towards *U.linza*. More importantly, several AmSiPU coatings maintained good FR performance towards *U.linza* despite the modification with the hydrophilic component PEG, which was evident from their comparable performance to the A4-20 internal control.

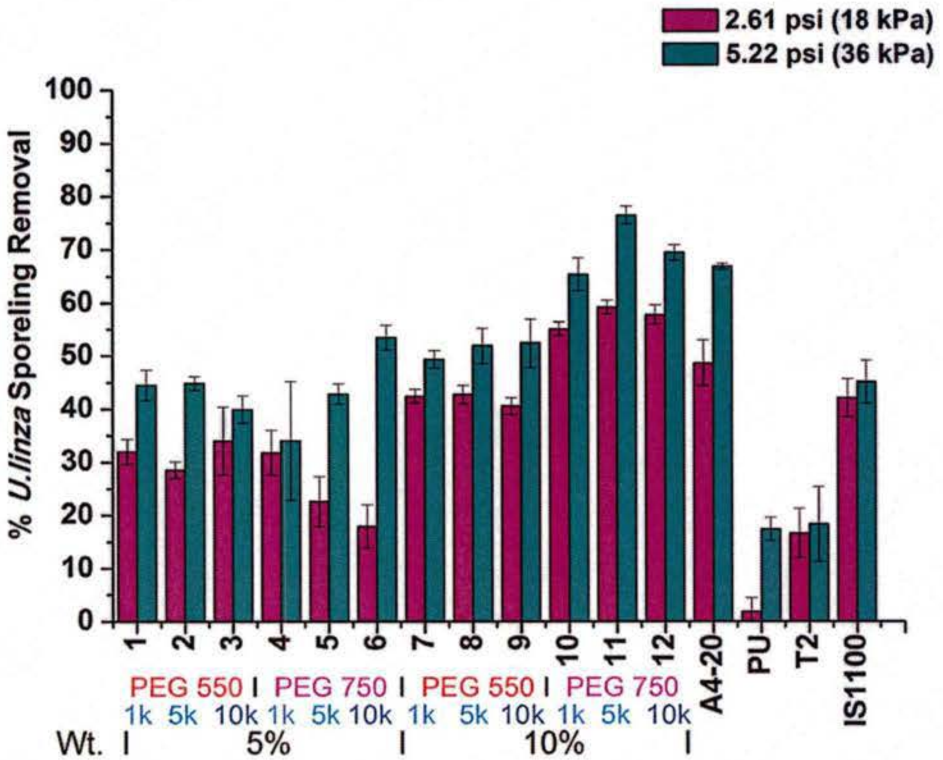

Figure 8: Percent removal of macroalgae (*U.linza*) sporelings at water jet treatments 18 and 36 kPa. Each bar represents the average percent removal of six measurements and corresponding standard deviation. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively.

The diatom (*N.incerta*) is a known slime forming microalgae. Fouling-release performance towards *N. incerta* was evaluated using a water-jetting assay. *N.incerta* has been shown to possess a higher affinity towards hydrophobic surfaces compared to hydrophilic surfaces.[44 46] In terms of cell attachment, most AmSiPU coatings displayed similar biomass compared to control coatings with the exception of Hempasil® X3 silicone hydrogel FR coating. Many AmSiPU coatings with 10% concentration of PDMS and PEG had a slightly lower amount of initial diatom cell attachment. Coating compositions 7, 10 and 11 showed the highest removal of diatoms after 20 psi water-jet treatment which was similar to the performance of Intersleek 1100® SR, Intersleek® 900, polyurethane, and Hempasil® X3 standard coatings. The same AmSiPU coatings also have ≈ 65% FR performance compared to the 1st generation SiPU coating (A4-20).[14] Coatings consisting of pre-polymer modified with 10% PEG 550 or PEG 750 showed the best FR performance towards the diatoms, suggesting that the amount of PEG may have an important role in affecting diatom adhesion strength. It is also important to point out that several AmSiPU coatings were on par with amphiphilic FR commercial standards considering their FR performance towards microalgae.

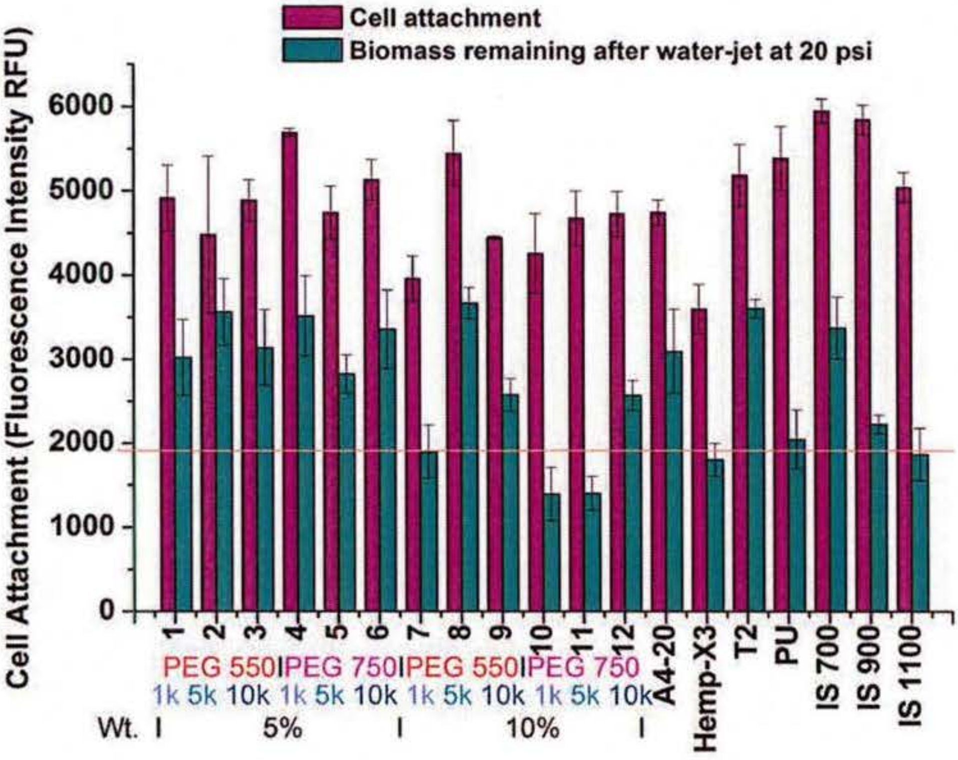

Figure 9: Microalgae (*N.incerta*) attachment and retention (i.e., biomass remaining) after water-jet treatment at 20 psi pressure. Each bar represents the average of 3 replicate measurements along with standard deviation. Pink colored line indicates the amount of biomass remaining on the IS 1100 commercial standard after water-jetting. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively.

Fouling release performance towards the marine bacterium *C.lytica* for experimental, standard and control coatings was evaluated in an assay similar to that of diatoms. Absorbance of crystal violet at 600nm wavelength is directly proportional to the biomass present on coating surface. Bacterial biofilm retention on some AmSiPU coatings was similar to the commercial control Intersleek® 1100SR, whereas some showed lower retention of biofilm which was comparable to Hempasil® X3. Several AmSiPU coatings showed almost no biofilm remaining after water jet treatment at 20 psi. It was noticed that many experimental coatings performed better than Intersleek® 900 and 700. Coatings 7, 9, 10, 11, 12 showed the best FR performance towards *C.lytica* comparable to Hempasil® X3 and exceeding A4-20. Figure 11 shows the visual appearance of biofilms on the coatings before and after water jetting. After water jetting, coatings 10 and 11 exhibited no visible/discernable crystal violet staining similar to Hempasil® X3, whereas silicone elastomer (T2) and polyurethane controls had a significant amount of staining which directly corresponded to the amount of biofilm retained after exposure to the water jet. From Figure 11 it is also indicated that coating 8 had a similar amount of biofilm to Intersleek® 1100 SR following water jet treatment. Results from the bacterial biofilm assay suggest that *C.lytica* has lower affinity towards IPDI-PEG-PDMS pre-polymer modified siloxane polyurethane coatings. It is also important to point out that introducing amphiphilic character to SiPU coatings has helped to improve the fouling release performance towards *C.lytica.*

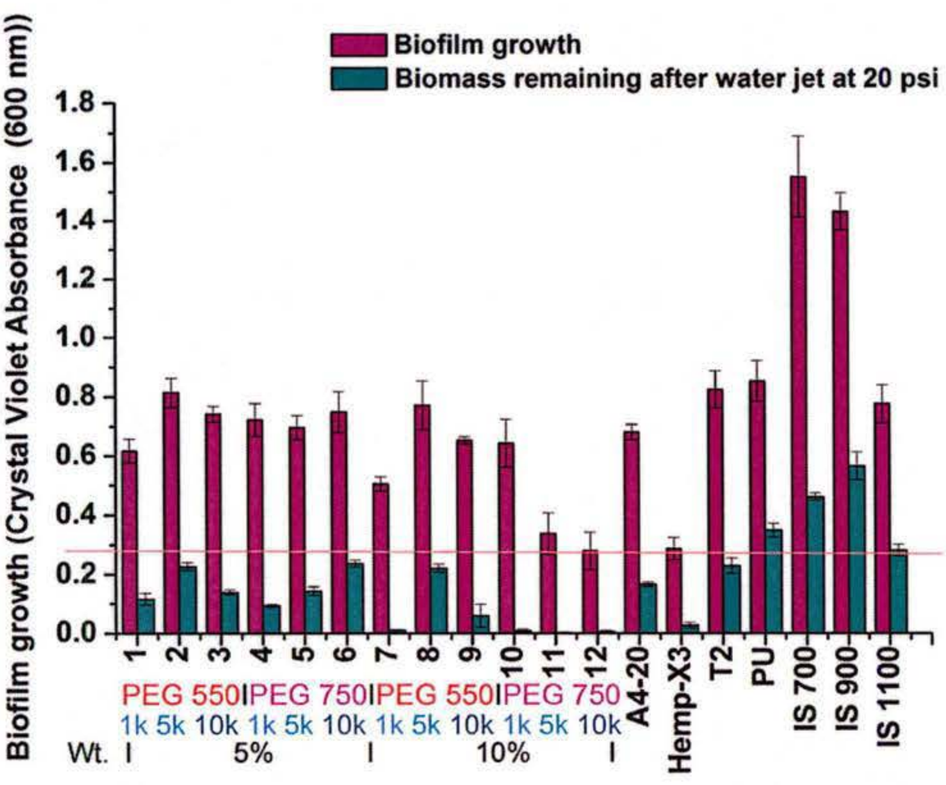

Figure 10: Bacterial biofilm (*C.lytica*) growth and retention after water-jet treatment at 20 psi pressure. Each bar represents the average of 3 replicate measurements along with standard deviation. Pink colored line indicates the amount of biomass remaining on the IS 1100 commercial standard after water-jetting. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively.

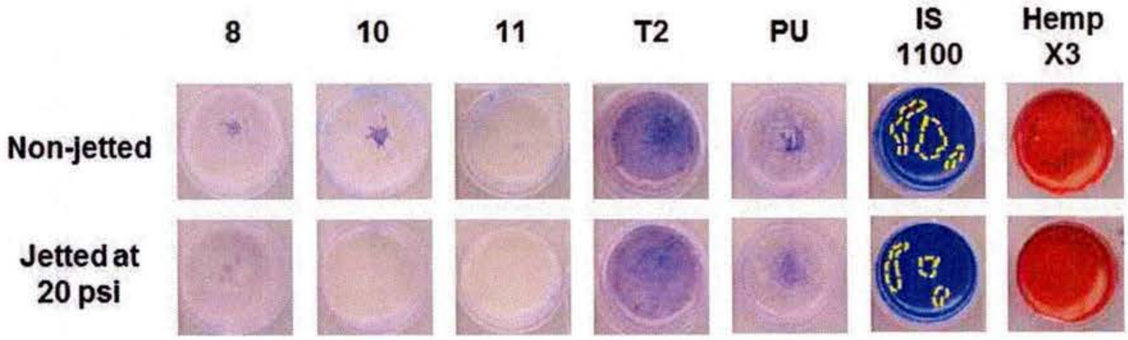

Figure 11: Photographs of crystal violet stained coating wells for AmSiPU coatings 8, 10, 11, standards Dow Corning® T2, polyurethane (PU), Intersleek® 1100SR and Hempasil® X3 before and after 20 psi water jet treatment. Biofilm on Intersleek® 1100SR is indicated by a highlighted yellow line.

Macrofouling organisms such as barnacles and mussels, can cause a significant reduction is operational efficiency of marine vessels. Barnacle adhesion strength towards coatings was evaluated using a two week reattachment assay followed by a push off test. Adhesion strength (or critical removal stress) was quantified by shear force for removal divided by barnacle basal plate area. The effects of PDMS MW was clearly seen by the barnacle adhesion strength for AmSiPU coatings (Figure 12). Coatings containing pre-polymers modified with shorter PDMS chains showed high barnacle adhesion strength. The opposite behavior was observed for coatings modified with longer PDMS chains (10000). Also the coatings with higher PDMS MW had no broken barnacles, which is further evidence that PDMS MW had a significant effect on easy release of barnacles attached to surfaces. Several experimental coatings showed non-attached barnacles and lower adhesion strengths that were comparable to Intersleek® 900 performance. Coatings 3, 6, 9, 11, and 12 displayed the best performance allowing removal of all reattached barnacles with lower adhesion strengths. On these coatings, several barnacles were unable to re-attach; further indicator of good FR performance. Coatings consisting of pre-polymer with 10% concentration of PDMS and PEG provided the better FR performance towards barnacles compared to those with 5%. Surface wettability and surface charge play an important role in barnacle settlement.[47] It is often observed that PDMS based materials show low critical removal stress of barnacles (*A.amphitrite*) which is attributed to their low surface energy.[47] However AmSiPU coatings with both hydrophilic PEG and hydrophobic PDMS displayed lower barnacle adhesion strengths. This assay demonstrates the important role of PDMS being an essential component in amphiphilic fouling release system. Compared to previous attempts of amphiphilic siloxane-PU coatings, IPDI-PDMS-PEG pre-polymer modified coatings were able to maintain good fouling release towards barnacles while improving performance towards microfoulers.[25] [29] The control coating polyurethane (no PDMS), showed the worst performance towards barnacles on which all reattached barnacles broke. Hempasil® X3 and Intersleek 1100SR showed the best performance by not allowing any barnacle to reattach during the two weeks of immersion in artificial sea water.

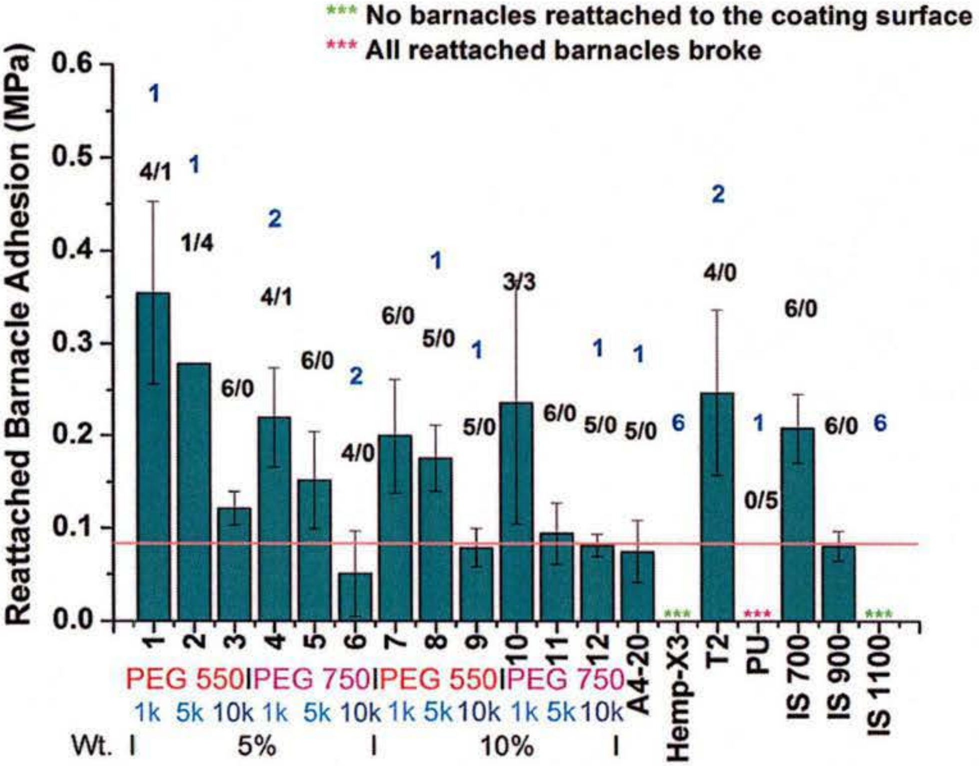

Figure 12: Reattached barnacle (*A. amphitrite*) adhesion strength. Six barnacles were used for each reattachment study, out of which blue numbers represent the non-attached barnacles. The ratio represents the number of released barnacles versus the number of broken/damaged barnacles during push off measurements. Each bar represents the average adhesion strength based on the number of successfully pushed barnacles. Pink colored line indicates the average adhesion strength for the IS 900 commercial standard. X-axis is labeled to indicate the coating

number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively.

Several experimental coatings with IPDI-PDMS-PEG pre-polymers showed no mussel attachment, suggesting that the coatings were either deterrent to mussel attachment or that they interfered with attachment (Figure 13). Similarly, Intersleek 900, Hempasil X3 and A4-20 control showed no mussel attachment. Some mussels did attach to the coating compositions that demonstrated excellent fouling release performance towards *U.linza*, bacteria, diatoms and barnacles but were easily removed with approximately 10N force. Out of the coatings that displayed some mussel attachment, coatings 10 and 11 showed the lowest number of attached mussels and lower force of removal suggesting good overall FR performance towards all organisms. Interestingly, mussels did not attach to coatings modified with PDMS MW 10000 regardless of compositional variation with PEG. Generally, mussels tended to have lower adhesion strength towards hydrophobic PDMS, which suggests that PDMS compositional changes in pre-polymers may have affected mussel adhesion.

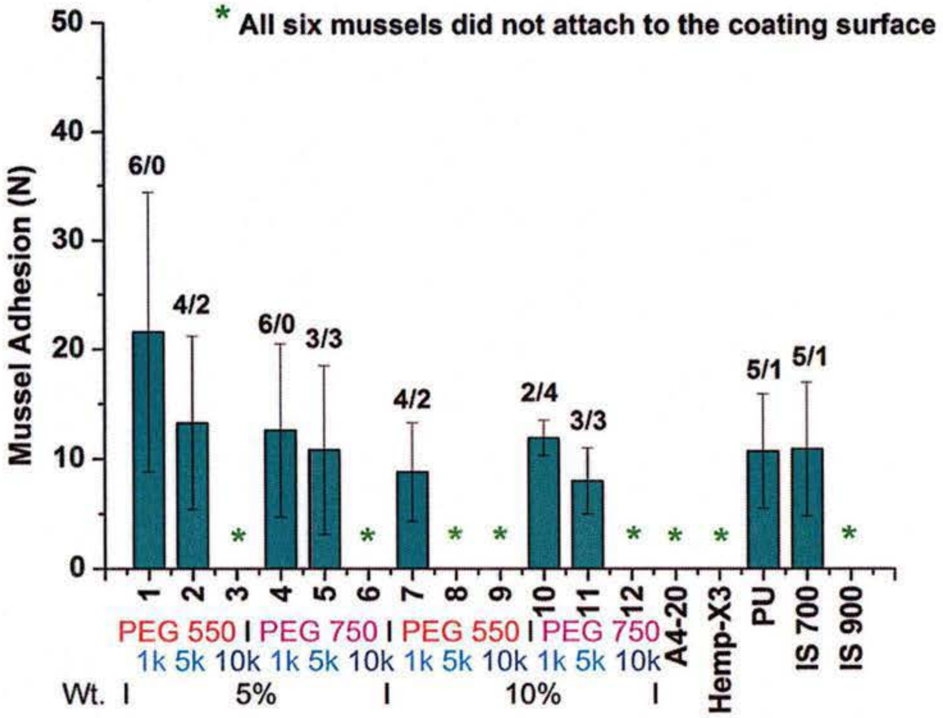

Figure 13: Marine mussel (*G. demissa*) adhesion evaluated with six attempted attachments for each coating. Each adhesion strength value represents the average force for removal of successfully attached mussels. The ratio represents the number of attached mussels over the number of non-attached mussels. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively.

In general, coating compositions 7, 9, 10, 11, and 12 exhibited broad-spectrum FR properties towards macroalage (*U.linza*), bacteria (*C.lytica*), diatom (*N.incerta*), barnacle (*A.amphitrite*) and mussel (*G.demissa*) and were comparable to or exceeded the performance of the commercially available FR standards such as Intersleek 900, 1100SR and Hempasil X3. Coatings comprising both 10% PDMS and PEG were more efficient at promoting the release of these organisms when compared to coatings based on 5% PDMS and PEG. Also PEG 750 showed enhanced FR properties towards microfouling as compared to PEG 550. Macrofouling release efficiency depended primarily upon the composition of PDMS, where macrofoulers were easily released from coatings containing the high PDMS MW. Surface characterization techniques demonstrated that both hydrophobic and hydrophilic moieties were present on the surfaces of the AmSiPU coatings. However, the surface morphology was clearly affected by the pre-polymer chemical compositional variations. Differences in surface morphology might also explain the improvement in fouling release performance of certain coatings compared to others. As SiPU coatings rely on self-stratification for fouling release properties, there are more variables that need to be considered for fine tuning surface properties of these AmSiPU which need to be addressed in future.

Conclusions

Several pre-polymers with compositional variation in PDMS and PEG were synthesized and incorporated into a siloxane polyurethane (SiPU) coating system. Coatings derived from these novel pre-polymers demonstrated amphiphilic surface properties. Surface wettability of the coatings remained mostly unchanged before and after water aging. Self-stratification of PDMS and PEG moieties was evident from ATR-FTIR, XPS and AFM characterization. ATR-FTIR suggests that both PDMS and PEG are present on the surface after water aging. Surface morphology of AmSiPU coatings were clearly affected by the variations in PDMS and PEG components used for pre-polymer synthesis. XPS spectra indicated that increasing PDMS MW in pre-polymers resulted in higher self-segregation of siloxane increasing the concentration of hydrophobic moieties. AFM images of AmSiPU coatings showed the presence of microdomains with soft and hard segments indicative of phase separation on the surface. Several coatings showed excellent FR performance towards bacteria (*C.lytica*), in terms of water jet removal of attached sporelings. In most cases, >90% of bacterial biofilms were cleaned off after a 20 psi water jet treatment. Fouling release performance of AmSiPU coatings also showed significant improvement in microalgae (*N.incerta*) compared to internal control A4-20 (1st generation SiPU). Interestingly, many of the AmSiPU coatings demonstrated comparable or superior fouling release properties towards bacteria and microalgae in comparison to the state-of-the-art commercial fouling release coatings. Biological assays for macroalgae (*U.linza*), suggest that AmSiPU coatings have similar fouling release performance compared to Intersleek 1100SR despite the inclusion of hydrophilic PEG. The adhesion strength of barnacles was very low and some non-attached barnacles were observed for several AmSiPU coatings. Generally most AmSiPU coatings displayed similar fouling release properties to Intersleek® 900 in relation to barnacle attachment. Marine mussel (*G.demissa*) adhesion was observed for coatings which performed well in microfouling release. However, the mussels were easily removed with a low force. In general, coatings comprised of pre-polymer with 10% of PDMS and PEG perform better than the ones derived from 5% PDMS and PEG. Also coatings made using PEG MW of 750 showed better FR properties in many assays when compared to the ones with PEG 550; which implies that longer PEG chain may be more effective in FR. A number of coatings provided broad-spectrum FR properties for a variety of representative marine organisms with diverse adhesion profiles, suggesting amphiphilic coatings are very effective in combating biofouling. Overall AmSiPU coatings showed superior or comparable FR properties to the leading commercial standards such as Intersleek® 900, Intersleek® 1100SR and Hempasil® X3 but with the additional desirable features of being tougher and more durable.

Acknowledgements

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Supplemental Information is available containing details of the coating compositions, AFM height images of the coatings, diatom and bacterial removal and macroalgae release performance data.

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Supplemental Information

Poly (ethylene) glycol modified amphiphilic siloxane polyurethane coatings and their performance as effective fouling release surfaces

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S1: Detailed formulations for pre-polymer portion of formulation 8

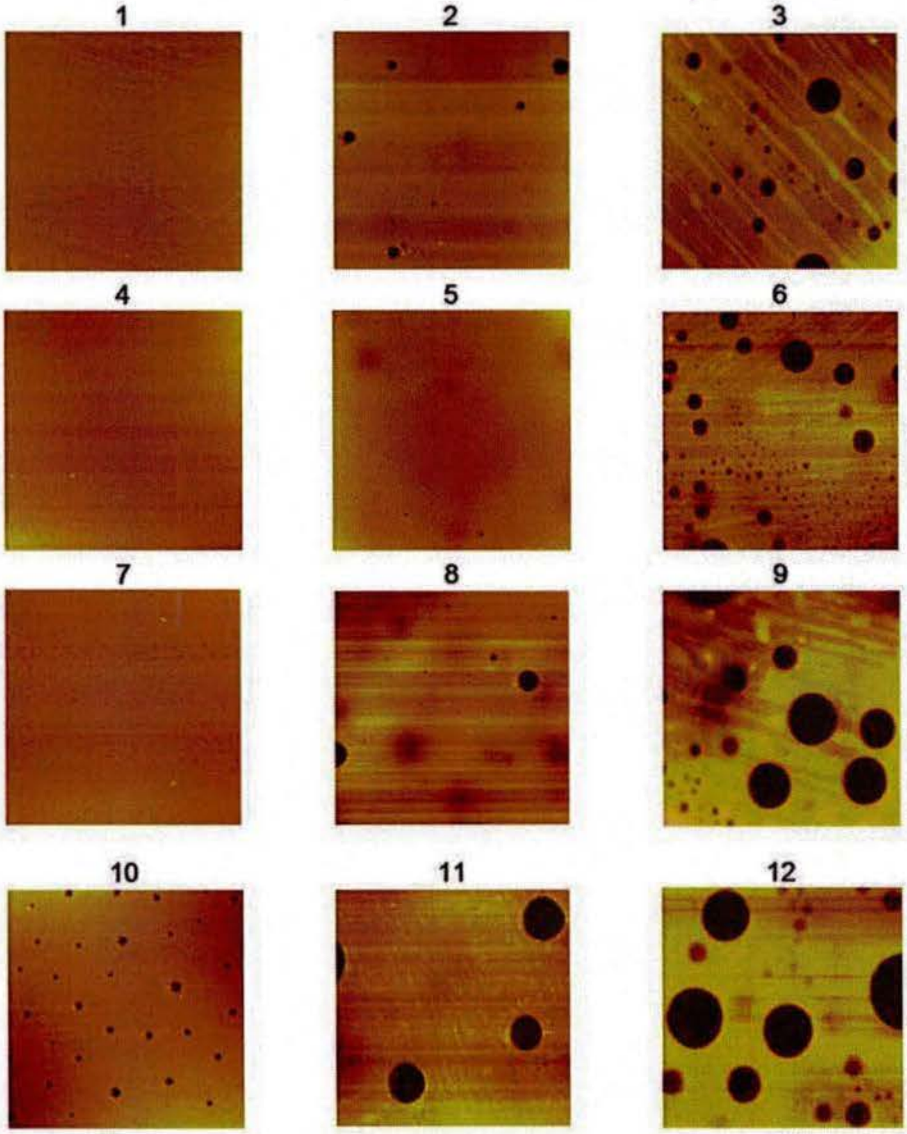
IPDI-M5KPDMS(10%)-550PEG(10%)-prepolymer F8

Ingredient	Mw (g/mol)	Amount (g)	Wt.%	Eq.Wt (g/eq)	Eq	%Solids	Amount Added (g)
Isocyanate (Desmodur Z 4470 BA)		1.7197	10.7480	355	4.84E-03	70	2.4567
EEP							1.6000
Monocarbinol terminated PDMS	5000	1.6000	10.0000	5000	3.20E-04	100	1.6000
Hydroxyl terminated PEG	550	1.6000	10.0000	550	2.91E-03	100	1.6000
DBTDAc (1% by wt. in MAK)		0.0032	0.0200			1	0.3200

S2: Compositions of pre-polymers investigated during this study

Pre-polymer	Wt of IPDI trimer (g)	Starting NCO Eq.	MW of PDMS (g/mol)	Wt of PDMS (g)	OH Eq. from PDMS (X_2)	MW of PEG (g/mol)	Wt of PEG (g)	OH Eq. from PEG (X_3)	EEP (g)	Ending NCO Eq.(X_1)
IPDI-5-1kPDMS-550PEG	1.7152	3.38E-03	1000	0.8000	8.00E-04	550	0.8000	1.45E-03	1.6000	1.13E-03
IPDI-5-5kPDMS-550PEG	1.2283	2.42E-03	5000	0.8000	1.60E-04	550	0.8000	1.45E-03	1.6000	8.08E-04
IPDI-5-10kPDMS-550PEG	1.1675	2.30E-03	10000	0.8000	8.00E-05	550	0.8000	1.45E-03	1.6000	7.68E-04
IPDI-5-1kPDMS-750PEG	1.4199	2.80E-03	1000	0.8000	8.00E-04	750	0.8000	1.07E-03	1.6000	9.33E-04
IPDI-5-5kPDMS-750PEG	0.9330	1.84E-03	5000	0.8000	1.60E-04	750	0.8000	1.07E-03	1.6000	6.13E-04
IPDI-5-10kPDMS-750PEG	0.8722	1.72E-03	10000	0.8000	8.00E-05	750	0.8000	1.07E-03	1.6000	5.73E-04
IPDI-10-1kPDMS-550PEG	3.4299	6.76E-03	1000	1.6000	1.60E-03	550	1.6000	2.91E-03	1.6000	2.25E-03
IPDI-10-5kPDMS-550PEG	2.4567	4.84E-03	5000	1.6000	3.20E-04	550	1.6000	2.91E-03	1.6000	1.62E-03
IPDI-10-10kPDMS-550PEG	2.3351	4.60E-03	10000	1.6000	1.60E-04	550	1.6000	2.91E-03	1.6000	1.54E-03
IPDI-10-1kPDMS-750PEG	2.8400	5.60E-03	1000	1.6000	1.60E-03	750	1.6000	2.13E-03	1.6000	1.87E-03
IPDI-10-5kPDMS-750PEG	1.8663	3.68E-03	5000	1.6000	3.20E-04	750	1.6000	2.13E-03	1.6000	1.23E-03
IPDI-10-10kPDMS-750PEG	1.7446	3.44E-03	10000	1.6000	1.60E-04	750	1.6000	2.13E-03	1.6000	1.15E-03

S3: AFM height images for AmSiPU coatings



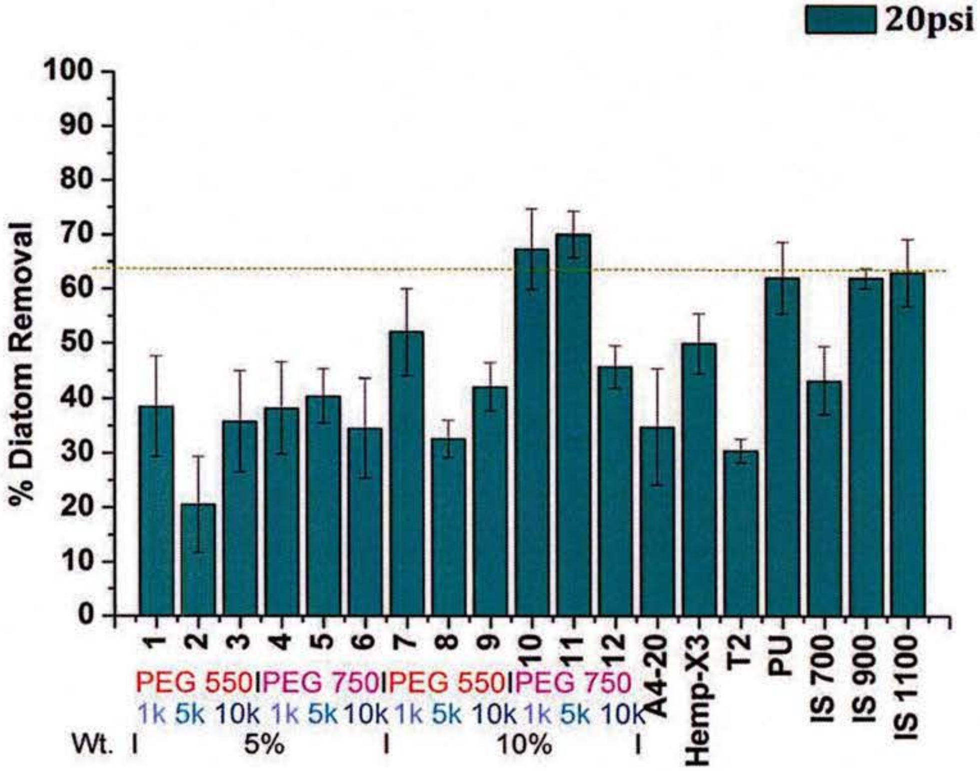
1 2 3

4 5 6

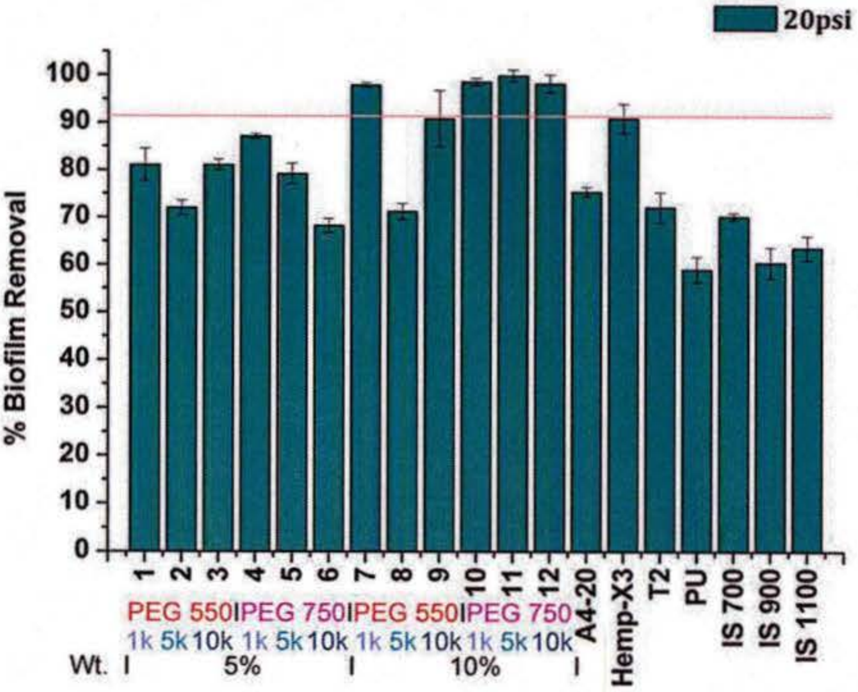
7 8 9

10 11 12

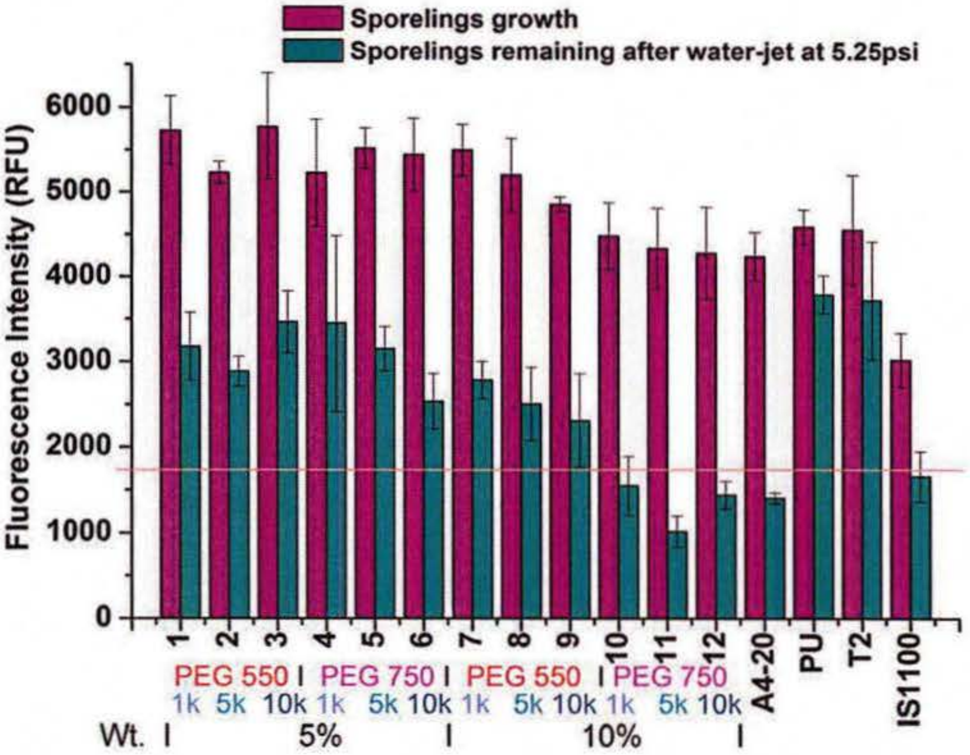
S4: Removal of diatoms (*Navicula incerta*) from coatings



S5: Removal of bacterial biofilm (*Cellulophaga lytica*) from coatings



S6: Macroalgae (*Ulva linza*) initial attachment and retention (i.e., biomass remaining) after water-jet treatment at 36 kPa pressure.



Appendix E

Fouling-Release Properties of Siloxane-Polyurethane Coatings from Acid Functionalized Polydimethyl Siloxane Blends.

Introduction

Marine biofouling has been an area of concern since man started sailing.[1] Unwanted settlement of marine organisms on any surface exposed to the marine environment leads to a decrease in performance and productivity.[2] For ocean going vessels, light fouling (slime) can result in additional powering penalties up to 10-16% and for ship hulls with heavy fouling these penalties may add up to 86%.[1 3 4] The United States Navy has estimated that the approximate cost of biofouling is around 180-260 million per year for their entire fleet; which highlights the magnitude of the economic impact of biofouling to ocean going vessels.[1 3 5]Also increased emissions and spread of fouling species around world (given the widespread network of shipping routes) may have a major impact on the environment. [3 6]

Anti-fouling coatings with active biocides remain the most widely used approach for biofouling control.[7 8 9] However non-toxic fouling-release (FR) coatings have gained the most recent interest in research and development of marine coatings.[10 11 12] Regulatory concerns and the process of authorizing new biocides can be extensive and time consuming.[10] Several risk assessment and toxicity studies are mandatory by the European Biocidal Products Directive in order to register and market new biocides for anti-fouling paints.[10] Currently Cu or CuO is used as the active ingredient in many anti-fouling paints and typically a high loading of Cu/CuO is required for long term performance. The use of Cu may also pose environmental concerns given the possibility of accumulation in the marine environment.[10] Low surface energy FR coatings are non-toxic, they may allow settlement of marine organisms on surfaces but perform as self-cleaning surfaces.[3 11] Settled fouling is removed due to hydrodynamic forces maintaining a clean and smooth ship hull.

Typical FR coatings are designed using siloxanes or fluoropolymers to obtain low surface energy materials.[13] In theory, low surface energy coatings help minimize the adhesion strength of marine organisms, thus allowing easy release upon exposure to hydrodynamic pressure. [1] Lately with profound understanding of adhesion processes of marine organisms have allowed continued development of non-toxic FR coatings.[14 15 16]

The diversity of marine organisms, their adhesion preferences and the complexity of their adhesives presents the biggest challenge in developing FR/ anti-fouling coatings. Biofouling on medical implants is considered to as serious an issue as on marine vessels.[17 18 19] The use of amphiphilic materials is an approach that has been widely explored in the area of biomedical research for controlling biofouling on implants and devices that are in contact with human body fluids.[17 18 20] This approach has become a recent area of interest for FR/ anti-fouling technology. The main difference between fouling on marine vessels and medical implants is attributed to the type of environment being exposed to demining the outcome and the extent of biofouling. It is widely understood that body fluids consist of complex macromolecules, proteins, glycoproteins which typically interact with freshly exposed surfaces preparing the surface for colonization of cells.[21 22] A significant amount of research has been focused on reducing or controlling the adsorption of these macromolecules.[22] Surfaces with mixed hydrophilic and hydrophobic character have shown promise in reducing the adsorption of macromolecules yet a material that is completely inert towards protein adsorption is still to be discovered.[20] Nevertheless designing FR coatings with amphiphilic surface characteristics can be helpful for broad resistance of marine biofouling given the recent developments in performance observed for coatings in academic research and in the marine coatings industry. [23 24 25 26 27]

One common hydrophilic group that has been extensively studied for amphiphilic materials is the carboxylic acid group. It is observed that COOH groups expressed on the surface may be deprotonated at slightly basic pH, providing a COO^- charged surface.[28] Surfaces with COO^-

groups have demonstrated easy elution of proteins in several studies.[29] In another study discussing the effects of surface chemistry on *Ulva linza* adhesion, surfaces with COOH moieties showed a drop in settlement of spores and higher biomass removal of sporelings.[30]

Siloxane polyurethane (SiPU) marine coatings are a practically sound approach to a tough and environmentally friendly FR solution.[31] [32] [33] [34] Unlike silicone elastomer based FR top coats, SiPU coatings have been able address the mechanical durability and adhesion concerns.[35] They have also demonstrated comparable FR properties to leading commercial standards in field immersion trials. Recently initial attempts of amphiphilic SiPU coatings were explored by incorporating carboxylic acid and polyethylene glycol groups.[36] [37] Although these new systems showed promise in improving the FR properties of SiPU coatings, an optimum hydrophilic/hydrophobic balance needs to be achieved for broad spectrum FR. More specifically, in an approach to use pendent acid functionalized siloxane resins in SiPU coatings, major improvements in the FR properties towards diatoms was observed, yet that of barnacles was compromised.[36] Therefore, to address the shortcomings of these previous studies, coatings with lower hydrophilic COOH content were prepared.

In this study, a 25% pendent acid functionalized aminopropyl terminated siloxane (APT-PDMS-25A) was synthesized and utilized in coating formulations. As an approach to manipulate the concentration of hydrophilic groups on coating surface, several coating formulations were prepared with varying the APT-PDMS-25A content from 20%, 16%, 12%, 8%, 4% and 0% by wt. In order to maintain a total combined siloxane content of 20% by wt, aminopropyl terminated siloxane (APT-PDMS) was blended in (at 0%, 4%, 8%, 12%, 16% and 20% respectively). Coating surfaces were characterized using water/methylene iodide contact angle measurements and atomic force microscopy (AFM). Coatings were tested for toxicity and FR properties towards microalgae (*Navicula incerta*), macroalage (*Ulva linza*), bacteria (*Cellulophaga lytica*), barnacles (*Amphibalanus amphitrite*), and mussels (*Geukensia demissa*) using laboratory biological assays.

Experimental

Materials

3-Aminopropyl terminated polydimethyl siloxane having a number average molecular weight of 875 (APT-PDMS-875), octamethylcyclotetrasiloxane (D_4), and 1, 3, 5, 7-tetramethyl- 1, 3, 5, 7-tetravinylcyclotetrasiloxane (D_{4V}) were purchased from Gelest Inc. Benzyltrimethyl ammonium hydroxide (40% in methanol), tetrahydrofuran (THF), hexanes, 2-heptanone, toluene, methanol-d, chloroform-d ($CDCl_3$), 3-mercaptopropionic acid (MPA), acetylacetone, dibutyltin diacetate (DBTDAc) were purchased from Sigma Aldrich. Polyisocyanate Desmodur Z 4470 BA was provided by Covestro. All reagents were used under as-received conditions. An acrylic polyol containing 80% butyl acrylate (BA) and 20% 2-hydroxyethyl acrylate (HEA) was utilized for this study and synthesized following a procedure reported previously.[38] An aminopropyl terminated poly(dimethylsiloxane) (APT-PDMS) of 20,000 g/mol molecular weight (MW) was also synthesized as reported previously.[34]

Acid Functional Aminopropyl Terminated Polydimethyl Siloxane (APT-PDMS-25A) Synthesis

Synthesis of the acid functionalized PDMS is a two-step process (Figure 1). First the vinyl functional copolymer of PDMS was synthesized (APT-PDMS-25V). Next the PDMS copolymer was acid functionalized through the vinyl groups using a thiol-ene click reaction. For this study APT-PDMS-25A copolymer with 25% acid functionality was synthesized. D_4 (187.31 g) and D_{4V} (75.89 g) cyclic siloxane monomers (3:1 molar ratio) were used to synthesize the copolymer. D_4 monomer was combined with catalytic amount of benzyltrimethyl ammonium hydroxide (0.653 g) in a 500 mL single neck round bottom flask. The content was rotary evaporated for about 30 mins. The dried monomer/catalyst mixture was then transferred into a four neck 500 mL round bottom flask containing APT-PDMS-875 oligomer (12.03 g) and D_{4V}. The reaction flask was also equipped with a mechanical stirrer, thermocouple, N_2 inlet, reflux cooling condenser and a heating mantle. Once the monomer mixture was transferred, the reaction mixture was heated to 80 °C while stirring. The reaction was allowed equilibrate for 48 hrs at 80 °C. After 48 hrs, the resin was heated to 165 °C for 1 hr to decompose the catalyst. Then the resin was cooled to room temperature and transferred into a glass container. The vinyl functional PDMS copolymer was characterized using GPC and ^{1}H NMR to confirm the successful synthesis.

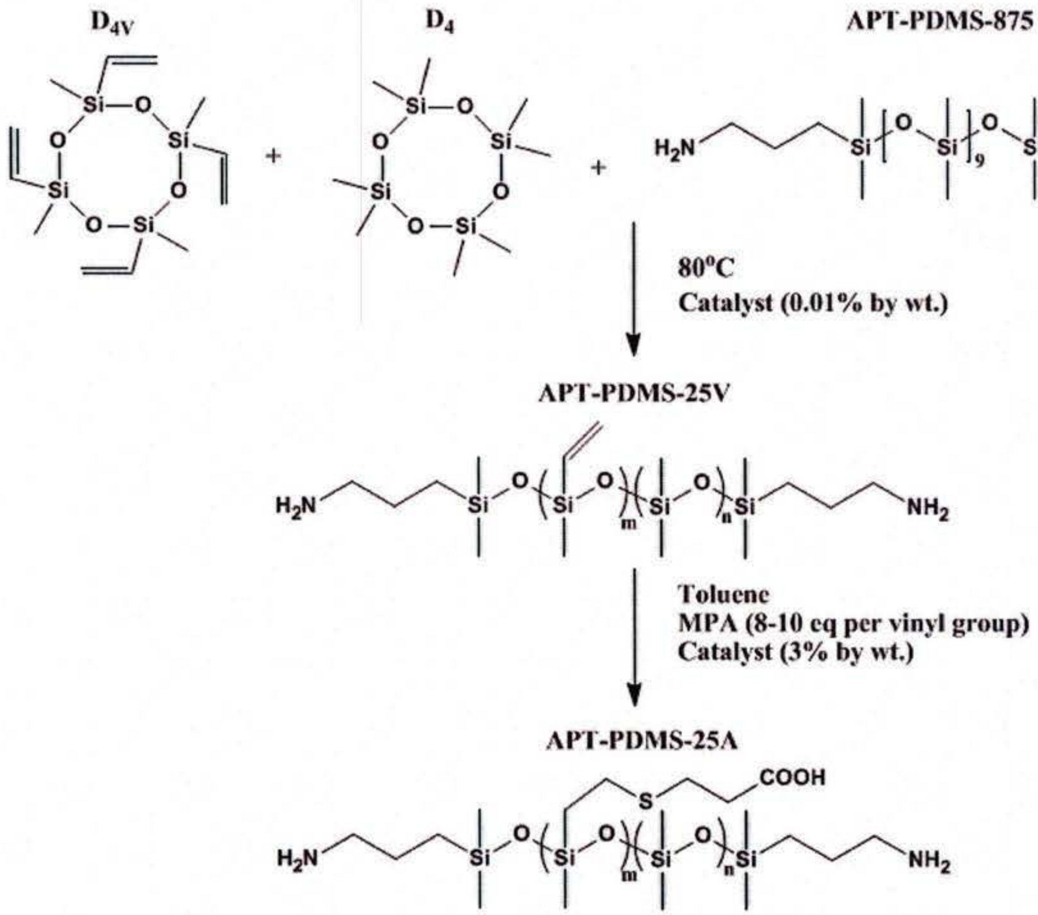


Figure 1: Reaction scheme for the synthesis of APT-PDMS-25A

The thiolene-click reaction was carried out in a 4 neck 3 L round bottom flask equipped with a mechanical stirrer, thermocouple, cooling condenser, N_2 inlet and heating mantle. The vinyl functional PDMS resin (150 g) from above, MPA (354.96 g; 8 equivalents of thiol per 1 vinyl equivalent) and toluene (1008.38 g were combined in the reaction flask and the mixture was heated to 80 °C. Catalyst solution containing Vazo 67 (9.08 g in 50 g of toluene) was added when the reaction temperature reached 80 °C. The reaction temperature was maintained at 80 °C while monitoring the disappearance of the vinyl peak using ^{1}H NMR very 2 hrs. The reaction was considered complete after complete disappearance of the vinyl peak around 5-6 ppm. The resin mixture was cooled to ambient temperature, the content was concentrated through rotary evaporation and transferred into a 1 L separatory funnel. The product was slightly diluted with THF (10-15mL portions each time) and excess acid was extracted using ice cold hexane for several times. Typically 8-10 extractions are required to complete removal of excess MPA. After purifying the product, the resin was concentrated and diluted in butyl acetate to obtain a 20% solid solution.

Gel Permeation Chromatography (GPC)

Approximate molecular weight of APT-PDMS-25V and APT-PDMS-25A were determined using a high-throughput GPC relative to polystyrene standard. For each resin, a polymer (approximately 5 mg/mL concentration) solution in THF was prepared. The samples were analyzed using Symyx® Rapid GPC equipped with an evaporative light scattering detector (PL-ELS 1000), 2× PLgel Mixed-B columns (10 µm particle size) while maintaining a 2.0 mL/min flow rate.

^{1}H NMR Characterization

The siloxane copolymers were characterized using ^{1}H NMR. Also ^{1}H NMR was utilized to determine the completion of the thiol-ene click reaction during acid functionalization of APT-PDMS-25V. All ^{1}H NMR spectra were obtained using the JEOL-ECA 400 (400 MHz) NMR spectrometer. In order to prepare samples for analysis, small amount of APT-PDMS-25V was diluted using $CDCl_3$ and APT-PDMS-25A samples were diluted using a solvent mixture consist of 80% $CDCl_3$ and 20% methanol-d by volume.

Coating Formulation

Coating formulations were prepared using the acid functionalized siloxane copolymer (APT-PDMS-25A), APT-PDMS, acrylic polyol, isocyanate (Desmodur Z4470 BA). Coating compositions prepared during this experiment are outlined in Table 1. A representative formulation procedure for coating 2 is described here. Siloxane resins APT-PDMS-25A (8.0 g) and APT-PDMS (0.4 g) were combined with acrylic polyol (10.0 g) and acetylacetone (1.0 g) in a 20 mL glass vial equipped with a magnetic stir bar. The content was allowed to mix overnight using a magnetic stir plate. After 24 hrs, Desmodur Z4470 BA (4.3 g) and DBTDAc catalyst solution (0.5 g) were added to the vial and allowed to mix under magnetic stirring before making coatings. After 1hr, the coating formulation was used to prepare drawdowns and depositions. Drawdowns were made on primed aluminum panels using a wire-wound drawdown bar and formulation (250µL sample/ well) was also deposited in to multi-well plates modified with primed aluminum disks. All coatings were allowed to cure under ambient conditions for 24 hrs and on the next day they were oven cured at 80 °C for 45 mins.

Table 1: Composition of Coatings

Coating #	APT-PDMS-25A (g)	APT-PDMS (g)	Acrylic Polyol (g)	Isocyanate (Desmodur Z4470 BA) (g)	Acetylacetone (g)	Catalyst (DBTDAc in MAK) (g)
1 (20PDMSA-0PDMS)	10.00	0.00	10.04	4.26	1.0	0.5
2 (16PDMSA-4PDMS)	8.00	0.40	10.04	4.26	1.0	0.5
3 (12PDMSA-8PDMS)	6.00	0.80	10.04	4.26	1.0	0.5
4 (8PDMSA-12PDMS)	4.00	1.20	10.04	4.26	1.0	0.5

5 (4PDMSA-16PDMS)	2.00	1.60	10.04	4.26	1.0	0.5
6 (0PDMSA-20PDMS)	0.00	2.00	10.04	4.26	1.0	0.5

Preparation of Standard Coatings

Commercial coating standards Dow Corning T2 (silicone elastomer), Intersleek®700 and Intersleek®900 (AkzoNobel International Paint) were prepared according to the manufacturer's specifications to serve as standards. A pure polyurethane formulation without APT-PDMS was also prepared to be included as a standard. All internal control coatings and commercial standards were prepared on both primed aluminum panels and in 24-well plates in order to be characterized in parallel with the experimental coatings.

Water Aging

All the coatings were pre-leached for 28 days using running tap water. Both multi-well plates and panels with coatings were placed in a tap-water aquarium system which automatically filled and emptied every 4 hrs. Another set of coatings were immersed in artificial sea water for 28 days (ASW) and water was manually changed every day.

Surface Characterization of Coatings

A Symyx® surface energy system was utilized to measure WCA and MICA for all experimental coatings. Three measurements of each liquid were obtained using First Ten Angstroms™ software. Then average WCA and MICA were used to calculate the SE for each coating by Owens-Wendt method.[39] Contact angle and SE analysis were performed both before and after water aging.

Atomic Force Microscopy (AFM) was used to observe the topography of the experimental coatings. A Dimension 3100 microscope with Nanoscope controller was used to scan the surface of the experimental coatings before and after water-leaching. A cantilever with a silicon probe (with a spring constant 0.1-0.6 N/m and resonant frequency 15-30 kHz) was used to scan a sample area of 20×20μm for each coating in tapping mode under ambient conditions.

Biological Laboratory Assays

Growth and Release of Macroalgae (*Ulva linza)*

Fouling-release assay for the microalga *U.linza* was conducted at Newcastle University, using a set of multi-well plates following 28 days of pre-leaching. More detailed procedure of the *U.linza* growth and removal assay using high throughput screening can be found elsewhere.[40] Before starting the experiment, all multi-well plates were equilibrated in 0.22μm-filtered artificial seawater (FSW) for 2 hrs. To each well, 1 mL *U.linza* spore suspension adjusted to 0.05 OD at absorbance 660 nm (3.3×10^5 spores ml^{-1}) in single strength enriched seawater medium was added. Spores settled on the plates were allowed to grow for 6 days inside an illuminated incubator at 18 °C with a 16:8 light: dark cycle (photon flux density 45 $\mu mol.m^{-2}.s^{-1}$) while renewing nutrients every 48 hrs (there was no washing performed to remove unsettled spores after settlement). After 6 days, the biomass generated was assessed from a single row of wells (6) from each plate. Single rows of wells on each plate were sprayed using the spinjet apparatus at 18, 67 and 111 kPa impact pressure. Chlorophyll extraction was performed by adding 1 mL of DMSO to each well followed by determining fluorescence at excitation at 360 nm and emission at 670 nm wavelengths. Fluorescence is directly proportional to the biomass present on each coating surface. The removal of sporelings at each pressure was compared with the unsprayed wells (that were used to assess sporeling growth above).

Growth and Release of Microalgae (*Navicula incerta)*

Microalgae (*N.incerta*) assay was conducted at NDSU using methods described previously.[41] [42] Pre-leached coatings were inoculated using a (1 mL per well) diatom (*N.incerta*) suspension with 4 x 10^5 cells/mL (adjusted to 0.03 OD at absorbance 660 nm) in Guillard's F2 medium. The plates were incubated for 2 hrs under ambient conditions to facilitate cell attachment. Three replicate wells (1st column) were left untreated to be used as a measurement of initial amount of cell attachment. Consequent coating wells were then subjected to water jet treatments, with water jet pressures 10 and 20 psi (138k Pa) for 10 seconds each. Biomass was quantified through chlorophyll extraction using 0.5 mL of DMSO and measuring fluorescence of the extracts (excitation wavelength at 360 nm; emission wavelength at 670 nm). The relative fluorescence from the extract is directly proportional to the algae biomass present on the coating surface before and after water jet treatment. Percent removal of diatoms was determined using relative fluorescence of non-jetted and water-jetted wells.

Bacterial (*Cellulophaga lytica*) Biofilm Adhesion

Fouling-release assay for marine bacterium *C.lytica* was performance following the procedure previously described by Stafslien *et al.*[42] [43] Multi-well plates containing coatings were inoculated by dispensing a 1 mL suspension of marine bacteria (*C.lytica*; 10^7 cells/mL) in FSW supplemented with 0.5 g/L of peptone and 0.1 g/L of yeast extract. The plates were subjected to static incubation for 24 hrs at 28°C. The first column of wells (3 wells) were untreated and used as the initial bacterial biofilm growth while the next columns (3 wells) were treated with subsequent water jet treatment at 10 and 20 psi (69 and 138 kPa) for 5 seconds. The coating surfaces were then stained with 0.3% crystal violet solution in deionized water. The stained crystal violet was extracted using 33% acetic acid solution and eluates were collected from each coating well. Then 0.15 mL aliquots of the resulting eluates were measured for absorbance at 600nm wavelength. The absorbance values were directly proportional to the amount of bacterial biofilm present on coatings. Biofilm removal from the coatings was quantified by comparing the relative absorbance values obtained for the non-jetted and water-jetted wells.

Re-attached Adult Barnacle (*Amphibalanus amphitrite*) Adhesion

Fouling-release performance towards barnacles were determined using an adult barnacle reattachment assay described by Stafslien *et al.*[44 45] Coatings were prepared on 8 x 4" panels and evaluated after 28 days of pre-leaching. Adult barnacles (~5 mm in diameter) were supplied by Duke University attached to silicone substrates. Barnacles were dislodged (n = 5) and immobilized onto the surface of experimental coatings using a custom template. The barnacles were allowed to reattach and grow while they were immersed in an artificial sea water aquarium tank system with daily feedings of Artemia nauplii (Florida Aqua Farms). A hand-held force gauge mounted to a semi-automated device was utilized to push of the attached barnacles (in shear) following 2 weeks attachment period. The peak force of removal for each barnacle was recorded. After each barnacle was dislodged, barnacle base plate area was quantified through Image analysis (Sigma Scan Pro 5.0). Barnacle adhesion strength (MPa) was calculated by taking the ratio of force for removal to basal plate area. The average barnacle adhesion strength for each coating was reported based on the total number of barnacles removed with a measureable force. Barnacles that were adhered strongly resulted in broken barnacles implying poor FR properties.

Mussel (*Geukensia demissa*) Adhesion

Another set of coatings prepared on 4" x 8" panels were used for the mussel adhesion assay. Marine mussels (*G.demissa*) were provided by Duke University Marine Laboratory in Beaufort, North Carolina, USA. Prior to attachment assay the mussels were modified by attaching a plastic rod. A 4 cm long acetal plastic rod (product# 98873A105, McMaster-Carr) was attached to each mussel perpendicular to the ventral edge, using a 3M® acrylic adhesive (product# 7467A135, McMaster-Carr). For this study, six mussels were immobilized on to each coating surface and placed PVC sheets (custom-designed template) firmly against the plastic rods in order to make sure that the mussels were in contact with the coating surface. The coatings with immobilized mussels were placed in the ASW aquarium system and fed daily with live marine phytoplankton (DTs Premium Reef Blend Phytoplankton) for three days. Then the coatings were removed from the ASW aquarium tank system and the total number of mussels showing attachment of byssus threads was recorded for each surface. The plastic rod from each mussel was attached to individual 5 N load cell of a custom built tensile force gauge. Then the mussels were pulled off (1 mm/s pull rate) simultaneously. The force required for detachment of all byssus threads was averaged and the pull-off value for each coating was recorded. The presence of non-attached mussels during the 3 day attachment period indicated good mussel deterrence properties of the coatings.

Results and Discussion

In this study 25% acid functionalized siloxane polymer (APT-PDMS-25A) was utilized to prepare SiPU coatings with hydrophilic COOH groups on the surface. First the siloxane resin with vinyl functional groups was synthesized using D_4 and D_{4V} cyclic siloxane monomers at a molar ratio of 3:1 via a ring opening equilibration reaction. Polymer from the first step was characterized using GPC and ^{1}H NMR. The number average molecular weight for APT-PDMS-25V was 18960 g/mol, which was close to the target value 20000 g/mol (Table 2). ^{1}H NMR indicated the presence of the vinyl peak at 5.5 ppm confirming the synthesis of APT-PDMS-25V (spectrum not shown). Then the siloxane copolymer was functionalized with COOH acid groups via thiol-ene click reaction and an apparent increase in MW was observed (22340 g/mol). The structure of the pendent acid functionalized siloxane was confirmed by ^{1}H NMR (Figure 1). The vinyl peak at 5.5 ppm has completely disappeared suggesting complete functionalization of APT-PDMS-25A. Also the OH peak from COOH was visible at 3.7 ppm. Using a slight excess of MPA established that all vinyl groups were reacted. Coatings were prepared according to formulations described in Table 1.

Total siloxane level was maintained at 20% by wt. for all formulations while blending the APT-PDMS-25A resin with APT-PDMS resin at several ratios. Blending the APT-PDMS resin with APT-PDMS and changing coating compositions provided a method to tune the amount of hydrophilic COOH groups present on the surface.

Table 2: Average molecular weight for siloxane resins synthesized or used for coating formulations.

Siloxane Resin	**Pendent Functionality**	**M_n (g/mol)**	**PDI**
APT-PDMS-25V	vinyl	18960	1.61
APT-PDMS-25A	COOH	22340	1.62
APT-PDMS	-	19760	1.70

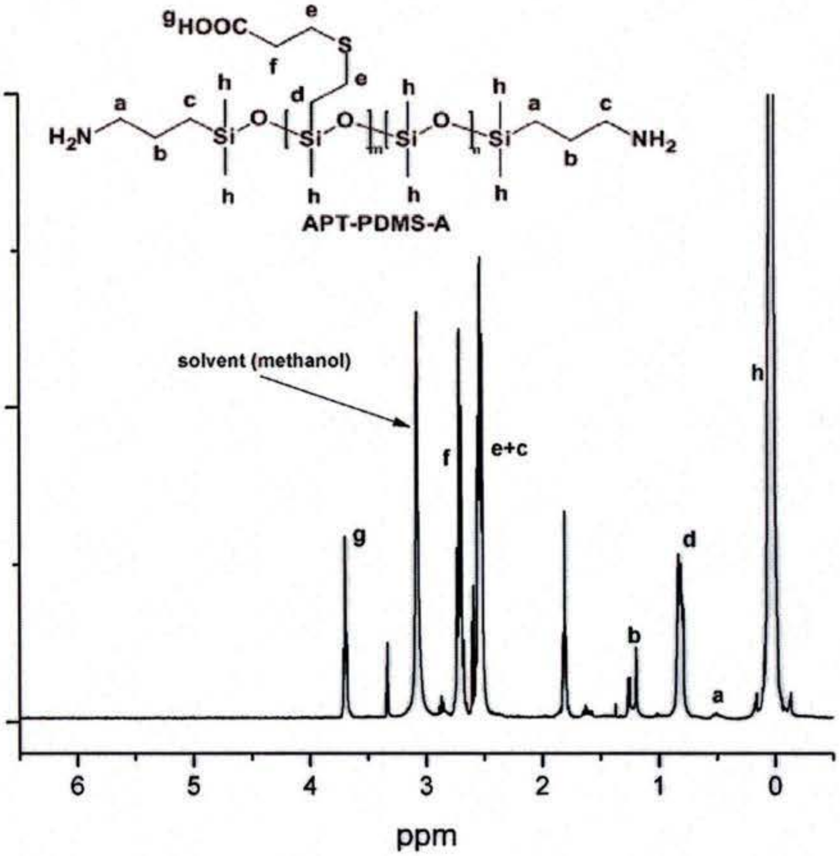


Figure 1: ^{1}H NMR of APT-PDMS-25A in solvent (80:20 mixture of $CDCl_3$: methanol-d)

Considering the coating compositions, the first 3 experimental coatings are APT-PDMS-25A rich whereas last three are APT-PDMS rich. Figure 2 shows the changes in WCAs and MICAs evaluated before and after water (pH ≈ 7) aging. Coatings 2-6 showed very similar WCAs before water immersion (above 100°), except coating 1 which showed a WCA around 85°. Coating 1 exclusively contained APT-PDMS-25A (20% by weight) as the siloxane component, thus the lower WCA may have resulted from having more COOH groups on the surface compared to other experimental coatings. The pKa of COOH is around 5 and it is reasonable to assume a major portion of COOH groups exposed to water can be in its deprotonated state (COO^-) which tends to attract water molecules. In general, APT-PDMS-25A rich coatings (1-3) showed a slight decrease in WCAs suggesting increased hydrophilicity following 28 days of water immersion. Given the thermodynamic and kinetic nature of Si-O bond, it is a strong possibility that the APT-PDMS-25A rich coatings may have undergone some surface rearrangement to expose more COOH groups resulting in increased hydrophilicity. On the other hand, the APT-PDMS rich coatings displayed similar or slight increase in WCAs after the water aging. Methylene iodide contact angle (MICA) for coatings 1-3 remained unchanged, although the PDMS rich coatings 4-6 showed an increase in MICA after exposure to tap water for 28 days.

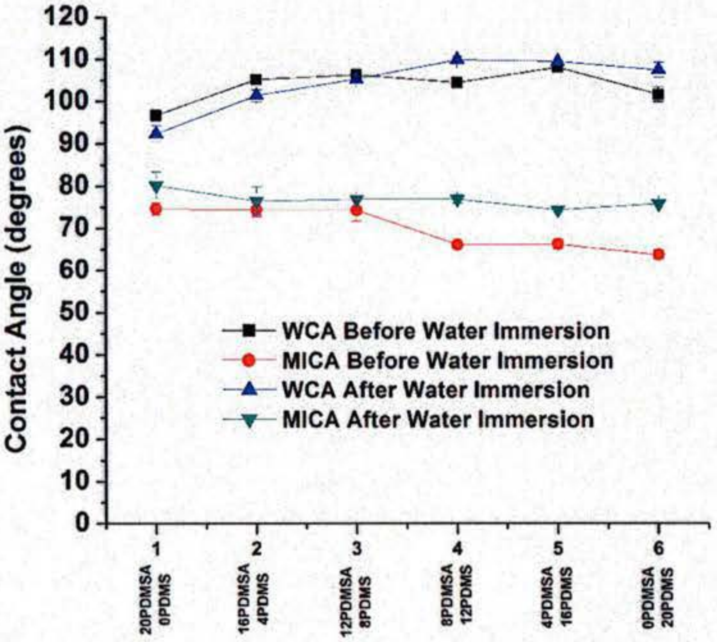


Figure 2: Water and methylene iodide contact angles of APT-PDMS-25A modified SiPU coatings analyzed before and after 28 days of tap water immersion. Each data point represents the average contact angle of three replicate measurements.

Figure 3 shows the change in WCAs and MICAs of experimental coatings before and after exposure to artificial salt water (ASW) (pH≈9). The pH of natural seawater typically ranges from 8-8.5 and COOH groups will tend to deprotonate at basic pH; therefore evaluating changes in wettability of coating surfaces when exposed to seawater can be important. Before ASW immersion, all the experimental coatings displayed similar WCAs and MICAs to those coatings used for the tap water immersion study. However post exposure to ASW for 28 days, a decrease in WCAs were observed for coatings 1-5. Interestingly coatings 1-5 contained APT-PDMS-25A ranging from 20% to 4% respectively. Coatings 1-5 demonstrated a linear trend in increasing WCA with respect to decreasing amount of APT-PDMS-25A incorporated into coating formulations. The observed in change in WCAs from coatings 1-5 may have resulted from deprotonation of COOH groups on the coating surface. Coating 6 does not contain any APT-PDMS-25A and thus explains the observed increase in WCA after immersion in ASW. Following 28 days of exposure to ASW, all experimental coatings except coating 2 displayed a slight increase in MICAs; a trend that was not obvious in regard to coating compositional variations. Coating 1 have very close values of WCA and MICA after ASW immersion. Higher pH of ASW may have resulted in more COO$^-$ groups on the coating surfaces resulting in the observed changes in WCA and MICA.

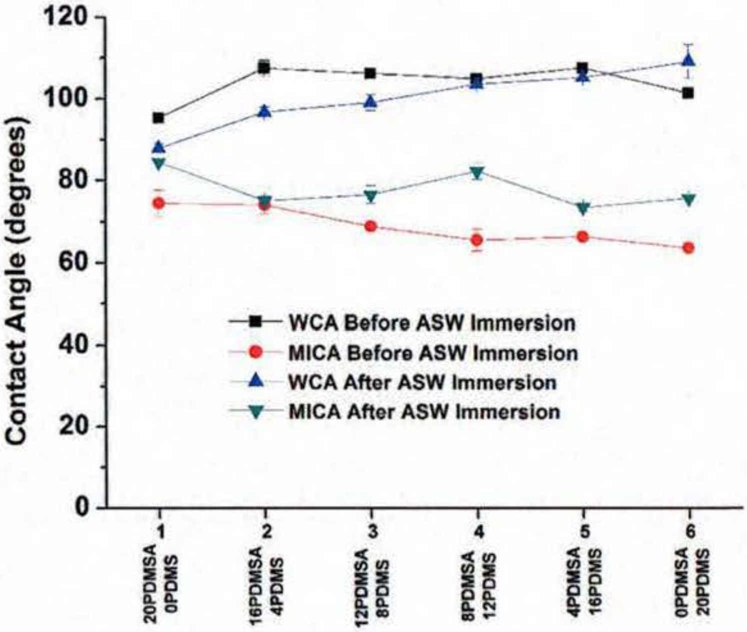


Figure 3: Water and methylene iodide contact angles of APT-PDMS-25A modified SiPU coatings analyzed before and after 28 days of ASW immersion. Each data point represents the average contact angle of three replicate measurements.

Surface energy of the coatings exposed to tap water and ASW aging were calculated using the Owens-Wendt method.[39] Before water immersion, SE for coatings with high APT-PDMS-25A content (1-3) were slightly lower than that of coatings with low APT-PDMS-25A content (4-6).

However after water immersion APT-PDMS rich coatings showed a decrease in SE, while SE of APT-PDMS-25A rich coatings remained more or less unchanged. A similar trend in SE change was observed for experimental coatings after exposure to ASW for 28 days.

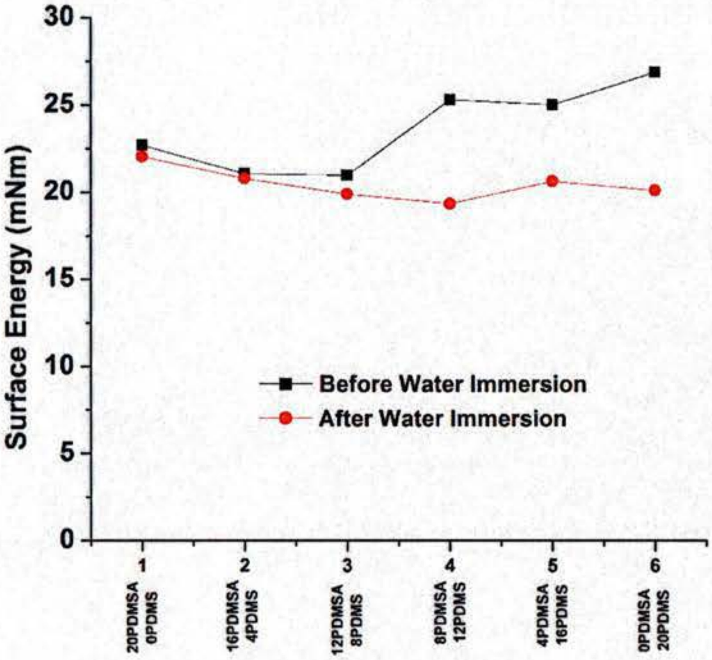


Figure 4: Surface energy of experimental coatings evaluated before and after water immersion. Each data point was calculated using the average WCA and MICA for each coating obtained from water aging study.

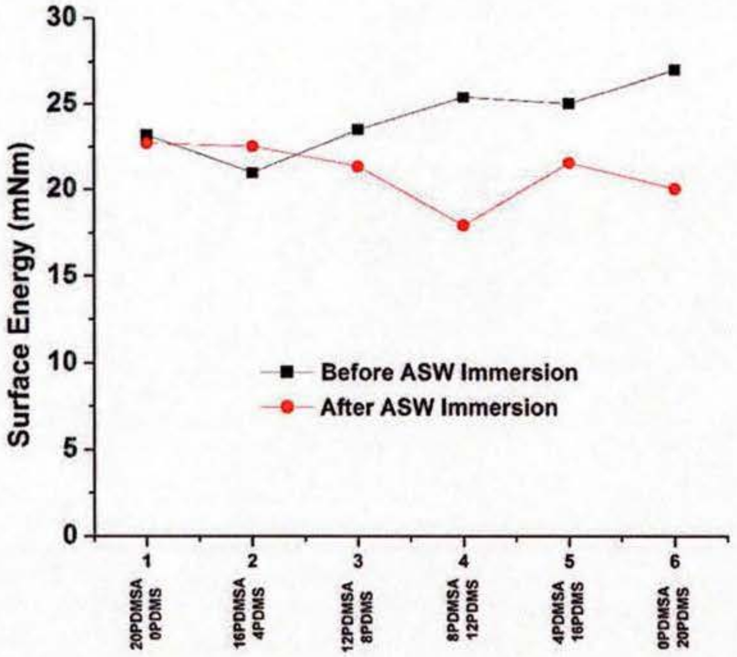


Figure 5: Surface energy of experimental coatings evaluated before and after ASW immersion. Each data point was calculated using the average WCA and MICA for each coating obtained from ASW water aging study.

Experimental coatings were analyzed using AFM before and after water aging. Coatings surfaces were observed to be smooth and did not show any significant surface features before water leaching. AFM images of the coatings after water leaching are shown in Figure 6. After 28 days of exposure to tap water, coatings with APT-PDMS-25A showed domains which may indicate the presence of COO^- groups on the coating surface. These domains seem to vary in size and distribution as the APT-PDMS-25A content was changed. Coatings 1 and 2 showed the highest density of domains after water immersion. It was apparent that domains became less significant as APT-PDMS-25A composition in coating formulation decreased (from 20%, 16%, 12%, 8% and 4% by wt. respectively). Following water aging, domains were not observed for coating 6 which did not contain any APT-PDMS-25A. Interestingly, observations made during AFM analysis strongly agree with surface wettability properties observed through contact angle analysis.

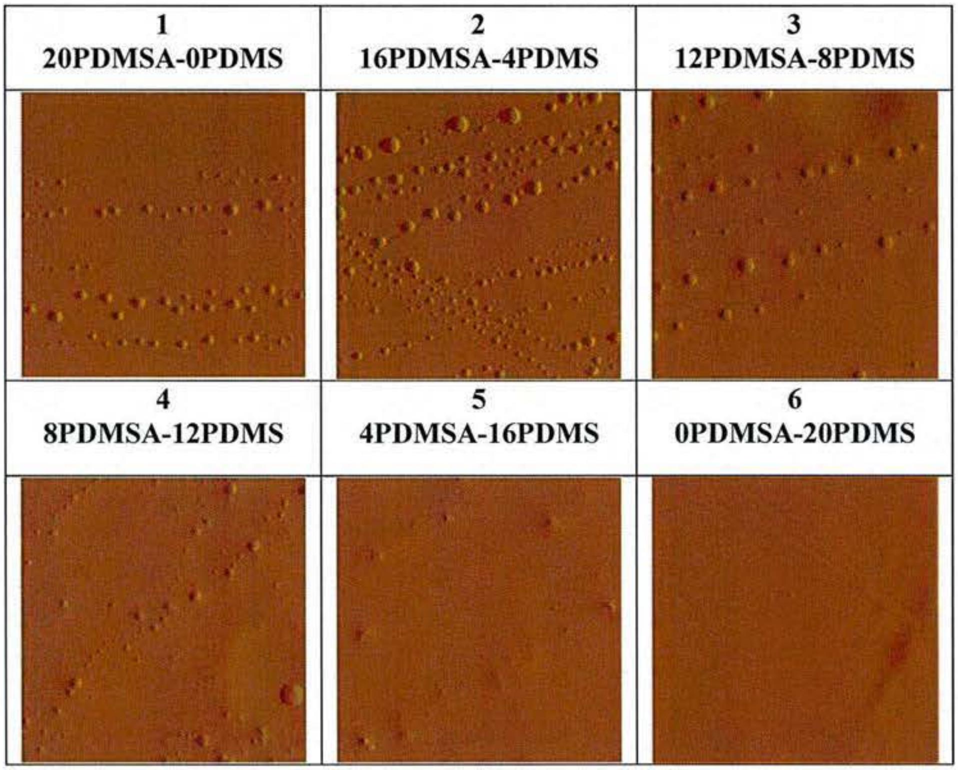


Figure 6: AFM scans of experimental coatings after 28 days of water aging.

The extent of *U.linza* sporeling growth (6 days of growth) for coatings is shown in Figure 7. Coatings 1 and 2 showed significantly lower biomass of *U.linza* sporelings compared to other experimental and standard coatings. Previous studies suggest that *U.linza* macroalgae are sensitive to surface wettability.[30] [46] Surfaces with COOH have shown to reduce the settlement of *U.linza* spores, yet those spores that settle tend to adhere strongly to surfaces with COOH groups.[30] Coatings 1 and 2 contained the highest amount of COOH functionalized PDMS thus resulting in lower settlement of *U.linza*. Coatings 4-6 showed similar amount of *U.linza* biomass as Intersleek® 900. Figure 8 represent the FR properties of experimental and standard coatings towards sporelings of *U.linza* when subjected to water jet treatment. Coatings 1 and 2 with the lowest *U.linza* biomass generated, displayed poor FR of sporelings supporting the theory previously discussed on settlement and adhesion strength of *U.linza*. However coatings 4 and 5 with a blend of APT-PDMS-25A and APT-PDMS displayed the best FR of sporelings which was comparable to Intersleek® 900 standard considering all three water jet pressures. The observed FR performance of coatings 4 and 5 may be attributed to their amphiphilic character. Contact angle measurements and AFM images suggested surface heterogeneity resulting from blending relatively hydrophilic APT-PDMS-25A with APT-PDMS.

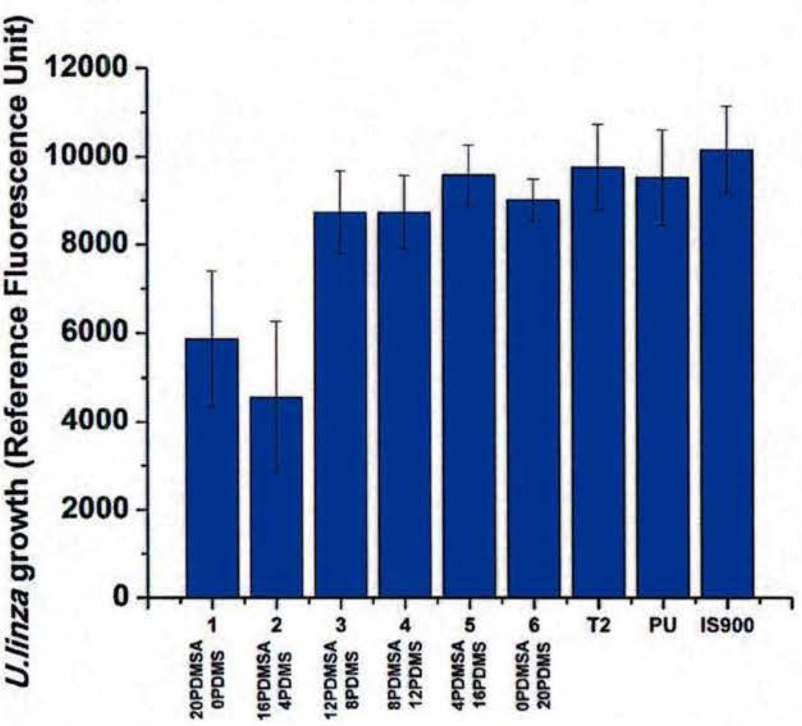


Figure 7: *U.linza* sporeling growth on experimental and standard coatings. Each bar represents the fluorescence of chlorophyll (averaged for 6 replicates per coating) which is directly proportional to amount of *U.linza* biomass present on the coating surface after 6 days of growth.

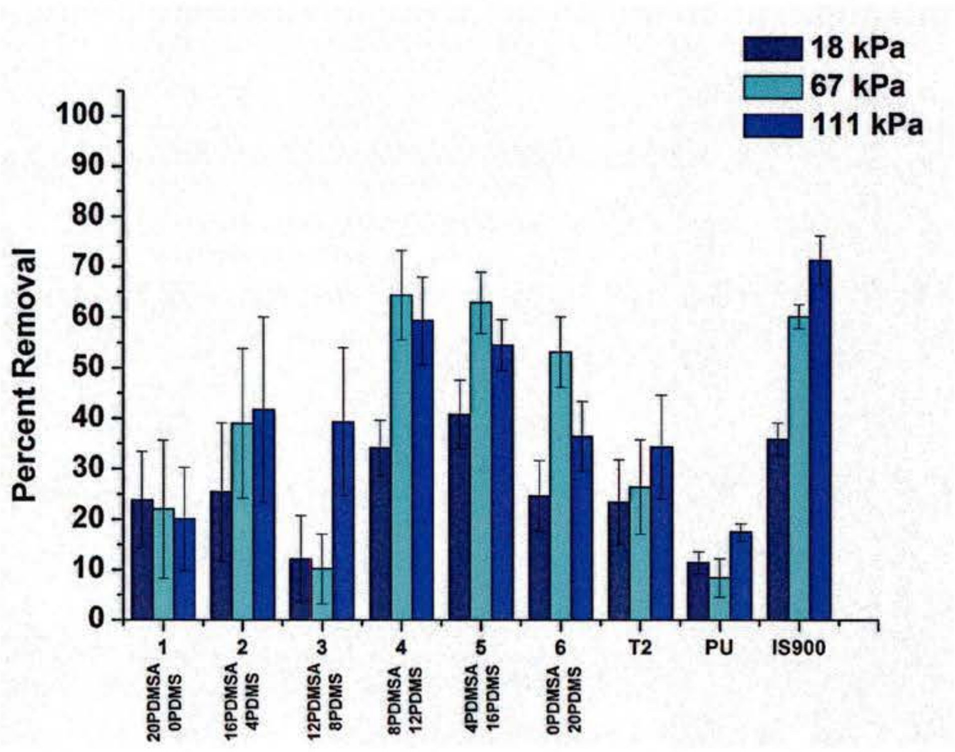


Figure 8: Removal of *U.linza* sporelings from coatings following water jet treatment at 18, 67, and 111 kPa. Each bar represent the average percent removal of 6 replicate measurements.

Bacterial biofilm removal of the coatings indicating the FR performance of coatings towards marine bacterium *C.lytica* is shown in Figure 9. All experimental coatings showed similar bacterial biofilm removal performance (at both water jet pressures) regardless of compositional variations of the coatings. On the other hand all experimental coatings displayed slightly better or comparable FR properties to silicone standards T2 and Intersleek 700. However Intersleek 900 showed the best FR of bacterial biofilm with almost complete removal of settled biofilm. In general, the incorporation of APT-PDMS-25A had no significant contribution to improve or impair *C.lytica* bacterial biofilm removal of SiPU coatings.

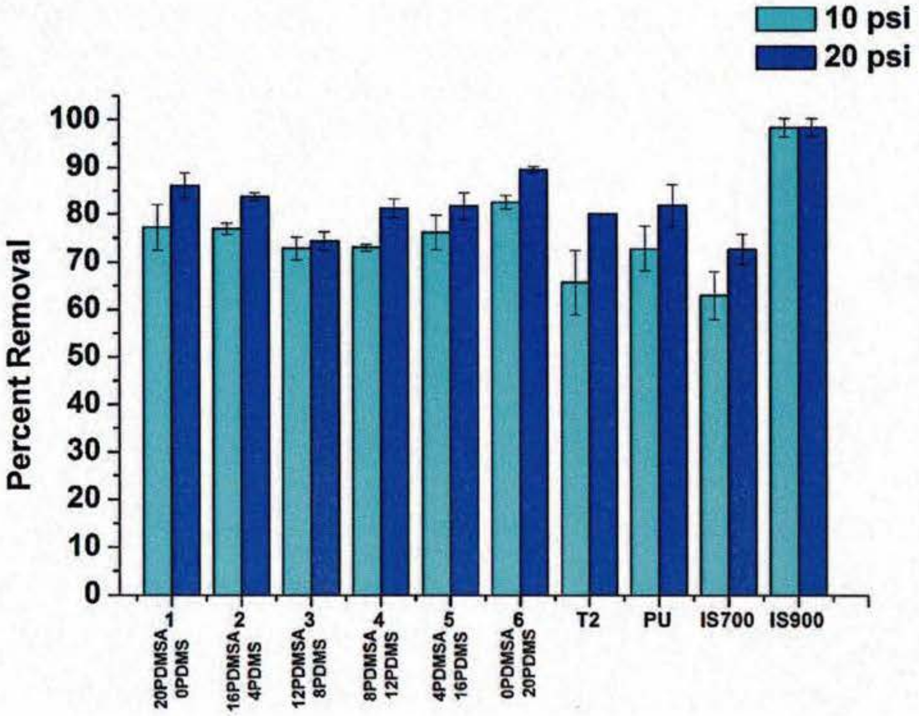


Figure 9: Removal of *C.lytica* bacterial biofilm form coatings following water jet treatment at 10 and 20 psi. Each bar represents the average percent removal of 3 replicate measurements.

N.incerta is a diatom which contributes to forming slime on ship hulls. The adhesion and settlement behavior of *N.incerta* has been studied previously and they tend to show lower adhesion strength towards more hydrophilic surfaces. [46] [47] [48] Most FR formulations are based on hydrophobic silicone elastomers which often have poor FR properties towards *N.incerta*. In a previous study, using COOH functionalized silicone resin in formulating SiPU marine coatings provided significantly improved FR properties towards diatoms.[36] Similarly, out of all experimental coatings, coating 1 containing the highest level of APT-PDMS-25A demonstrated the best FR properties towards diatoms. Coating 1 showed comparable removal of diatoms as Intersleek 900 at 10 psi water jet pressure. However at 20 psi water jet pressure, Intersleek® 900 outperformed all coatings in terms of diatom removal. Coating 1 also showed similar FR of diatoms as other standard coatings Intersleek 700, T2 and PU at both water jet pressures. Experimental coating compositions with APT-PDMS-25A and APT-PDMS blends did not show good FR performance towards *N.incerta* removal. Low concentration of COOH groups in blend coatings may have resulted the low removal of diatoms.

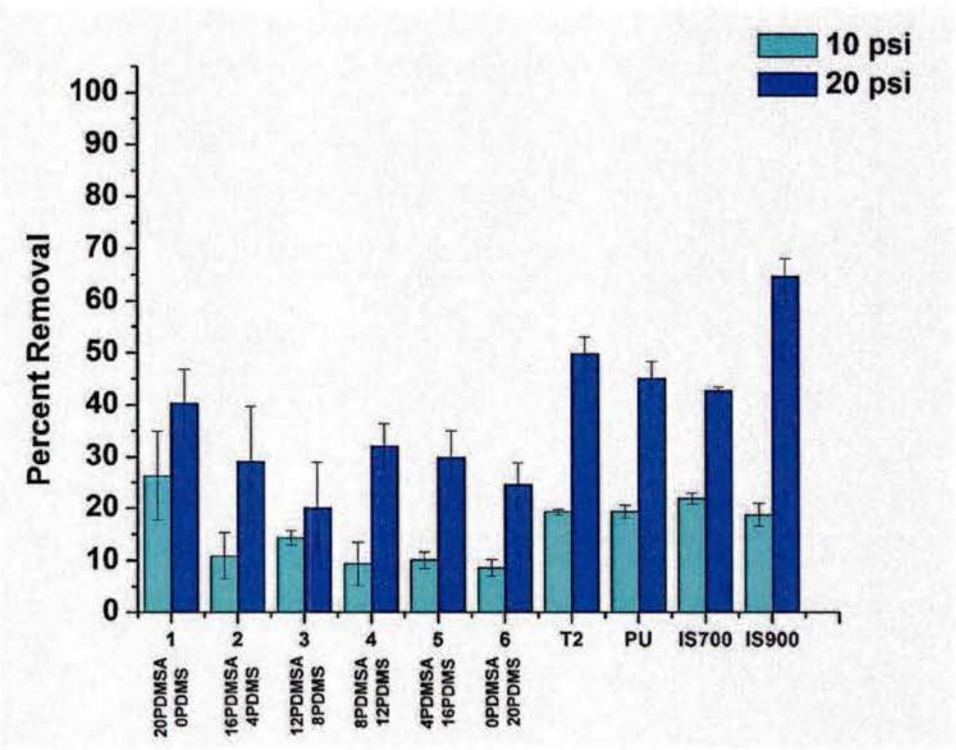


Figure 10: Removal of *N.incerta* microalgae from coatings after water jet treatment at 10 and 20 psi pressures. Each bar represents the average percent removal of 3 replicate measurements.

Barnacles are one of the most common macrofouling organisms costing severe fuel penalties if allowed to accumulate. Previously, the use of COOH functionalized siloxane provided excellent FR properties towards diatoms yet barnacles adhered very strongly to these coatings.[36] Several reattached barnacles broke/damaged during the push off test indicating poor FR properties of coatings with acid functionalized siloxane.[36] Therefore it was hypothesized that reducing the hydrophilic COOH groups on the surface may improve the release of barnacles. In fact the data obtained from 2 week reattachment study for experimental coatings supported this hypothesis (Figure 11). Decrease in APT-PDMS-25A in coating compositions resulted in low barnacle adhesion strength with easy removal of many barnacles with no damage. The coating 1 which contained the highest APT-PDMS-25A content (20% by wt.) showed the highest barnacle adhesion strength and several broken/damaged barnacles signifying the worst barnacle release performance out of all experimental coatings. On the other hand coating 6 without any APT-PDMS-25A showed the lowest barnacle adhesion strength which was comparable to Intersleek® 900 and 700 coatings. All 5 barnacles reattached to the pure polyurethane coating resulted in broken barnacles suggesting that it was a poor FR surface.

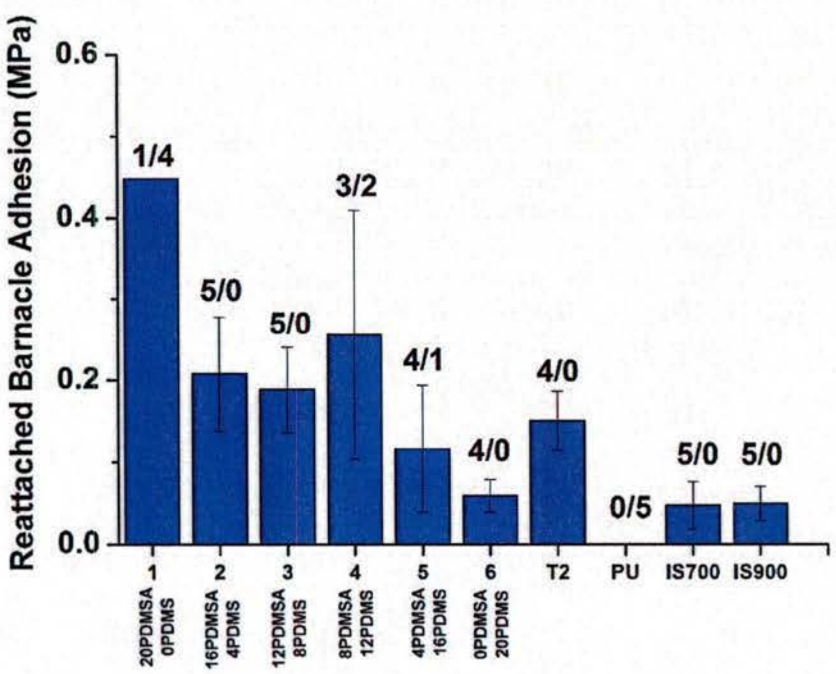


Figure 11: Adhesion strength of reattached barnacles (*A.amphitrite*) for coatings. Five adult barnacle reattachments were attempted for each coating. Each adhesion strength value represent the average of total number of reattached barnacles released without damage. The ratio represent the number of measured barnacles over the number of broken/damaged barnacles.

Figure 12 shows the adhesion strength of marine mussels towards the experimental and standard coatings. Adhesion of marine mussels followed a similar trend that was observed for barnacle adhesion. Coating 1 with the highest level of APT-PDMS-25A had the highest adhesion force. Coatings 5 and 6 with more of the APT-PDMS (16% and 20% by wt. respectively) showed no mussel attachments displaying anti-fouling properties and being similar in performance to Intersleek 900. Coatings 2 and 3 with a blend of APT-PDMS-25A and APT-PDMS showed better FR properties towards mussels compared to standard coatings T2 and PU.

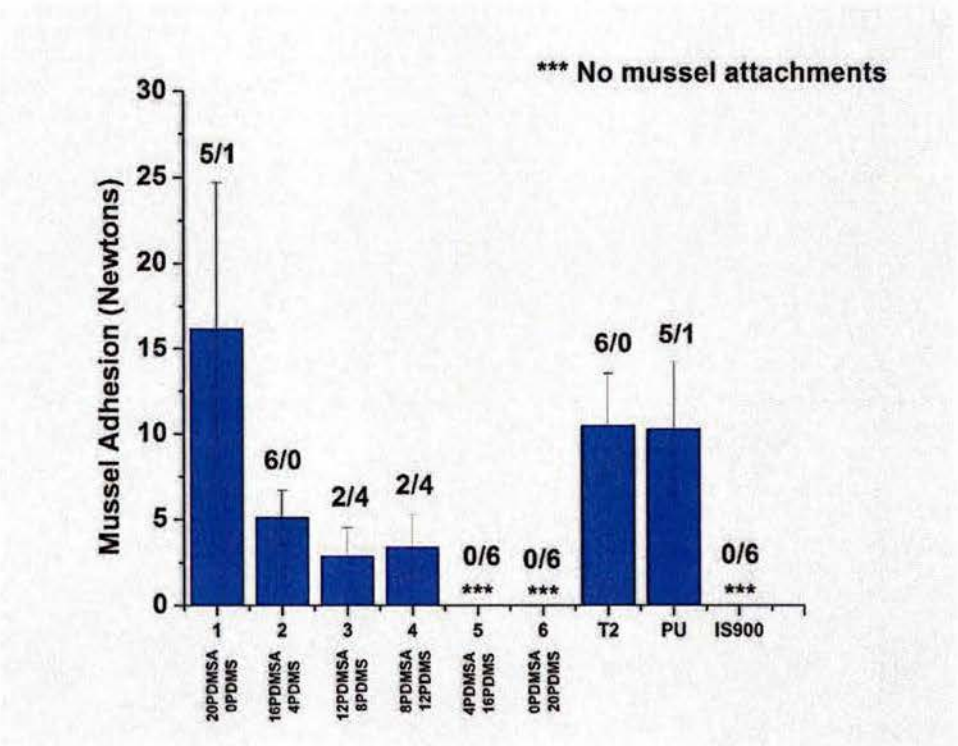


Figure 12: Adhesion of mussel (*G.demissa*) to coatings. Six mussel attachments were attempted for each coating. Each adhesion strength value represent the average of total number of attached mussels released from the surface. The ratio represent the number of attached mussels over the number of non-attached mussels.

Overall, reducing the hydrophilic COOH groups on SiPU coatings have improved the macrofouling-release properties towards barnacles and mussels compared to the previous study. However, the decrease in hydrophilic moieties negatively affected the *N.incerta* FR properties. Coating compositions containing mixtures of APT-PDMS-25A and APT-PDMS provided the best

FR properties towards *U.linza* sporelings compared to coatings with resins individually. Bacterial biofilm removal remained unchanged regardless of changes in coating compositions. Experimental coatings also showed comparable performance to standard coatings in several of the FR laboratory biological assays.

Conclusions

Acid functionalized APT-PDMS-25A resin was successfully synthesized in two steps. First a vinyl functional APT-PDMS-25V copolymer was synthesized through ring opening equilibration of D_4 and D_{4V} monomers at a molar ratio of 3:1. The vinyl groups of APT-PDMS-25V were functionalized with COOH via thiol-ene click reaction. The resulting polymer was used to prepare SiPU coatings. The APT-PDMS-25A resin was blended with APT-PDMS as a way to control the hydrophilic content of coatings. Water contact angle measurements showed an increased hydrophobicity with decreasing content of APT-PDMS-25A in formulations. After water and ASW immersion for 28 days, coatings with high APT-PDMS-25A content displayed decrease in WCAs implying presence of COO^- groups on the surface. Coatings with 20% and 16% APT-PDMS-25A minimized the settlement of *U.linza* spores, yet settled spores adhered strongly resulting in poor release of sporelings. The coating compositions with APT-PDMS-25A and APT-PDMS blends had comparable or better at FR of *U.linza* sporelings as Intersleek 900. Reducing the APT-PDMS-25A resin content lead to impaired FR properties towards diatoms although significantly improved that for barnacles. While this study did not result in the identification of a materials having good FR performance for all of the marine fouling organisms studied, it is clear that the adhesion of the organisms is highly responsive to the chemistry of the surfaces. The amphiphilic approach is still a viable option to find solutions to biofouling. However new coating systems need to be explored using other hydrophilic moieties for broad spectrum FR. Obtaining the optimum hydrophilic/hydrophobic balance suitable for marine fouling applications still remains a challenge.

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Appendix F

Siloxane-polyurethane marine coatings with hydrophilic side chains for fouling release applications.

Introduction

Developing an effective non-toxic coating solution to marine biofouling is a modern day challenge given the number of marine organisms in the oceans and their diverse surface preferences. Constant colonization and accumulation of marine organisms on ocean immersed structures is known as marine biofouling.[1] The magnitude of the economic and environmental costs of biofouling is well recognized and an environmentally friendly solution is being sought after to benefit the global shipping industry.[2-4] Coatings with active tri-butyl-tin (TBT) were very effective against biofouling although they were soon found to be causing detrimental effects to non-targeted marine life.[4] In 2003, use of TBT in marine paints was prohibited by the International Maritime Organization (IMO).[1, 4] Due to the prohibition of tri-butyl-tin (TBT) based antifouling (AF) coatings, copper oxide based AF coatings and fouling-release (FR) coatings gained popularity.[3-5] However, FR coatings have gained market attention as a completely non-toxic and eco-friendly approach to contend with biofouling.

Fouling-release coatings do not release toxins, rather only allowing weak attachment of marine organisms which facilitate easy removal of organisms when subjected to hydrodynamic pressure or light cleaning.[3, 4] Polydimethyl siloxane (PDMS) combines several required material elements for such fouling release applications.[1, 4] Therefore, most commercial FR coating systems are often formulated with PDMS elastomers. Although early versions of PDMS based FR coatings have demonstrated excellent fouling release behavior at higher ship speeds, settlement of fouling during idle periods leads to decrease in performance over time.[6] Also, it is widely accepted that some microfouling organisms settle easily on static surfaces compared to dynamic surfaces.[7] On the other hand, the slime resulting from microfouling is difficult to release even with high hydrodynamic forces given the low surface profile of slime (typically a thin layer).[8-10] However slime fouling can significantly affect fuel consumption due to increased frictional drag. Studies have shown heavy slime can result in 10.1% increase in fuel costs.[11] Recent developments in FR technology has been focused on inhibiting settlement of microfouling organisms during idle periods.

The attachment and settlement of marine animals on surfaces is a significantly dynamic process which involves complex interfacial interactions between the organisms and the surfaces. These interactions involve physico-dynamic events which biologists have attempted to understand, although the exact nature and triggers for such behavior still remains a mystery.[1 12] Recent studies have suggested that the primary interaction of marine organisms with surfaces is through the conditioning layer of adsorbed adhesive proteins and macromoclecules.[13] Therefore, protein resistant materials are being widely explored for non-toxic marine coatings to delay the settlement of fouling specially during idle periods. Polyethylene glycol (PEG) is more commonly investigated for protein resistant materials given its ability to inhibit protein adsorbtion.[14] PEG-modified surfaces display protein resistance properties due to hydrophilic interactions with water.[5] PEG chains on the surface can bind water molecules through hydrogen bonding, creating a highly hydrated water layer minimizing the interfacial surface energy.[15] Studies have shown that water content inside the surface grafted PEG chains can be very high (about 80% by volume).[5] Disrupting the highly organized PEG-water complex is energetically costly for proteins and organic molecules, which is in fact thermodynamically unfavorable.[16, 17] Also, on the other hand, when in contact with water, PEG has an interfacial low surface energy (5 mNm^{-1}) compared to that of PDMS (52 mNm^{-1}) minimizing protein adsorption.[5] Although there is active discussion about the role of PEG in protein resistance, factors such as number of repeat units of ethylene glycol and surface density of PEG have been observed to affect the degree of protein resistance.[5] Self-assembled mono-layers (SAM) containing PEG are commonly explored as protein-resistant materials for biomedical applications.[14 18] Several studies have demonstrated that protein resistant properties of SAMs can be tuned by variations introduced through the PEG component.[7, 19] However, practical application of SAM for marine applications can be an over reach.[20]

Zwitterionic surfaces are also investigated as a potential non-toxic fouling resistant strategy. In contrast to PEG, protein resistant properties of zwitterionic surfaces arise from a very strongly bound electrically induced hydration layer.[3] Therefore, coatings prepared using zwitterionic polymers provide low fouling and FR properties. Zwitterionic coatings are often superhydrophillic, attributing to the tightly and commonly used poly (sulfobetaine) and poly (carboxybetaine) polymers with strong chemical stability.[21, 22] Zwitterionic coatings can also overcome the shortcomings associated with PEG based systems. Several studies have shown that zwitterionic coatings greatly reduce the settlement of marine organisms (*Ulva linza* and barnacles) while demonstrating FR properties towards those organisms.[21-23] Although a commercial product based on this approach is yet to be introduced, current developments show future potential.[24]

Recently developed FR coatings attempted to combine the fouling inhibition and FR properties in order to provide a more effective solution to biofouling and extend the life time of coating systems. Lately, several patent applications has been submitted claiming fouling resistant non-toxic coating compositions; an improvement upon earlier versions of FR coatings in addition to FR properties.[25-27] Also, multiple commercial FR coating products has been introduced to the market. Intersleek 1100SR from International paint and Hempasil X3 from Hempel AF are the newest line of FR coatings that are being promoted as fouling inhibiting/releasing marine coatings.[25] The coating compositions revealed that PDMS still remains as the major ingredient while a surface active PEG modified siloxane or fluoropolymer component is used to enhance the fouling resistance via the formation of a highly hydrated surface.

Siloxane Polyurethane (SiPU) coatings were developed as non-toxic marine coatings having superior mechanical performance and durability compared to commercial FR systems.[28, 29] Previous studies have shown that SiPU coatings can have FR properties on par with commercial standards while not requiring tie coat for adhesion and having a magnitude higher bulk modulus values.[30-32] Also, the system can be tuned for optimum FR application.[23, 32-34] Therefore modifications to the SiPU system with hydrophilic groups were explored as a way to improve the FR properties. In this study, polyisocyanates were modified with sulfobetaine, PEG, and PDMS side chains to be incorporated into SiPU coatings. Commercially available polyisocyanate resins were subjected to modification with hydrophilic groups such as sulfobetaine and PEG. The synthesis of the resins were confirmed by FTIR and isocyanate titrations. The modified resins were then used to prepare pre-polymers with other components and incorporated into SIPU coatings. The coatings had various combinations of side chains; sulfobetaine-PEG, sulfobetaine-PDMS, PEG-PDMS, and just PEG. Non-reactive ethylene oxide functionalized siloxane additives were also used in small quantities in coating formulations. Coating surfaces were characterized using water contact angle (WCA) measurements. The effects of these side groups and hydrophilic additives on fouling release properties were investigated through a number of laboratory biological assays for bacteria (*Cellulophaga lytica*), microalgae (*Navicula incerta*), barnacles (*Amphibalanus amphitrite*) and marine mussels (*Geukensia demissa*)

Experimental

Materials

Polyisocyanates Bayhydur 304 and Desmodur Z4470 BA were provided by Covestro LLC. Monofunctional carbinol terminated polydimethyl siloxane (PDMS) (MCR-C18: 5000MW, $PDMS_{5k}$), difunctional carbinol terminated PDMS (DMS-C23: 10000MW, and DMS-C21: 5000MW) as well as PEG modified siloxane (non-reactive) hydrophilic additives (DBE-821: 4400MW with 80-85% ethylene oxide and DBE-621: 2500MW with 50-55% ethylene oxide) were purchased from Gelest Inc. Polyethylene glycol methyl ether (PEG_{16}: 750MW and PEG_8: 350MW), polyethylene glycol (PEG_{13}: 600MW) and dimethylformamide (DMF), toluene, acetylacetone, dibutyl-tin diacetate (DBTDAc prepared as 1% by wt. in 2-heptanone) were purchased from Sigma

Aldrich. An acrylic polyol composed of 80% butyl acrylate and 20% 2-hydroxyethyl acrylate was synthesized via conventional free radical polymerization and diluted to 50% with toluene. Aminopropyl terminated polydimethyl siloxane (APT-PDMS) with molecular weight 20000g/mole was also synthesized at NDSU through a ring-opening equilibration reaction. Detailed descriptions of synthesis procedures for both acrylic polyol and APT-PDMS can be found elsewhere.[33]

AkzoNobel International Paint provided the commercial FR standards Intersleek® 700 (IS 700), Intersleek® 900 (IS 900), Intersleek® 1100 (IS 1100) commercial FR coatings and Intergard 264 marine primer. Hempasil® X3 commercial FR coating was provided by Hempel. Silicone elastomer, Silastic® T2 (T2) was provided by Dow Corning. Aluminum panels (4 x 8 in., 0.6 mm thick, type A, alloy 3003 H14) purchased from Q-lab were sand blasted and primed with Intergard 264 using air-assisted spray application. Multi-well plates were modified using circular disks (1 inch diameter) of primed aluminum.

Synthesis of sulfobetaine modified monofunctional poly (ethylene oxide) methyl ether containing polyisocyanate (SB-BAY-304)

Polyisocyanate Bayhydur 304 is based on hexmethylene diamine (HDI) and modified with emulsifying PEG chain. This resin was further modified to contain sulfobetaine functionality (4:1 equivalence of NCO to hydroxyl). Bayhydur 304 (28.03 g), toluene (28.00 g), and N,N'-dimethylethanolamine (2.72 g) were combined in a 250 mL 3-neck round bottom flask equipped with mechanical stirring, N2 inlet, and thermocouple. The reaction mixture was heated to 40°C using a heating mantle. The DBTDAc catalyst solution (0.57 g) was added once the reaction mixture reached the set temperature. The reaction was allowed to equilibrate for 24 hrs. Next day reaction mixture was further diluted with toluene (40.01 g) and 1,3-propanesultone (3.74 g) was added. The reaction was carried out for another 24 hrs at 40°C. The presence of sulfobetaine groups were confirmed by FTIR analysis. Also, the isocyanate content of the modified resin was determined post reaction.

Synthesis of sulfobetaine modified isophone diisocyanate based polyisocyanate (SB-IPDI)

Isophorone diisocyanate-based polyisocyanate (Desmodur Z4470 BA) (38.54 g) was combined with toluene (17.72 g), and N,N'-dimethylethanolamine (2.38 g) were combined in a 100 mL 3-neck round bottom flask equipped with mechanical stirring, N_2 inlet, and thermocouple. The reaction mixture was heated to 40°C using a heating mantle. Once the set temperature was reached, DBTDAc catalyst solution (0.44 g) was added and allowed the reaction to equilibrate for 24 hrs. Next day, 1,3-propanesultone (3.21 g) was added. The reaction was carried out for another 24 hrs at 40°C. During the reaction, NCO to hydroxyl equivalent ratio was maintained at 3:1. Post functionalization the presence of sulfobetaine groups were confirmed by FTIR and isocyanate titrations.

Synthesis of poly (ethylene oxide) modified isophone diisocyanate based polyisocyanate (PEG-IPDI)

Desmodur Z4470 BA resin was modified with PEG chains. In a 40 mL glass vial, Desmodur Z4470 BA (20.56 g), PEG 350 (4.94 g) and DBTDAc catalyst solution (0.16 g) were combined (3:1 NCO to hydroxyl equivalents). The vial was purged with N2 and allowed to react overnight at 35 °C under mechanical stirring. The functionalization was confirmed by FTIR analysis and isocyanate titrations.

Isocyanate Titrations

Isocyanate titration was used to confirm the presence of NCO groups after the pre-polymer synthesis. In general, a sample of pre-polymer (0.3-0.5g) was placed in Erlenmeyer flask and diluted with isopropanol. Then, 25mL of 0.1N dibutyl amine solution was added to the flask followed by additional isopropanol (25 mL). Next, the solution was mixed for 15 mins. A few drops of bromophenyl blue indicator were added and titrated using a standardized 0.1N hydrochloric acid solution until the end point of blue to yellow. A blank prepared only with 25 mL of dibutyl amine solution was also titrated using the same acid solution and then the % NCO of the pre-polymer was determined.

Characterization

Fourier Transform Infrared (FTIR) spectroscopy was used to characterize the modified polyisocyanate resins using a Thermo Scientific Nicolet 8700 FTIR instrument. The resin sample was spread on a potassium bromide (KBr) plate as a thin film prior to obtaining the spectrum. Non-volatile content of resins were determined following the ASTM D2369 standard.

Synthesis of Pre-polymers Part 1

First part of the pre-polymers were prepared using the components outlined in Table 1. A general synthesis procedure is described here. Modified isocyanate resin was diluted with 0.5 g of DMF and combined with monofunctional PEG and/or PDMS component in a 40mL vial equipped with a magnetic stir bar. The first part of the pre-polymer synthesis was catalyzed with 0.02g of the DBTDAc solution and the content was thoroughly mixed using a vortex mixer for 5 min followed by magnetic stirring for 24 hrs.

Synthesis of Pre-polymers Part 2

Formulation components for part 2 were directly added to appropriate formulation from part 1. First, the modified IPDI based isocyanate component was added to the vial followed by the difunctional PEG 600 and PDMS (DMS-C23 or DMS-C21) components. Small amount of catalyst solution (0.05g) was also added to the mixture. Then the content was mixed using the vortex for 5 min and allowed to mix overnight on a magnetic stir plate.

Table 1: Pre-polymer compositions

Pre-polymer	Part 1					Part 2				
	SB-BAY 304 (g)	**BAY-304 (g)**	**DMF (g)**	**PEG$_{16}$ (g)**	**PDMS$_{5k}$ (g)**	**PEG$_{13}$ (g)**	**DMS-C23 (g)**	**DMS-C21 (g)**	**SB-IPDI (g)**	**PEG-IPDI (g)**
1	5.49	-	0.51	1.21	-	0.82	2.04	-	3.43	-
2	2.04	-	0.50	-	3.00	0.82	-	1.20	5.91	-
3	-	3.51	0.51	1.86	-	0.82	2.02	-	-	4.70
4	-	0.90	0.50	1.21	1.81	0.82	-	1.22	-	4.18
5	5.51	-	0.51	1.26	-	0.80	2.01	-	3.40	-
6	2.09	-	0.51	-	3.00	0.81	-	1.21	5.93	-
7	-	3.48	0.51	1.87	-	0.81	2.02	-	-	4.73
8	-	0.92	0.51	1.29	1.81	0.82	-	1.20	-	4.15
9	2.06	-	0.51	-	3.01	-	-	-	-	-
10	1.82	-	0.50	1.21	1.80	-	-	-	-	-
11	2.07	-	0.51	-	3.00	-	-	-	-	-
12	-	1.80	0.50	1.21	1.80	-	-	-	-	-

Coating formulation

Coating formulations were prepared by adding acrylic polyol, additional polyisocyanate (Desmodur Z4470 BA), hydrophilic additive, catalyst solution, and pot-life extender into a vial containing the pre-polymer (Table 2). Then, the contents were thoroughly mixed using the vortex for 5 min and allowed to mix for 1 hr by magnetic stirring. After mixing, coating formulations were deposited into multi-well plates using an automatic repeat pipette (250 µL of formulation was deposited into each well in multi-well plate). Drawdowns were made on primed 8"×4" aluminum panels using a wire-wound drawdown bar with a wet film thickness of 80µm. All coatings were allowed to cure under ambient conditions for 24 hrs followed by oven curing at 80 °C for 45 min.

Table 2: Bulk coating formulation compositions.

Coatings	Acrylic Polyol (g)	Desmodur Z4470 BA (g)	DBE-821 (g)	DBE-621 (g)	DBTDAc in MAK (g)	Pot-life extender (g)
1	16.03	5.90	1.03	-	0.03	0.05
2	14.57	5.21	1.00	-	0.03	0.05
3	15.18	5.50	1.02	-	0.03	0.05
4	14.61	5.16	1.01	-	0.03	0.05
5	16.03	5.91	0.51	0.52	0.03	0.05
6	14.58	5.24	0.52	0.50	0.03	0.05
7	15.20	5.55	0.50	0.51	0.03	0.05
8	14.54	5.16	0.52	0.52	0.03	0.05
9	20.02	8.64	1.01	-	0.05	0.06
10	20.65	6.68	1.01	-	0.05	0.06
11	20.02	8.66	0.51	0.51	0.05	0.06
12	20.67	6.67	0.51	0.51	0.05	0.06

Control and Standard Coatings

Commercial standards were prepared following manufacturer's specifications. Control A4-20 was prepared following the procedure outlined in a previous study.[33] Similar to experimental coatings all control and standards were also prepared on 8" x 4" primed aluminum panels and multi-well plates. Table 3 contains detailed descriptions of the control and standard coatings used for this study.

Table 3: List of control and standard coatings used in the study

Coating	Name	Description
13	A4-20%	Internal Siloxane-PU FR Control
14	Hempasil X3	Silicone Hydrogel based Commercial FR Standard
15	NDSU-PU	Pure Polyurethane Standard
16	Dow T2	Silicone Elastomer Standard
17	IS 700	Intersleek Commercial FR Standard
18	IS 900	Intersleek Commercial FR Standard
19	IS 1100	Intersleek Commercial FR Standard

Water contact angle measurements

All experimental coatings were characterized using water contact angles (WCA) using the Symyx® surface energy system prior to water aging. The WCAs of coatings were obtained at 0, 2, 4, 6, 8, and 10min time intervals. Three measurements of WCA were obtained using First Ten Angstroms™ software. Then average WCA for each time was recorded with standard deviation of the mean. Similarly, WCAs of control A4-20 and commercial standards IS 900 and Hempasil X3 were measured.

Water Aging

All the coatings were pre-leached for 28 days in running tap water. Coated multi-well plates and panels were placed in a tap-water aquarium system equipped with automated filling/emptying capability where the tank water was emptied and refilled every 4 hours.

Biological Laboratory Assays

Bacterial (*Cellulophaga lytica*) Biofilm Adhesion

Fouling-release properties towards bacteria was evaluated using retention and adhesion assays described previously.[35] [36] [37] A suspension consisting of the marine bacterium *Cellulophaga lytica* at 10^7 cells/mL concentration in ASW containing 0.5 g/L peptone and 0.1g/L yeast extract was deposited in to 24-well plates (1 mL/well). The plates were then incubated statically at 28°C for 24 hours. The ASW growth medium was then removed and the coatings were subjected to water-jet treatments. The first column of each coating (3 replicate wells) was not treated and served as the initial amount of bacterial biofilm growth. The second column (3 replicate wells) was subjected to water-jetting at 10 psi for 5 seconds. Following water-jet treatments, the coating surfaces were stained with 0.5 mL of a crystal violet solution (0.3 wt. % in deionized water) for 15 minutes and then rinsed three times with deionized water. After 1 hour of drying at ambient laboratory conditions, the crystal violet dye was extracted from the coating surfaces by adding 0.5 mL of

33% acetic acid solution for 15 minutes. The resulting eluates were transferred to a 96-well plate (0.15 mL/coating replicate) and subjected to absorbance measurements at 600nm wavelength using a multi-well plate spectrophotometer. The absorbance values were considered to be directly proportional to the amount of bacterial biofilm present on coating surfaces before and after water-jetting treatments. Percent removal of bacterial biofilm was quantified by comparing the mean absorbance values of the non-jetted and water-jetted coating surfaces.[38]

Growth and Release of Microalgae (*Navicula incerta*)

Laboratory biological assay to evaluate FR properties of coatings towards diatom (*Navicula incerta*) was conducted at NDSU following a similar procedure described previously.[39] [36] Briefly, a suspension with 4×10^5 cells/mL of *N. incerta* (adjusted to 0.03 OD at absorbance 660 nm) in Guillard's F/2 medium was deposited into each well (1 mL per well) and cell attachment was stimulated by static incubation for 2 hours under ambient conditions in the dark. Coating surfaces were then subjected to water-jet treatments.[35] First column of wells (3 wells) were not water-jetted so that initial cell attachment could be determined and the next column of wells (3 wells) were water-jetted at 20 psi for 10 seconds. Microalgae biomass was quantified by extracting chlorophyll using 0.5 mL of DMSO and measuring fluorescence of the transferred extracts at an excitation wavelength of 360 nm and emission wavelength at 670 nm. The relative fluorescence (RFU) measured from the extracts was considered to be directly proportional to the biomass remaining on the coating surfaces after water-jetting. Percent removal of attached microalgae was determined using relative fluorescence of non-jetted and water-jetted wells.

Adult Barnacle (*Amphibalanus amphitrite*) Adhesion

An adult barnacle reattachment and adhesion assay was used to evaluate the fouling-release properties of the coatings towards macrofoulers.[40] [41] Coatings prepared on 8 x 4" panels after water aging were utilized for this laboratory assay. Barnacles were dislodged from silicone substrates sent from Duke University and immobilized on experimental coatings (6 barnacles per coating) using a custom-designed immobilization template. The immobilized barnacles were allowed to reattach and grow for 2 weeks while immersed in an ASW aquarium tank system with daily feedings of brine shrimp *Artemia* nauplii (Florida Aqua Farms). After the 2 week attachment period, the number of non-attached barnacles was recorded and the attached barnacles were pushed off (in shear) using a hand-held force gauge mounted onto a semi-automated stage. Once the barnacles were dislodged, their basal plate areas were determined from scanned images using Sigma Scan Pro 5.0 software program. Barnacle adhesion strength (MPa) was calculated by taking the ratio of peak force of removal to the basal plate area for each reattached barnacle. The average barnacle adhesion strength for each coating was reported as a function of the number of barnacles released with a measureable force and that exhibited no visible damage to the basis or shell plates.

Mussel (*Geukensia demissa*) Adhesion

Slightly modified version of previously published protocol was used to evaluate adhesion of marine mussels to coatings in a laboratory assay.[42] [43] [44] Marine ribbed mussels (*Geukensia demissa*; 3-5 cm length) were received from Duke University Marine Laboratory in Beaufort, North Carolina, USA. Prior to the attachment study, each mussel was modified with a 4 cm long acetal plastic rod (product# 98873A105, McMaster-Carr) (perpendicular to the ventral edge) glued to the it using a 3M® acrylic adhesive (product# 7467A135, McMaster-Carr). Six mussels were then immobilized on to each coating surface using a custom-designed template fabricated from PVC sheets. The coatings with immobilized mussels were then placed in an ASW aquarium system and fed daily with live marine phytoplankton (DTs Premium Reef Blend Phytoplankton) for 3 days. After 3 days, the coatings were removed from the ASW aquarium tank system and the total number of mussels exhibiting attachment of byssus threads was recorded for each coating. The plastic rod glued to each attached mussel was then affixed to individual 5 Newton load cells of a custom-built tensile force gauge where all mussels were pulled off simultaneously (1 mm s^{-1} pull rate). The total force (Newton) required to completely detach all byssus threads for each mussel was recorded and the mean value of the total number of attached mussels for each coating was calculated.

Results and Discussion

In this study, polyisocyanates were modified with sulfobetaine, PEG, and PDMS side chains to be incorporated into SiPU coatings. Commercially available polyisocyanate resins were subjected to modification and successful modification was confirmed by FTIR and isocyanate titrations. The coatings had various combinations of side chains; sulfobetaine-PEG, sulfobetaine-PDMS, PEG-PDMS, and just PEG. The effects of these side group on fouling release properties were investigated through a number of laboratory biological assays.

Modifying polyisocyanates to have sulfobetaine functional groups is carried out by sequential reactions. Figure 1 shows the reaction scheme for functionalization. First, the isocyanate groups (1 equivalent) were reacted with N,N'-dimethylethanolamine catalyzed by DBTDAc at slightly elevated temperature. Then, after 24 hrs, 1,3-propanesultone was added. Tertiary amine from the N,N'-dimethylethanolamine readily reacts with 1,3-propanesultone to form sulfobetaine group (common synthesis route used for obtaining sulfobetaine group). Since the sulfobetaine groups are highly polar resins, they need to be diluted with solvents to achieve workable viscosity. Sulfobetaine modified polyisocyanates of Bayhydur 304 and Desmodur Z4470 BA were prepared for this study. They are denoted as SB-BAY 304 and SB-IPDI. Another derivative resin from Desmodur Z4470 BA was synthesized using short chain PEG to be used in coating formulations (IPDI-PEG). Polyethylene glycol methyl ether with Mn=350 was reacted with IPDI trimer with the presence of DBTDAc maintaining a NCO:OH equivalent ratio of 3:1.

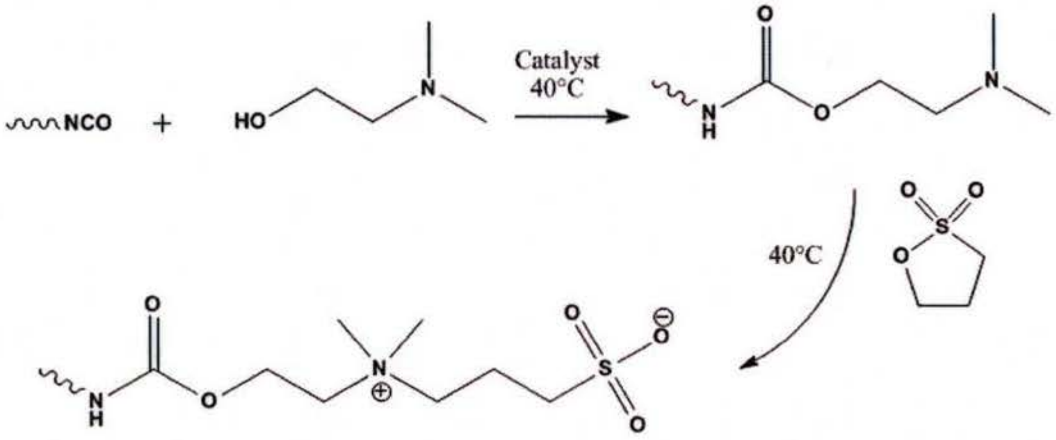

Figure 1: Sulfobetaine functionalization of polyisocyanates

Table 4 shows the experimentally determined isocyanate content of the modified polyisocyanate resins. The modified isocyanate resins should have the majority of isocyanate groups intact after functionalization which will be used for crosslinking later. Isocyanate titration method was used to confirm the presence of remaining NCO groups. Following modification with sulfobetaine and PEG, polyisocyanate resins displayed isocyanate values that were closely to that of theoretical. This indicates that the modifications to polyisocyanate resins were successful and that they can be used for coating formulation.

Table 4: Comparison of percent isocyanate of modified polyisocyanates

Modified Polyisocyanate Resin	Percent solid (%)	Theoretical %NCO	Experimental % NCO
SB-BAY 304	34.2	10.15	9.91±0.05
SB-IPDI	55.2	9.41	8.92±0.25
PEG-IPDI	74.2	7.95	7.12±0.04

Figure 2 shows the FTIR spectra of the modified polyisocyanate resins. For all three modified polyisocyanates, the peak at 2270 cm^{-1} indicated the remaining isocyanate which was later used for crosslinking reactions. The peak at 3200-3400 cm^{-1} indicated the presence of the -N-H stretching from the carbamate group. However the -N-H stretching was more prominent on PEG-

IPDI compared to sulfobetaine modified resins. All three resins show the carbamate carbonyl (-C=O') around 1696 cm^{-1} indicating the successful reaction of corresponding side chains. The other carbonyl (-C=O*) arise from the PEG-urethane linkage. The presence of the ether group (-C-O-C-) was evident from the peak at 1210 cm^{-1} and the ether peak was strong on the IPDI-PEG compared to sulfobetaine modified resins. Bayhydur 304 polyisocyanate has some PEG modification thus explaining the presence of the small ether peak at 1210 cm^{-1}. The peaks at 1193 cm-1 and 1044 cm-1 are indicative of -S=O groups and suggest successful modification of polyisocyanate resins with sulfobetaine.

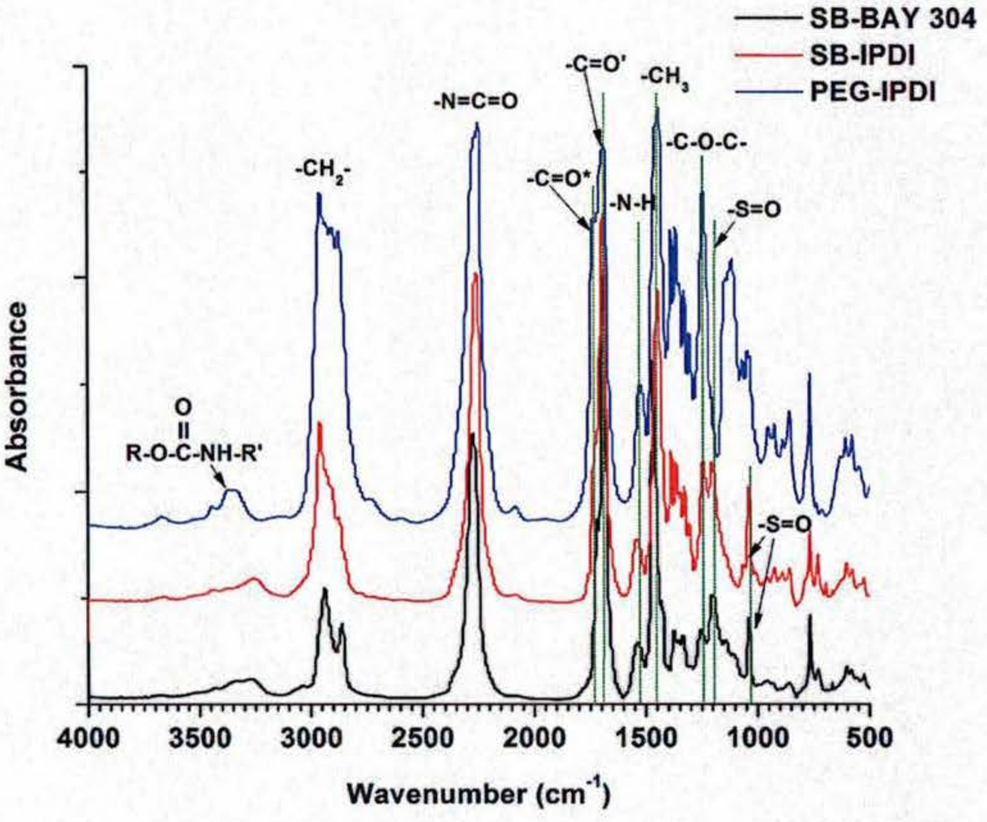

Figure 2: FTIR spectrum of modified polyisocyanate resins SB-BAY 304, SB-IPDI, and PEG-IPDI.

Coating formulation consists of 3 distinct stages. First the polyisocyanate resins were reacted with PEG$_{16}$ (750 MW) or PDMS$_{5k}$ (5000 MW) side chains. A representative structure for pre-polymer from Part 1 is shown in Figure 3. Remaining NCO groups are indicated by X and the possible side chain modifications are indicated by Y. Formulation 1 and 2 are based on SB-BAY 304 resin, difference being 1 having PEG_{16} and 2 having $PDMS_{5k}$ (Y from Figure 3 can be sulfobetaine and PEG_{16} or sulfobetaine and $PDMS_{5k}$). Formulation 3 and 4 are based on unmodified Bayhydur 304 with PEG_{16} and $PDMS_{5k}$ side chains respectively (Y from Figure 3 can be exclusively PEG_{16} or a combination of PEG_{16} and $PDMS_{5k}$). After the first step, additional difunctional PEG_{13}, PDMS (DMS-C21 or DMS-C23) were added along with modified IPDI polyisocyanate (SB-IPDI or PEG-IPDI). Finally, the formulations were completed with the addition of acrylic polyol, additional isocyanate, pot-life extender, catalyst and non-reactive hydrophilic additive (DBE-821). The formulations 5-8 consists of the same composition except a combination of non-reactive hydrophilic additives was used (DBE-821 and DBE-621). Formulation 9, 10, 11 and 12 only consist of part 1 for pre-polymer preparation. Pre-polymer for formulation 9 and 10 were based on SB-BAY 304. While formulation 9 was with sulfobetaine and $PDMS_{5k}$ side chains, formulation 10 additionally contained PEG_{16} side chains as well (F9, Y could be sulfobetaine and $PDMS_{5k}$, for F10, Y could be sulfobetaine, $PDMS_{5k}$ and PEG_{16}). Coatings 11 and 12 consisted of the same pre-polymer as in 9 and 10 respectively yet had a combination of the non-reactive hydrophilic additive.

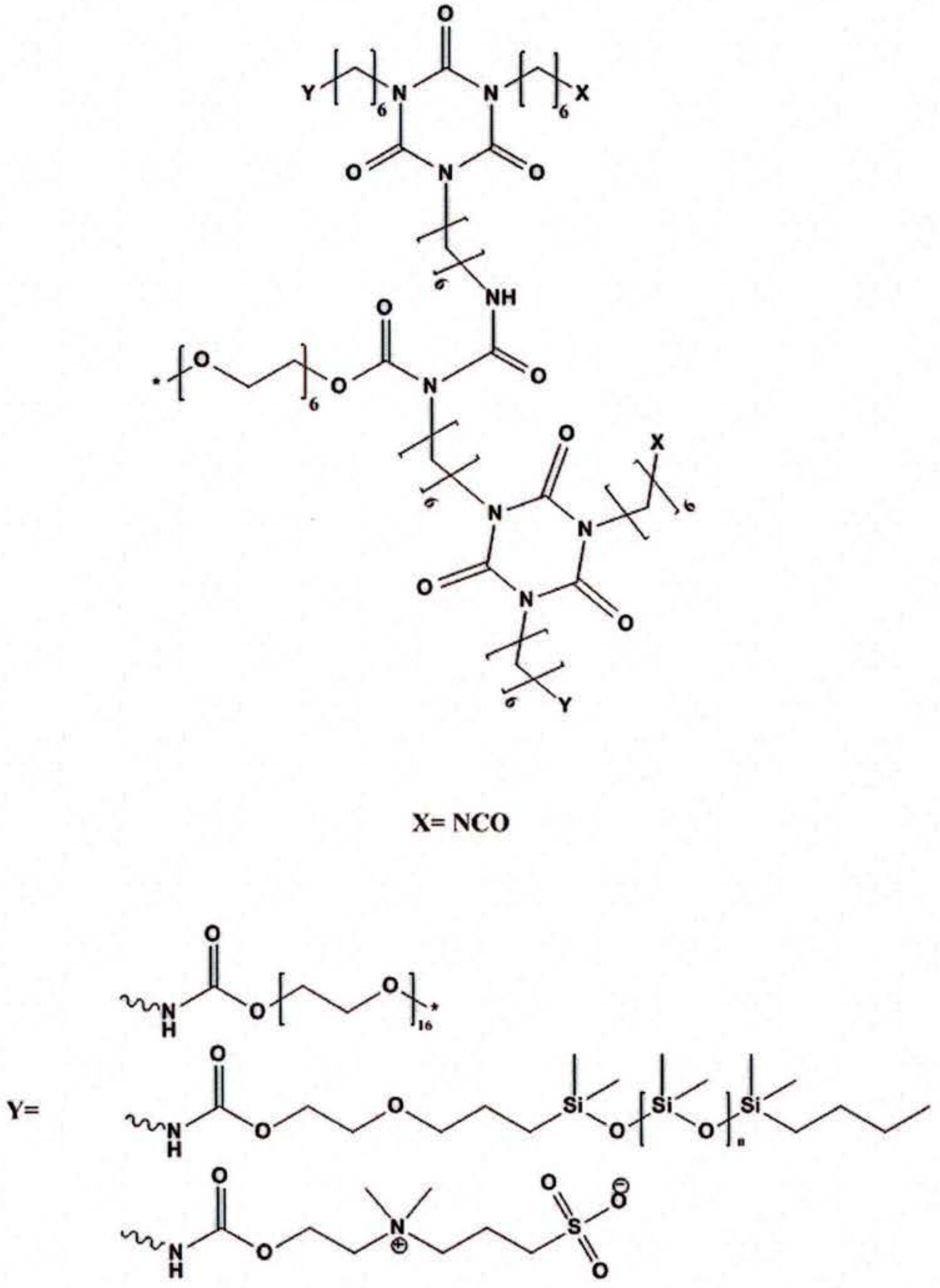

Figure 3: General representative structure for pre-polymers (part 1)

Figure 4 shows the water contact angle measurements of the coatings taken every two minutes over a period of ten minutes. Several of the coatings prepared for this study displayed a change in WCA over time. Almost all experimental coatings showed a change in WCA from hydrophobic to hydrophilic whereas some changed more than others. In general all the experimental coatings showed WCA of equal or less than 100° initially. Coating 1 (with sulfobetaine-PEG side chains) displayed a higher drop in WCA at each time interval compared to Coating 2 (with sulfobetaine-PDMS side chains). Coating 3 (PEG side chains) showed a more gradual decrease in WCA while coating 4 (PEG-PDMS side chains) showed a significant drop in WCA initially and very little change over time. Coatings 5-8 displayed lower WCA angles than that of coatings 1-4. The WCAs for coatings 5-8 suggest that the surfaces were more hydrophilic compared to those of coatings 1-4. After 10 min coating 5, 7, and 8 show WCA in 35-40° range. Since coatings 5-8 were made using the same pre-polymers used in coatings 1-4, the observed difference in WCA may be attributed due to the addition of the non-reactive hydrophilic additive DBE-621. Coatings 9-12 also showed decreasing WCA with time, yet having a combination of multiple hydrophilic additives vs. a single hydrophilic additive did not affect the WCAs of the coatings significantly. Commercial standards Hempasil X3 and IS 900 also demonstrated decreasing WCAs, a trend comparable to that observed for several experimental coatings. However, IS 900 was relatively hydrophilic to begin with compared to Hempasil X3. Results suggest that during WCA experiment, coatings 1, 2, 3, and 6 behaved similarly to Hempasil X3 while coatings 5, 7, 8, 10 and 12 behaved similarly to IS 900. This rapid change in surface wettability has not been observed for SiPU coating systems previously. In fact, the A4-20 control did not show much change in WCA with time. This new feature may influence the FR properties of SiPU coatings. However, further characterization of surface morphology is needed to identify the underlying principle for rapid surface wettability change in coatings. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) may provide in depth details of the coating surface compositions.

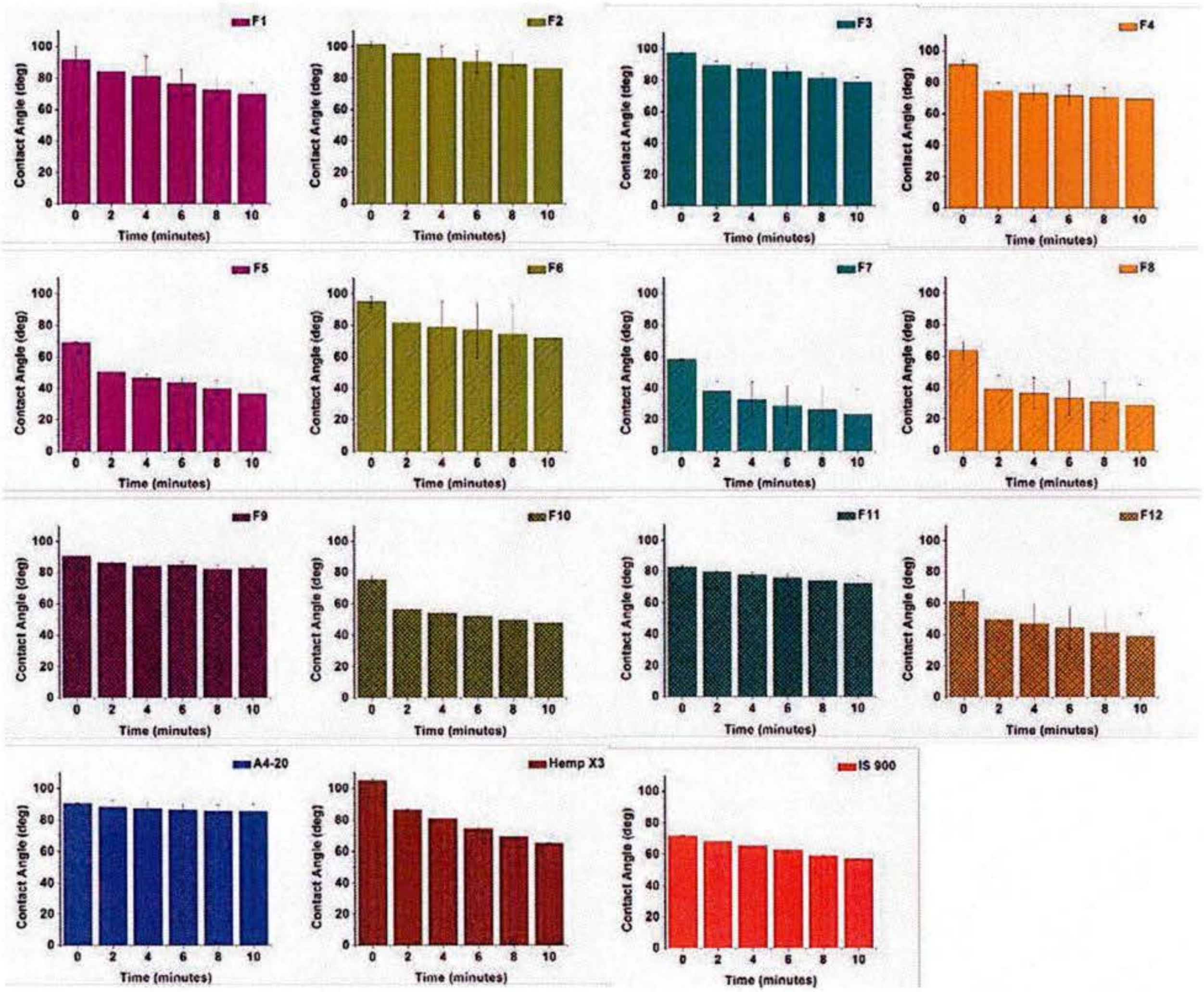

Figure 4: Water contact angles for coatings observed over 0, 2, 4, 6, 8, and 10 min. Each bar represents the average of 3 replicate measurements and the error bars represent the standard deviation of the mean.

Fouling release properties of coatings were evaluated using the *C.lytica* bacterial biofilm growth and removal assay. Figure 5 shows the amount of biomass on coatings before and after water jet treatment. The absorbance of crystal violet at 600nm is directly proportional to the biomass present on the coating surface. Many experimental coatings showed bacterial biofilm growth similar to silicone standard T2 and commercial FR standard IS 1100. However coatings 9, 11, and 12 showed slightly lower biomass compared to other experimental coatings and the amount of biofilm growth was similar to that of Hempasil X3 FR standard. All experimental coatings show very little bacterial biofilm remaining after a 20 psi water jet treatment, suggesting excellent FR properties. More specifically, coatings 4, 8, and 12 showed almost complete removal of *C.lytica* biofilm just like Hempasil X3. Interestingly, coatings 4, 8 and 12 contained the pre-polymers with high amount of PEG_{16} and $PDMS_{5k}$ side chains. It was noticed that IS 900 only allowed very little biofilm growth (IS 900 had some toxicity during the leachate toxicity assay). Figure 6 presents the removal of bacterial biofilm from the coatings. Coatings 3, 4, 8, 10, 11, and 12 released more than 90% of the *C.lytica* biofilm grown on the surface; an improvement compared to the internal control SiPU coating (A4-20). All experimental coatings outperformed standards IS 700, T2 and PU. Coatings with sulfobetaine side chains (1, 2, 5, and 6) demonstrated similar biofilm removal compared to IS 1100 yet not quite good as IS 900 and Hempasil X3 standards. Coatings 4, 8, and 12 showed the best FR performance towards *C.lytica* (≈100% biofilm removal) which was on par with commercial FR standards HempasilX3 and IS 900.

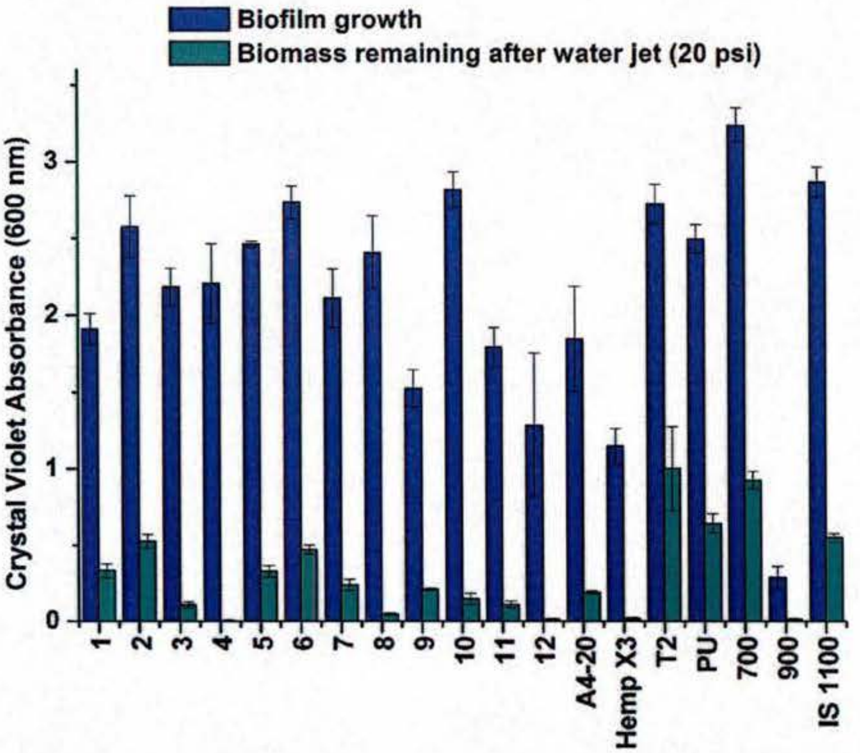

Figure 5: Bacterial biofilm (*C.lytica*) growth and retention after water-jet treatment at 20 psi pressure. Each bar represents the average of 3 replicate measurements and the error bars represent the standard deviation of the mean.

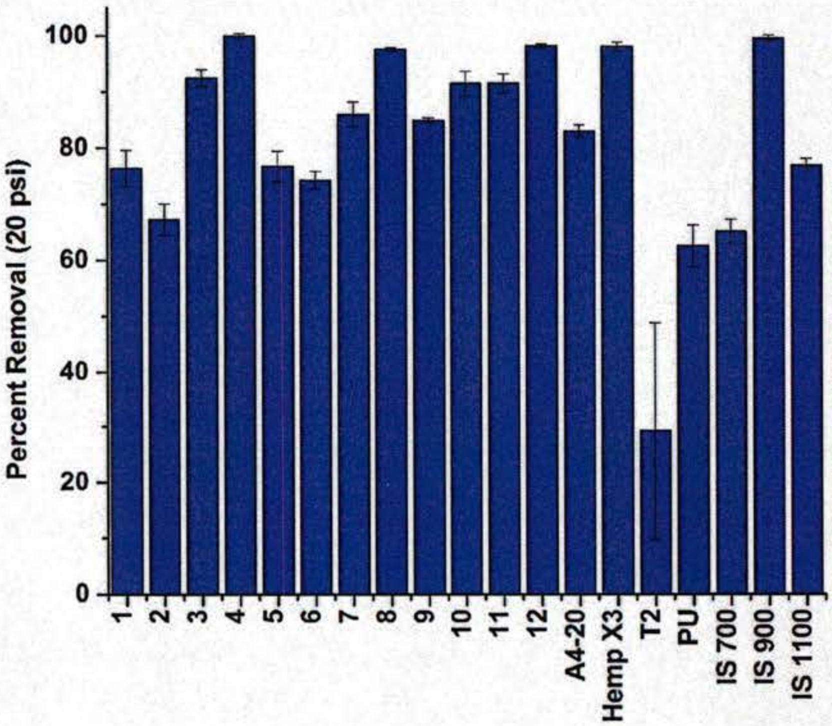

Figure 6: Removal of *C.lytica* biofilm from coatings. Each bar represents the average of 3 replicate measurements and the error bars represent the standard deviation of the mean.

Diatoms are microalgae that contribute to forming slime. When settled *N.incerta* is difficult to release from hydrophobic surfaces attributed to their adhesion preference behavior. [7 45] Previous studies have shown that the SiPU system had relatively poor FR performance towards diatoms given the hydrophobic surface characteristics. However, recent approaches to prepare amphiphilic coating may have helped to improve the FR of SiPU coatings towards diatoms. All experimental coatings showed lower *N.incerta* cell attachment compared to A4-20, T2, PU and IS 1100 (Figure 7). Coatings 10, 12, Hempasil X3, and IS 900 displayed very low diatom cell attachment. After water jet treatment at 20 psi, several experimental coatings (5, 9, 10, 11, and 12) showed low biomass remaining which was comparable to that of commercial standards IS 1100, Hempasil X3, and IS 900. Diatom removal is shown in Figure 8. Coatings with pre-polymer modified with difunctional components did not show efficient diatom removal as suggested by the presence of high biomass reaming after water jet (low removal). However coatings with pre-polymers modified with just monofunctional components (9, 10, 11, and 12) displayed the best FR performance towards diatoms which was on par with leading commercial FR standards Hempasil X3, IS 900, and IS 1100. They also showed much better diatom removal compared to the A4-20 internal standard. Although it is necessary to confirm using surface analysis techniques, observed trend in diatom removal suggests that the pre-polymers modified with monofunctional components may allow better surface expression of functional groups compared to those with both mono and difunctional components. Also using a combination of hydrophilic additives helped to achieve slight improvement in FR properties of coatings rather than using just DBE-821.

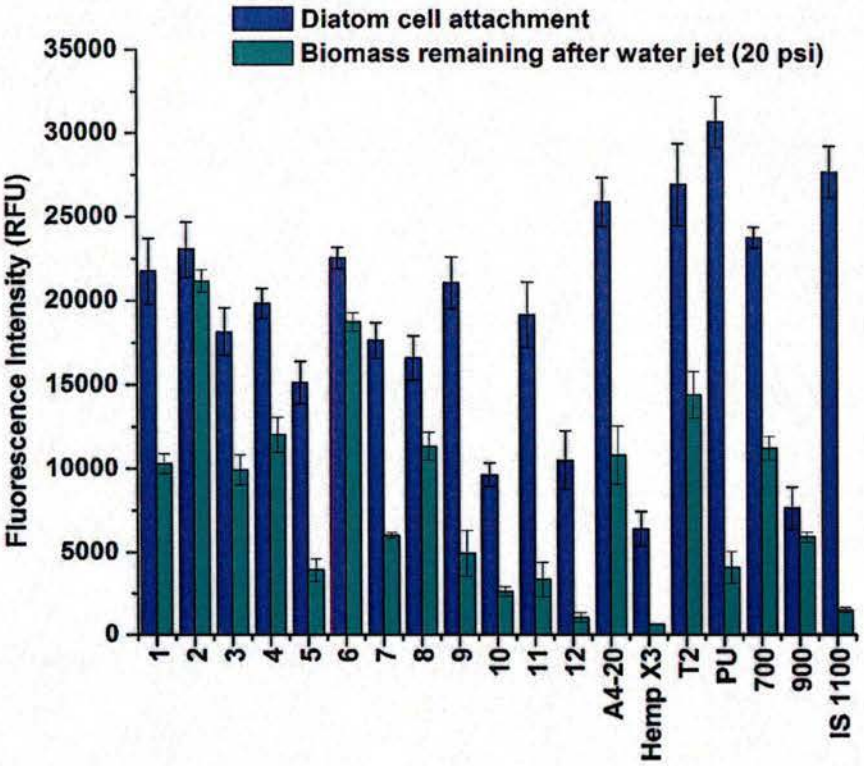

Figure 7: Microalgae (*N.incerta*) cell attachment and retention (i.e., biomass remaining) after water-jet treatment at 20 psi pressure. Each bar represents the average of 3 replicate measurements along with standard deviation.

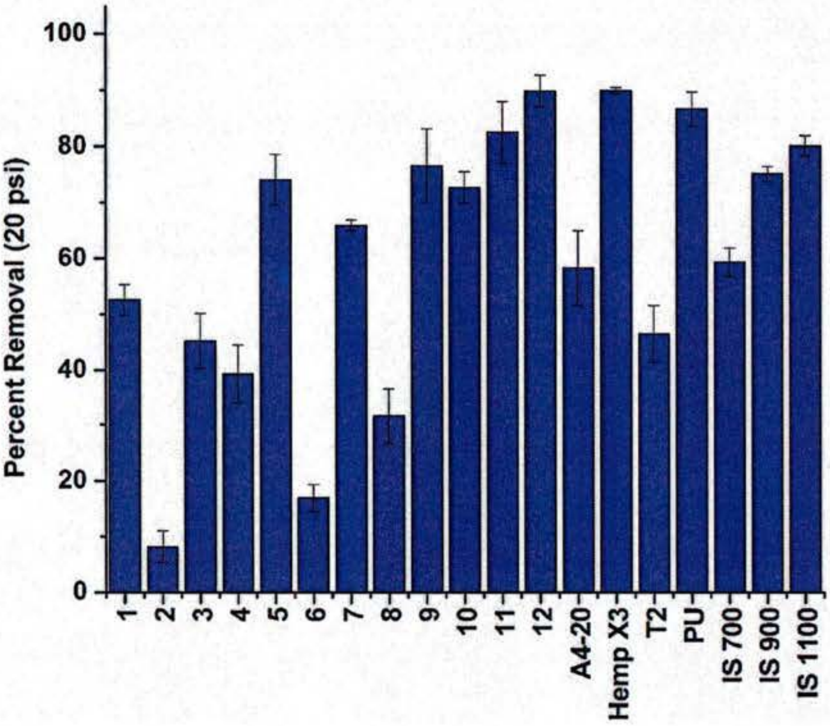

Figure 8: Removal of diatom (*N.incerta*) from coatings. Each bar represents the average of 3 replicate measurements and the error bars represent the standard deviation of the mean.

Macrofouling organisms such as barnacles contribute to heavy calcareous fouling on ship hulls leading to a significant increase in frictional drag, impairing fuel efficiency.[9] Studies have found that heavy calcareous fouling can increasing power costs by 85%.[3] Therefore, FR properties towards barnacles is important for effective FR coating system. Figure 9 shows the barnacle adhesion strength for the coatings. All experimental coatings except for coatings 3 and 11 showed non-attached barnacles; some had more than others. Although not as efficient as Hempasil X3 and IS 1100, coatings 1, 4, 5, and 9 had less than 50% of the attempted barnacles attached showing anti-fouling behavior. Also many experimental coatings (except for 2, 8, 10, and 12) showed very low barnacle adhesion strength comparable to IS 900. The A4-20 internal control displayed excellent FR/AF properties towards barnacles yet relatively behind in diatom removal compared to experimental coatings. Standard PU had the worst FR performance towards barnacles as it showed the highest barnacle adhesion strength. In general using a combination of DBE-621 and DBE-821 provided a slight edge over just using DBE-821 in terms of FR properties of coatings. It is important to note that having hydrophilic moieties did not impair the FR properties of SiPU coatings as *A. amphitrite* is known to adhere strongly on hydrophilic surfaces.[46]

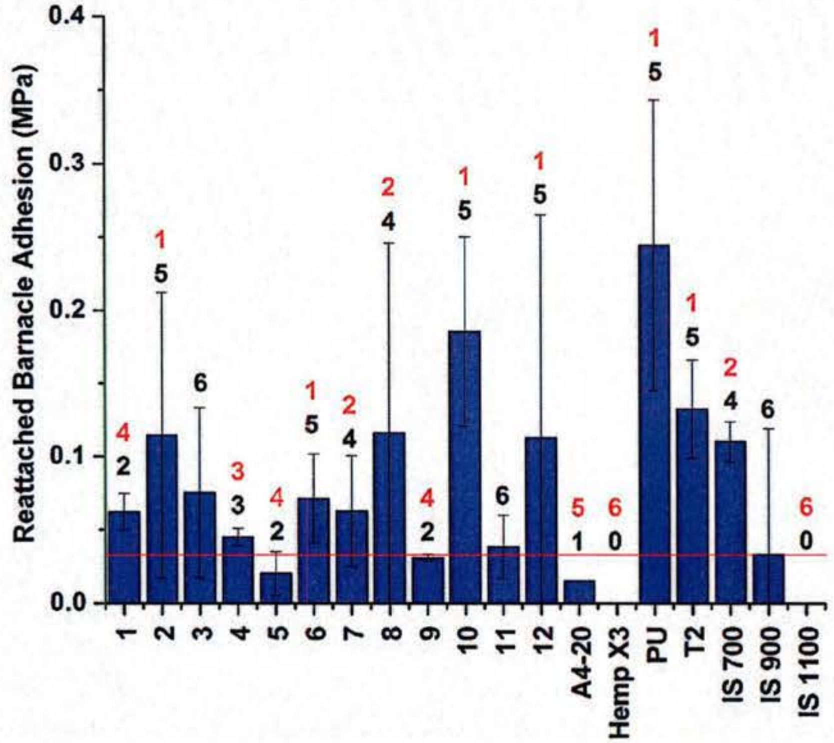

Figure 9: Reattached barnacle (*A. amphitrite*) adhesion strength. Six barnacles were used for each reattachment study, out of which red numbers represent the non-attached barnacles and the black numbers represent the successfully reattached barnacles. No broken/damaged

barnacles were reported during push off measurements for this study. Each bar represents the average adhesion strength based on the number of successfully pushed barnacles and the error bars represent the standard deviation of the mean. Red colored line indicates the average adhesion strength for the IS 900 commercial standard.

Figure 10 shows the adhesion of marine mussels to the coatings. Several experimental coatings did not allow any mussel attachments suggesting AF behavior. Among the coatings that had a few mussels attached, mussels were removed with a very small force (most cases < 5 N). Coatings 1, 4, 7, 9, 11 had no mussels attached which was a similar result observed for commercial standard Hempasil X3 and control A4-20. Polyurethane standard showed the highest adhesion of mussels with a removal force > 20 N. It is difficult to extrapolate a distinct trend in mussel adhesion in relation to coating composition given that most coatings did not allow mussel settlement.

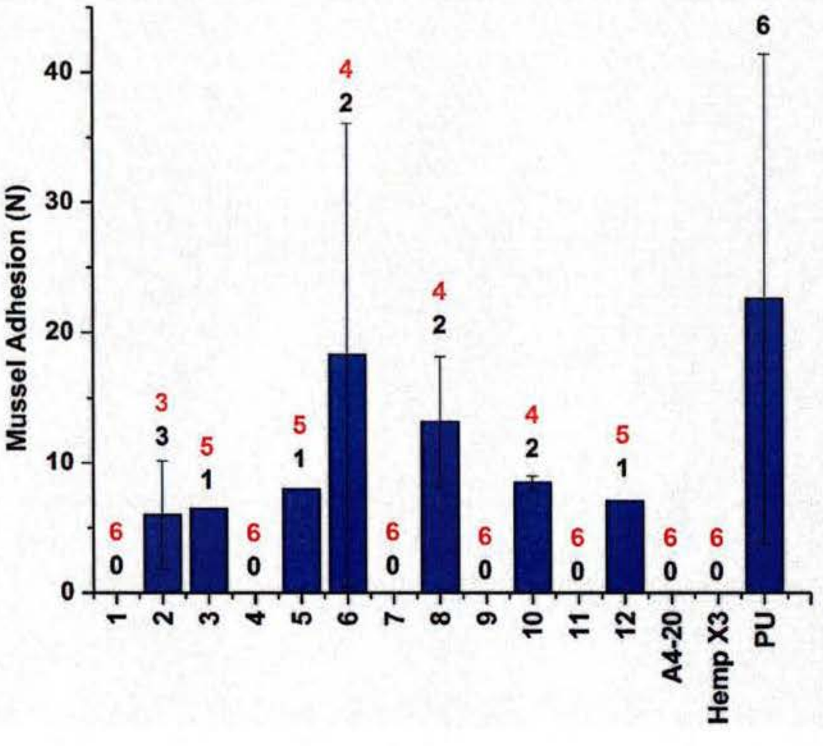

Figure 10: Marine mussel (*G. demissa*) adhesion evaluated with six attempted attachments for each coating. Each adhesion strength value represents the average force for removal of successfully attached mussels. Error bars represent the standard deviation of the mean. The red number indicates the number of non-attached mussels and the black number indicates the number of attached mussels.

In general, many hydrophilic side chain modified pre-polymer based SiPU coatings displayed comparable FR properties to commercial standards during laboratory biological assays for a variety of marine organisms. Many of the experimental coatings showed > 90% biofilm removal and low biomass remaining after water jet treatment. Coatings 9, 10, 11, and 12 showed excellent removal of diatoms on par with leading FR standard Hempasil X3, IS 900, and IS 1100. Many experimental coatings also displayed similar adhesion strength of barnacles comparable to IS 900, although Hempasil X3 and IS 1100 outperformed them during this assay. Mussels did not attach to a number of coatings. The few coatings that did have mussels attached, only allowed a small amount which were easily removed with little force. Coatings 5, 7, 9, and 11 can be regarded as surfaces with broad spectrum FR properties.

Conclusions

Polyisocyanate resins were modified with hydrophilic side chains and used to prepare poly isocyanate pre-polymers. SiPU coatings were prepared incorporating the polyisocyanate pre-polymers and hydrophilic additives. All experimental coatings displayed surfaces transitioning from hydrophobic to hydrophilic with increasing contact time with water. Coatings with hydrophilic additive combination provided coatings that transform to being hydrophilic quickly, whereas using of a single (DBE-821) additive provided a more swiftly changing surface with exposure to water. Side chain combination of PEG-PDMS seems to provide excellent FR properties for marine bacteria which was on par with commercial FR standards. Excellent FR performance towards diatoms were displayed by coatings prepared only using monofunctional components. Many coating compositions showed improved FR properties compared to that of the A4-20 control considering microfouling. Several experimental coating also displayed good AF and FR properties towards barnacles and mussels. More in depth surface characterization would provide better understanding of observed trends for adhesion and release of marine organisms. This work will provide the foundation to further develop SiPU coating surfaces with hydrophilic character for FR applications. Tailoring the surface balance of protein resistant hydrophilic groups will enable broad spectrum FR properties.

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Appendix G

Novel Non-Isocyanate Siloxane-Polyurethane Coatings

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Abstract

A novel non-toxic siloxane-polyurethane coating system was developed using non-isocyanate chemistry. The resultant coatings combined the properties of polyurethanes with the convenient epoxy-amine crosslinking reactions. Varying amounts of functional polydimethylsiloxane (PDMS) were incorporated into the resins and then used to make self-stratified coatings having low surface energy. Formulations were crosslinked using a series of amine crosslinkers in varying stoichiometric ratios. The resins were analyzed using FTIR and NMR. Cured coatings were characterized for solvent resistance and mechanical properties like hardness and impact strength. Thermal behavior of the cured coatings was studied using DSC, TGA and DMA. Contact angle experiments were conducted on the cured coatings to determine the stratification of PDMS to form a hydrophobic surface.

Introduction

Epoxy and polyurethane polymer systems are popularly used in a variety of applications like protective coatings, industrial coatings, composites and adhesives.[1, 2] The high mechanical strength, toughness, chemical and abrasion resistance of polyurethanes can be attributed to the presence of intermolecular bonds within the matrix.[2, 3] Epoxy resins can be conveniently crosslinked through the reaction with amines.[4] The type and stoichiometric ratio of amine crosslinkers determines the rate of curing of epoxy resins. The resultant coatings show excellent corrosion resistance and adhesion to substrates. Glycidyl carbamate (GC) functional resins combine the properties of polyurethanes with the convenience of epoxy-amine chemistry. GC resins can be synthesized by the reaction of isocyanates with glycidol to form carbamate (-CO-NH-) linkages. GC resins can be cured using amines and the resultant thermosets possess excellent mechanical strength and chemical resistance. In the past, Webster et al. have studied viscosity modification of GC resins,[2] sol-gel modified systems[5] and water dispersible resins[6] containing polyethylene glycol. In this work, GC resins were explored as fouling-release (FR) coatings for marine applications. Silicone elastomer-based commercial FR coatings lack the strength and adhesion to the substrate, required for long term viability. In an attempt to overcome the shortcomings of the commercial systems, siloxane-polyurethane (SiPU) coatings were developed in the Webster research group.[7, 8] Further, GC resin technology shows potential to reduce the hazards of isocyanates in 2K coating formulations. Therefore, GC systems are explored as potential substitutes for regular polyurethanes to make self-stratified FR coatings.

In this study, a siloxane modified GC resin was synthesized using isocyanates, siloxane and glycidol. Formulations were made by crosslinking the resin with different diamines such as PACM, polyamines and polyamides. Stoichiometric ratios of epoxy to amine hydrogen equivalent weight were also varied during the study. Additional aminopropyl terminated PDMS was added to the formulations to find the optimum formulation suitable for FR applications. Properties of the resultant coatings were analyzed according ASTM standard tests for mechanical strength, solvent resistance, impact strength and thermal behavior. Surface energy of select coatings was determined using contact angle measurements.

Experimental Section

Materials

Glycidol was supplied by Dixie Chemicals. To reduce the formation of impurities, glycidol was refrigerated.[9] Covestro (Bayer MaterialScience) provided hexamethylene diisocyanate (HDI) trimer (Desmodur 3300A). Isocyanate equivalent weight was determined by ASTM D 2572. Dicarbinol polydimethylsiloxane (PDMS) with molecular weight 5000 gm/mol was purchased from Gelest. Dibutyltin diacetate (DBTDAc), ethyl-3-ethoxy propionate (EEP) and toluene were purchased from Sigma Aldrich. Amine crosslinkers were provided by Air Products.

Aminopropyl terminated polydimethylsiloxane (APT-PDMS) was synthesized in a fashion similar to the one described in prior publication.[7] Briefly, siloxane monomer (D_4), benzyltriammonium hydroxide solution in methanol and blocker bis(3-aminopropyl)-tetramethyldisiloxane (BAPTDMS) were equilibrated at 80°C for 24 hours in a round bottom flask. The flask was equipped with a nitrogen inlet, condenser, heating mantle and temperature controller. To decompose catalyst, the temperature was increased to 170°C for 2 hours. After the completion of the reaction, the mixture was cooled to room temperature and stored. D_4, benzyltriammonium hydroxide solution and BAPTDMS were purchased from Dow Chemical, Sigma Aldrich and Gelest, respectively.

Synthesis of siloxane modified glycidyl carbamate (IGC_PDMS)

A four necked round bottom flask was fitted with a condenser, nitrogen inlet, thermocouple and a mechanical stirrer. For this reaction, the ratio of equivalents of NCO: PDMS: glycidol was maintained at 6:2:4. Also, a 50/50 w/w mixture of EEP and toluene was used as the solvent to achieve a theoretical target of 50% solids. In the first step, the flask was charged with HDI and EEP solvent. A slight excess of isocyanate was added during synthesis. Difunctional PDMS (5% equivalents of HDI) and catalyst DBTDAc (0.05% weight of total solids) were dissolved in the required amount of toluene. The solution was then added to the flask. The reaction scheme is shown in Figure 1. Temperature was maintained at 80°C for 1-1.5 hours.

In the next step, temperature was reduced to between 40-45°C before the addition of glycidol. Glycidol was then added to the flask, when the temperature dropped to ~40°C. The reaction of glycidol with isocyanate is highly exothermic; therefore, an ice bath may be required to cool the flask while adding glycidol to control the rise in temperature. The reaction was allowed to proceed at 45-50°C for another 1.5 hours. Completion of the reaction was determined as the disappearance of the NCO peak at 2272 cm^{-1} as observed using FTIR.

Resin characterization

A Thermo Scientific Nicolet 8700 was used for FTIR measurements. A small amount of resin sample was coated onto a potassium bromide plate. 32 scans were taken for the resin sample. A dilute solution of the resin in $CDCl_3$ was analyzed using Bruker 400 ^{13}C-NMR. To determine experimental percent solids, ~1 gm resin, measured accurately, was added to aluminum pans. The pans were heated in an oven at 120°C for 1 hour. Weight of the resin before and after heating were used to calculate the experimental value of percent solids. Average of three percent solids values was used for further experiments. Epoxy equivalent weight (EEW) was determined experimentally according to ASTM D 1652. ~1 gm of the resin, accurately measured up to fourth decimal place, was added to an Erlenmeyer flask. 10-15 ml chloroform was added to the flask. The resin was allowed to dissolve completely in chloroform. Crystal violet was used as the indicator. The resin solution was titrated against standardized 0.1 N HBr solution. Color change from violet to blue-green was considered to be the end point of titration. EEW titrations were conducted three times and the average value was considered to make formulations.

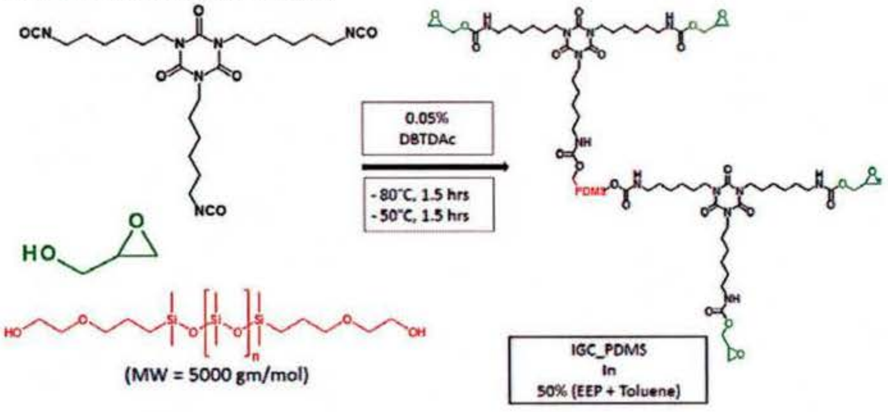


Figure 1: Reaction scheme for synthesis of siloxane modified glycidyl carbamate (IGC_PDMS) resin.

Coating formulations

Amine crosslinkers such as PACM, polyamines (Ancamine 2143 and Ancamine 2432) and polyamides (Ancamide 2634 and Ancamide 2767) were used to crosslink the synthesized resin. Different formulations were made using IGC_PDMS, amine crosslinkers in different stoichiometric amounts and varying amounts of additional APT-PDMS. During the study, the epoxy: AHEW ratios were varied as 1:1, 1:2 and 2:1. Further, the amounts of additional APT-PDMS were varied as 0, 1, 2, 3, 4, 5, 10, 15, 20 and 30% weight of resin solids in the formulations.

Table 1 shows labels for the formulations made using IGC_PDMS resin. All the formulations were mixed using a magnetic stirrer for 20 min. To minimize film defects caused due to bubbling, all the formulations were sonicated for 10 min prior to coating application. Coatings were made using a drawdown bar with wet film thickness of 8 mils. Steel, aluminum and glass panels were used as substrates, which were degreased using isopropanol before use. Coatings with PACM were oven- cured at 80°C for 45 min. Coatings crosslinked using polyamines and polyamides were cured under ambient laboratory conditions for 3 weeks.

Table 1: Different coating formulations included in the study.

Amine crosslinkers	Curing Conditions	Labels[a]
PACM	80°C, 45 min	PACM_r_Fx
Ancamine 2143	Room temperature, 3 weeks	2143_r_Fx
Ancamine 2432	Room temperature, 3 weeks	2432_r_Fx
Ancamide 2634	Room temperature, 3 weeks	2634_r_Fx
Ancamide 2767	Room temperature, 3 weeks	2767_r_Fx

[a]Labels are of the format amine crosslinker_epoxy: AHEW ratio_F%APT-PDMS in formulations.

Coating Characterization

After completion of the curing, the coatings were characterized for their solvent resistance, mechanical properties and impact strength. Methyl ethyl ketone (MEK) double rubs test (ASTM D 5402) was conducted to assess the chemical resistance and extent of crosslinking. A 26-oz hammer with three layers of cheesecloth was soaked in MEK. The hammer head was rewet with MEK after 100 double rubs. The number of double rubs that resulted in surface mar were noted. König pendulum hardness (ASTM 4366) was measured and reported in seconds. Reverse impact strength of the coatings was determined according to ASTM D 2794 using a Gardener impact tester. The maximum drop height was 43 in. and the drop weight was 3.92 lb. The results were reported as crazing or loss of adhesion or film failure in inch–pounds (in-lbs). Flexibility of coatings was determined conical mandrel bend (ASTM D 522). The results were reported as no failure or the length of the crack formed during experimentation. Based on the results obtained from the above experiments combined with the overall appearance of the coatings, select coatings were further characterized for their thermal behavior.

Thermal analysis of select coatings was conducted using TA Instruments Q1000 Differential Scanning Calorimetry (DSC). Coating samples were subjected to heat-cool-heat cycle for temperature ranges between -20°C to 250°C. Heating and cooling rates were maintained at 10°C/min and 5°C/min respectively. Glass transition temperature (T_g) was determined as the temperature of inflection at mid-point. Degradation behavior of select coatings was determined using a TA Instruments Q500 Thermogravimetric Analysis (TGA). Samples were heated to 800°C at a heating rate of 10°C/min. Storage modulus and tan delta curves for select coatings were determined using a TA Instruments Q800 Dynamic Mechanical Analysis (DMA). Crosslink density ($\boldsymbol{v}_e$) of the select coatings was calculated using T_g values obtained from the experiment. Free coating films, ~30 mm in length, 5 mm in width and 0.03-0.05 mm in thickness, were heated in a temperature range from -20°C to 180°C. Heating rate was maintained at 10°C/min at a frequency of 1 Hz. Then, $\boldsymbol{v}_e$ was calculated using the storage modulus value in the rubbery region and the T_g values from tan delta curves, using $E' = 3\boldsymbol{v}_e RT$, where E', storage modulus in MPa; $\boldsymbol{v}_e$, crosslink density (mol/L); R, universal gas constant (8.31 J/K/mol) and T, temperature in K. Further, coatings were analyzed using Symyx Coating Surface Energy Measurement System to measure water contact angles (WCA) and methylene iodide contact angles (MICA). WCA and MICA values were used to calculate surface energy (SE) of the coatings by Owen-Wendt method.

Results and Discussion

A siloxane-modified glycidyl carbamate resin (IGC_PDMS) was synthesized by the reaction between HDI, difunctional PDMS and glycidol. Amount of PDMS was 5% equivalents of HDI trimer. The resin was characterized using FTIR and ^{13}C-NMR. Figure 2 shows the FTIR spectrum for the synthesized resin. Completion of the reaction was determined from the disappearance of the isocyanate peak at 2272 cm^{-1}. The small peak seen in the scan maybe due to the presence of excess isocyanate added during synthesis. Wavenumbers at 910 cm^{-1}, ~1100 cm^{-1}, ~3400 cm^{-1} represent epoxy rings, Si-O-Si vibrations and NH groups respectively in the resin. Figure 3 shows the ^{13}C-NMR spectrum for the IGC_PDMS resin. Chemical shifts at 1 ppm, 44 and 49 ppm and 149 ppm indicate C atoms from PDMS, oxirane rings and carbamate linkages respectively. Experimental determination of percent solids and EEW values showed the synthesized resin was made with 50% solids with EEW value of 435 gm/mol.

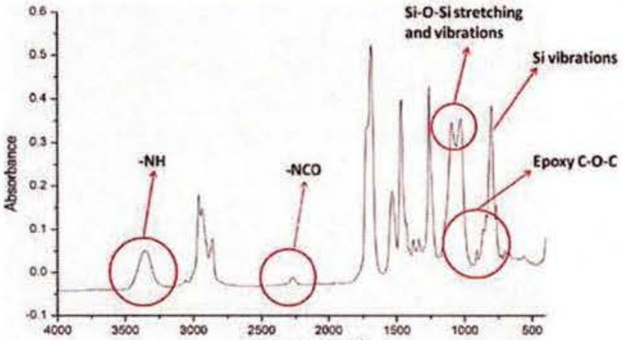


Figure 2: FTIR spectrum of IGC_PDMS resin.

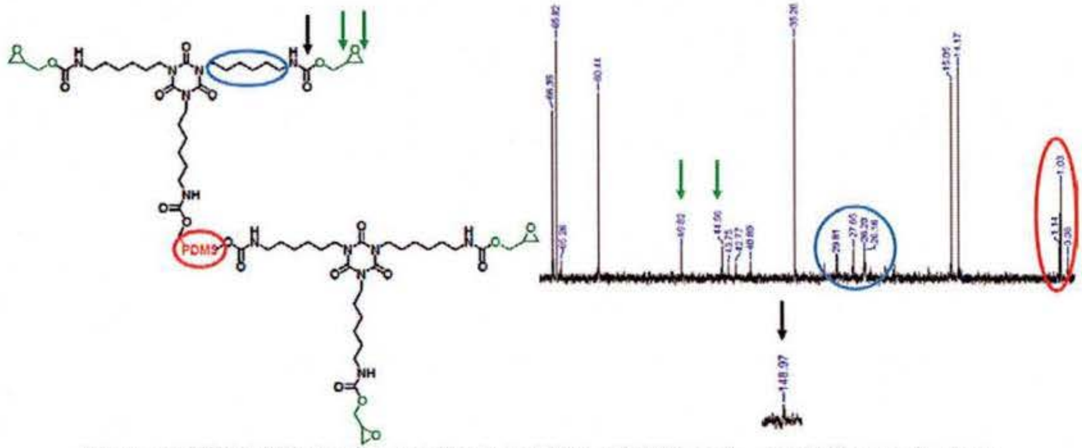


Figure 3: ^{13}C-NMR for the synthesized IGC_PDMS resin. All shifts are in ppm.

Diamines such as PACM, polyamines and polyamides, in varying epoxy:AHEW ratios, were used to crosslink the synthesized resin. Additional APT-PDMS was incorporated into the formulations to identify the formulation that gives optimum FR performance. The amount of APT-PDMS was varied as 0, 1, 2, 3, 4, 5, 10, 15, 20 and 30% weight of resin solids in formulations. Wet film thickness of the coatings was maintained at 8 mils. PACM_r_Fx coatings (Table 1) were cured at 80°C for 45 min. Coatings cured using the polyamines and polyamides were cured at room temperature for 3 weeks. Upon completion of the respective curing schedules, all coatings were characterized for their solvent resistance, mechanical and impact strength. Dry film thickness of the coatings lied in the range from 30 to 60 µm. The results for coatings with varying epoxy: AHEW ratios are shown in Table 2 to Table 4.

Table 2 shows characterization results for coatings cured with epoxy:AHEW = 1:1. PACM_r_Fx coatings exhibited a combination of good solvent resistance, high hardness and high impact strength and appearance. The coatings also showed high gloss. PACM-cured coatings were devoid of phase separation on the surface of the coatings. This smooth, uniform, glossy appearance of PACM_r_Fx coatings may be attributed to the use of oven-curing; higher temperature of 80°C may have compatibilized all the different components during the curing reaction. Significant increase in hardness König pendulum hardness and pencil hardness values were observed with coatings containing 4% APT-PDMS.

In general, coatings crosslinked with polyamines and polyamides resulted non-uniform coatings with phase separation on the surface. Ambient curing also resulted in coatings with sticky or oily surfaces. Curing the coatings at ambient conditions may have resulted in inhomogeneity in the bulk of the coatings. Coatings with polyamines showed better properties compared to polyamides. After 3 weeks of curing at ambient conditions, 2143_1:1_Fx and 2432_1:1_Fx coatings, up to 4% additional APT-PDMS, were completely cured (MEK > 400). The completely cured 2143_1:1_Fx coatings showed high pencil hardness values, but poor impact resistance. On the other hand, 2432_1:1_Fx appeared softer than 2143_1:1_Fx coatings, but showed comparatively higher impact resistance. Similar to PACM_1:1_F4, the hardness and impact resistance of the polyamine cured coatings increased with the addition of 4% APT-PDMS. 2634_1:1_Fx and 2767_1:1_Fx did not cure completely (MEK < 400) after 3 weeks, except 2634_1:1_F1, 2634_1:1_F2, 2632_1:1_F4, 2767_1:1_F0 and 2767_1:1_F4. In spite of the incomplete cure, coatings cured using polyamides showed high values for pendulum hardness. The high hardness combined with incomplete network formation may have caused poor impact resistance of 2767_1:1_Fx coatings. Except for the improvement in solvent resistance, the polyamide cured coatings with 4% APT-PDMS showed similar hardness and impact resistance performance. Coatings cured using the polyamines and polyamides did not cure at %APT-PDMS values higher than 5%.

Table 3 shows ASTM test results for coating formulations with epoxy:AHEW = 1:2. For coatings cured using PACM and the polyamines, increasing the amount of amines resulted in a significant increase in pendulum hardness values, as compared to the coatings with epoxy: AHEW = 1:1. Furthermore, 2432_1:2_Fx coatings showed improved pencil hardness values. Conversely, for the coatings cured using the polyamides, the hardness values decreased, but 2767_1:2_Fx coatings showed improved pencil hardness values compared to 2767_1:1_Fx. PACM_1:2_Fx coatings appeared smooth and uniform with a homogeneous surface, while the coatings cured using polyamines and polyamides appeared non-glossy with sever phase separation on the surface. Similar to F4 formulations with epoxy: AHEW = 1:1, hardness of PACM_1:2_F4 and 2432_1:2_F4 formulations improved with 4% APT-PDMS. Coatings with %APT-PDMS greater than 4% will be formulated and characterized in the future.

Table 4 shows characterization results for coatings cured at epoxy:AHEW = 2:1. ~50% of all the formulations did not cure when the amount of amines was reduced. All the coatings were non-uniform, soft and elastomeric to touch. Due to the incomplete formation of networks, the coatings showed comparatively lower impact resistance behavior. Formulations with %APT-PDMS above 3% showed incomplete network formation (MEK < 400).

Based on all characterization results in Table 2 and Table 3, low baking conditions of 80°C for 45 min resulted in better compatibilization of all the phases in the coating during curing reactions, giving a smoother, glossier appearance to the coatings. Coatings with 4% APT-PDMS showed the best performance with highest hardness and impact resistance values. Increasing the amount of APT-PDMS above 4% caused lowering of the mechanical properties of the coatings. It was also evident from coating characterizations that coatings with lower amount of amines (epoxy: AHEW = 2:1) resulted in incomplete crosslinking reactions. Presence of PDMS in the formulations may have caused plasticization of the coatings and interfered with the curing process. Therefore, a minimum of stoichiometric amount of the amine crosslinker (epoxy: AHEW = 1:1) is required to obtain a complete network (MEK > 400) of the IGC_PDMS resin. In decreasing order of amine performance combined with appearance of the final coatings, PACM > polyamines >> polyamides.

Table 2: Results for coatings with epoxy:AHEW ratio of 1:1.

Amines_ratio	F%APT-PDMS	MEK Double Rubs	König Pendulum (s)	Pencil Hardness	Impact (in.lbs)	[a]Mandrel Bend	60° Gloss
PACM_1:1	F0	>400	78	2H	>160	NF	82.37
	F1	>400	74	HB	>160	NF	87.30
	F2	>400	68	B	>160	NF	85.70
	F3	>400	62	2B	>160	NF	85.27
	F4	>400	95	6H	>160	NF	89.86
	F5	>400	79	HB	>160	NF	92.03
	F10	>400	67	B	47.04	NF	82.87
	F15	>400	74	HB	74.48	NF	86.20
	F20	>400	77	3B	66.64	NF	82.90
	F30	>400	73	2B	>160	NF	77.60
2143_1:1	F0	>400	68	6H	78.40	NF	57.13
	F1	>400	76	7H	70.56	NF	57.67
	F2	>400	78	5H	70.56	NF	60.63
	F3	>400	75	6H	70.56	NF	54.43
	F4	>400	98		>160	NF	95.83
2432_1:1	F0	>400	64	3B	117.6	NF	85.77
	F1	>400	64	3B	94.08	NF	75.87
	F2	>400	67	2B	109.76	NF	71.13
	F3	>400	67	3B	125.44	NF	67.07
	F4	>400	87		141.22	NF	67.33
2634_1:1	F0	220	88	B	86.24	NF	13.67
	F1	>400	83	B	117.6	NF	17.47
	F2	>400	82	HB	141.12	NF	45.13
	F3	175	82	HB	[b]-	NF	41.77
	F4	>400	93		>160	NF	92.90
2767_1:1	F0	>400	104	6H	39.20	NF	45.30
	F1	300	99	6H	39.20	NF	35.70
	F2	200	100	5H	19.60	1 cm tear	60.53
	F3	75	101	5H	35.28	1 cm tear	73.13
	F4	>400	100	2B	>160	NF	40.43

[a] NF indicates no failure in the film after experiment.

[b] Non-uniformity of the coating surface resulted in large variations in impact strength values.

Table 3: Results for coatings with epoxy:AHEW ratio of 1:2.

Amines_ratio	F%APT-PDMS	MEK Double Rubs	König Pendulum (s)	Pencil Hardness	Impact (in.lbs)	[a]Mandrel Bend	60° Gloss
PACM_1:2	F0	>400	92	H	>160	NF	100.9
	F1	>400	88	2H	>160	NF	86.33
	F2	>400	87	H	>160	NF	74.53
	F3	>400	84	2B	>160	NF	80.97
	F4	>400	106	5H	>160	NF	85.20
	F5	>400	88	HB	>160	NF	94.20
	F10	>400	79	HB	>160	NF	88.17
2143_1:2	F0	>400	70	7H	>160	NF	42.60
	F1	>400	59	8H	>160	NF	41.67
	F2	>400	69	7H	>160	NF	34.27
	F3	>400	106	8H	94.08	NF	31.03
	F4	>400	65	2H	>160	NF	88.10
2432_1:2	F0	>400	111	7H	78.40	NF	52.20
	F1	>400	94	5H	74.48	NF	28.20
	F2	>400	84	2H	>160	NF	47.53

	F3	160	79	HB	156.8	NF	48.80
	F4	>400	103	B	>160*	NF	38.03
2634_1:2	F0	>400	77	5H	>160	NF	12.83
	F1	>400	79	2H	>160	NF	6.83
	F2	>400	107	3H	137.20	NF	7.53
	F3	>400	78	5H	117.60	NF	5.97
	F4	150	112	H	>160*	NF	[b]88.03
2767_1:2	F0	>400	84	2H	94.08	NF	59.47
	F1	200	86	2H	>160	NF	28.63
	F2	220	81	H	156.80	NF	35.90
	F3	180	77	H	23.52	NF	20.53
	F4	100	84	H	>160*	NF	[b]87.97

[a]NF indicates no failure in the film after experiment.

[b]Gloss measurements will be redone.

*The coating films remained intact after impact, but delamination of the film was observed around the point of impact.

Table 4: Results for coatings with epoxy:AHEW ratio of 2:1.

Amines_ratio	**F%APT-PDMS**	**MEK Double Rubs**	**König Pendulum (s)**	**Pencil Hardness**	**Impact (in.lbs)**	**[a]Mandrel Bend**	**60° Gloss**
PACM_2:1	F0	>400	44	4B	133.28	NF	97.27
	F1	>400	47	4B	137.20	NF	86.83
	F2	140	41	5B	141.12	NF	86.53
	F3	>400	41	5B	>160	NF	74.97
	F4	340	44	3H	>160	NF	78.13
2143_2:1	F0	>400	34	8B	86.24	NF	54.03
	F1	158	32	8B	47.04	NF	49.53
	F2	>400	31	8B	39.20	NF	43.83
	F3	>400	34	8B	23.52	NF	44.30
2432_2:1	F0	250	29	8B	109.76	NF	83.73
	F1	>400	30	8B	141.12	NF	46.87
	F2	>400	35	8B	86.24	NF	49.07
	F3	160	40	8B	152.88	NF	54.13
2634_2:1	F0	80	45	HB	156.80	NF	74.40
	F1	320	46	HB	152.88	NF	66.47
	F2	220	49	B	>160	NF	58.70
	F3	180	46	B	>160	NF	47.17
2767_2:1	F0	300	81	2H	23.52	1 cm tear	79.77
	F1	300	73	2H	11.76	1 cm tear	73.97
	F2	100	76	H	23.52	1 cm tear	71.50
	F3	80	73	F	11.76	NF	66.57

[a]NF indicates no failure in the film after experiment.

Based on the results obtained with the ASTM tests (Table 2 to Table 4) combined with the appearance of the coatings, PACM_1:2_Fx, 2143_1:2_Fx and 2432_1:2_Fx coatings were selected for further characterization using thermal analysis techniques. Figure 4 shows DSC scans and T_g values for the select coatings. 2143_1:2_Fx showed highest T_g values between 85-90°C (Figure 4(a)). Addition of APT-PDMS resulted in slight variation in T_g, with the values dropping with 1% APT-PDMS and then increasing again. T_g values for PACM_1:2_Fx coatings lied in the range from 75-80°C (Figure 4(b)), with no particular change upon addition of APT-PDMS. Ancamine 2432 resulted in coatings with the lowest T_g (Figure 4(c)). The coatings showed ~5°C drop in T_g values from 68°C to 63°C with increasing amount of APT-PDMS.

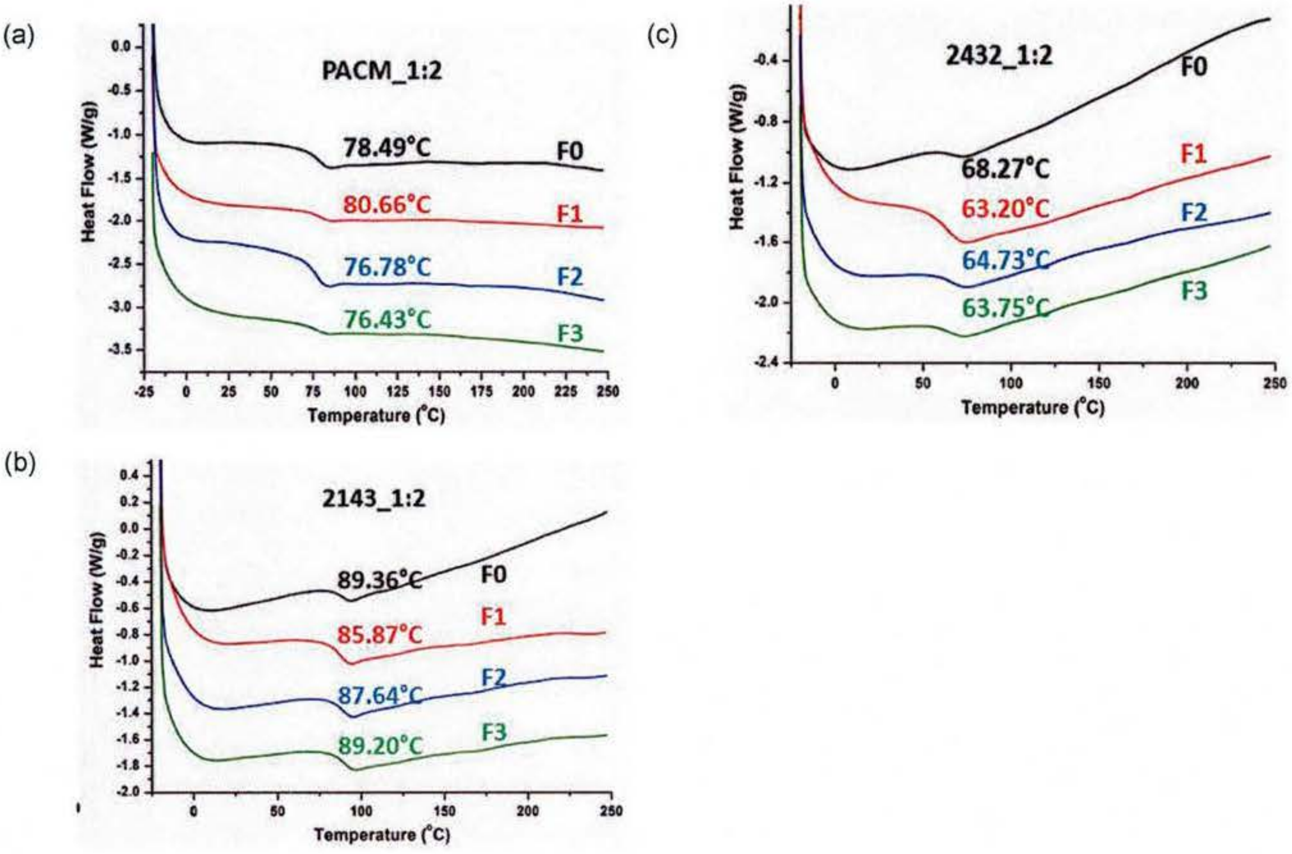
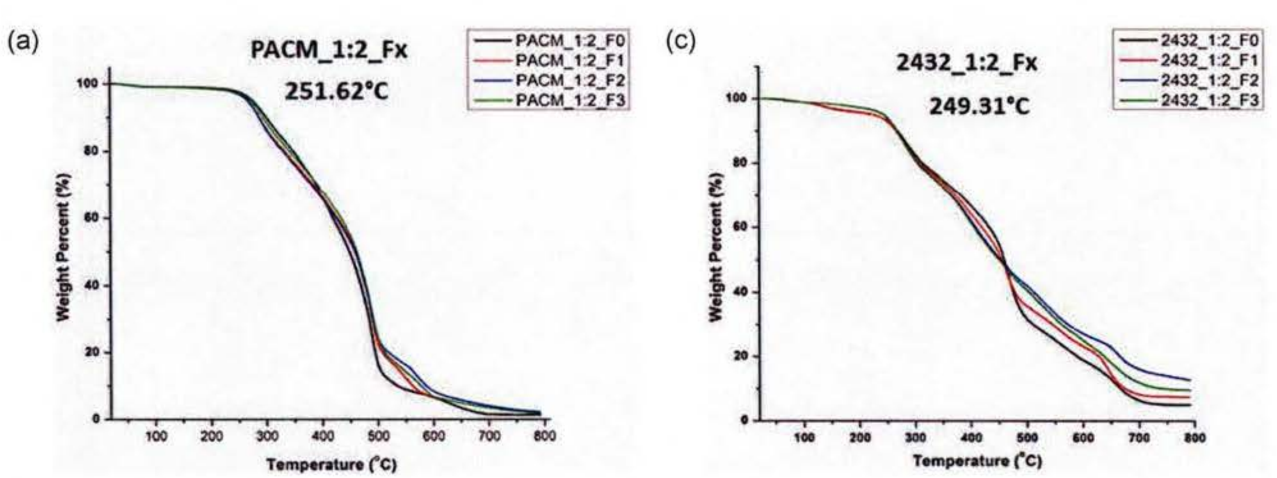


Figure 4: DSC scans for coatings crosslinked with (a) PACM, (b) Ancamine 2143 and (c) Ancamine 2432. Coatings with APT-PDMS content greater than 3% will be characterized using DSC.

Figure 5 shows degradation behavior of select coatings. PACM_1:2_Fx, 2143_1:2_Fx and 2432_1:2_Fx showed similar degradation temperature of between 245-250°C. Coatings with PACM showed 1-2% initial weight loss, while the polyamine cured coatings showed almost 7% initial weight loss. This difference may be attributed to the difference in curing conditions of the coatings. Most of the solvents may have evaporated during the curing process of PACM_1:2_Fx coatings at 80°C. On the other hand, higher amount of solvent may have remained in the polyamine coatings after curing under ambient conditions.



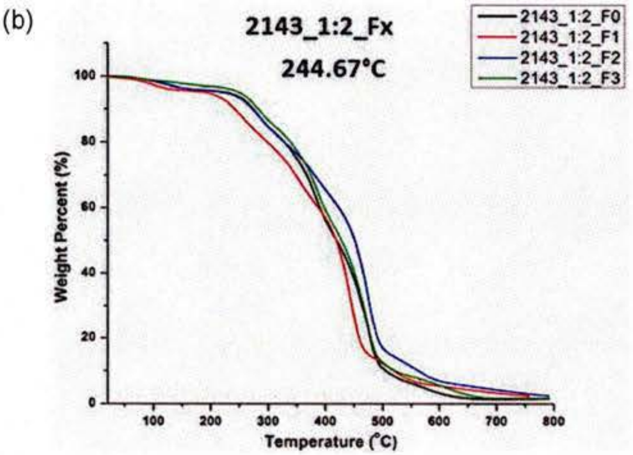


Figure 5: TGA thermograms for coatings crosslinked with (a) PACM, (b) Ancamine 2143 and (c) Ancamine 2432.

Figure 6 shows storage modulus data for PACM_1:2_Fx, 2143_1:2_Fx and 2432_1:2_Fx. Storage modulus values at 25°C for 2432_1:2_Fx coatings were highest among the select coatings. Incorporation of additional APT-PDMS did not show significant changes in storage moduli of the coatings. PACM_1:2_Fx coatings showed the lowest storage moduli in the range from 225 to 290 MPa at 25°C. With 2143_1:2_Fx coatings, addition of APT-PDMS resulted in a drastic increase in storage modulus values from 226 MPa for F0 to 440 MPa for F1. The moduli further increased to 527 MPa with 2% APT-PDMS, but dropped to 300 MPa with 3% APT-PDMS. In general, for coatings curing using the polyamides, addition of APT-PDMS appeared to be a "reinforcement" in the coating networks. APT-PDMS did not cause significant plasticization of the coatings in any formulations.

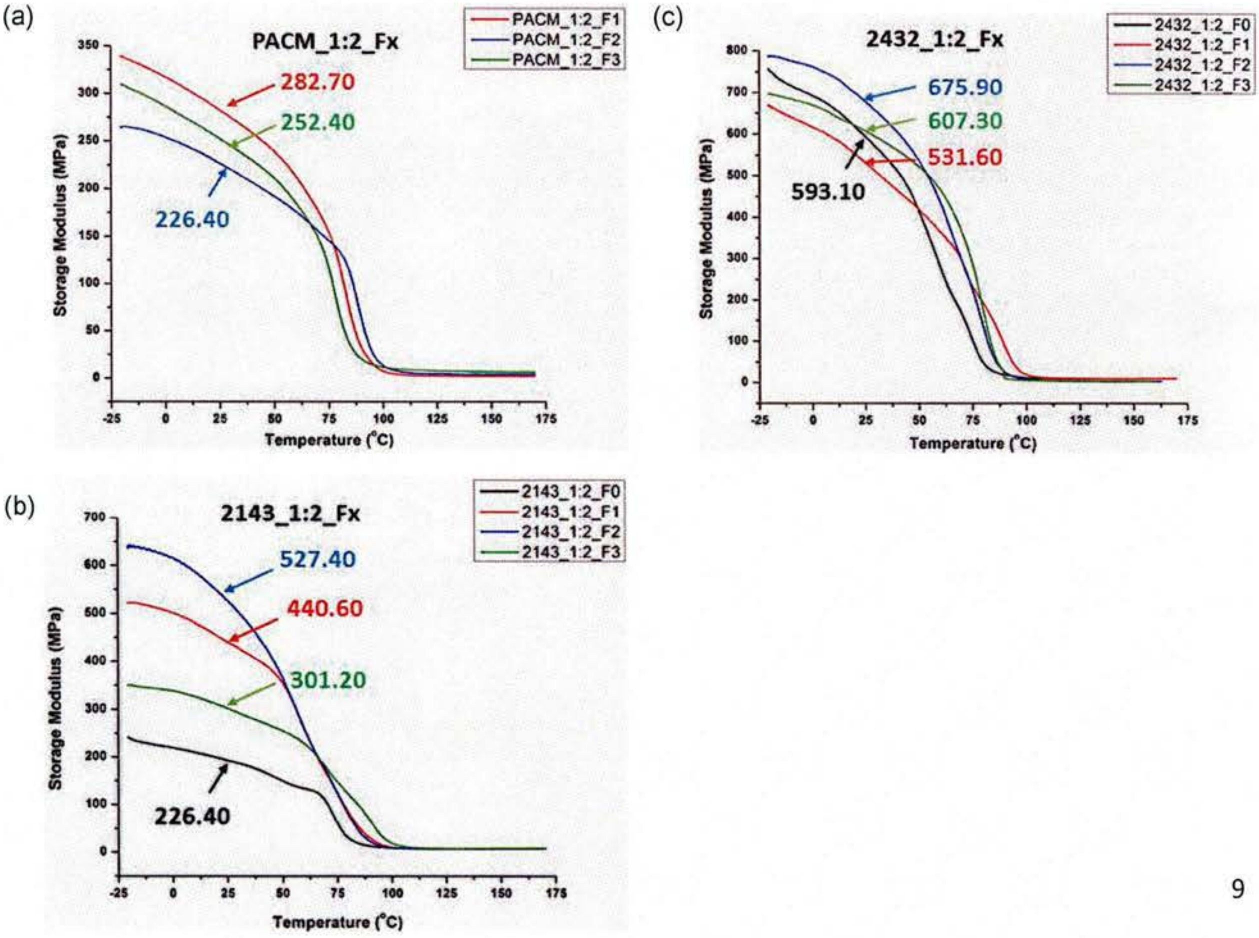


Figure 6: Storage modulus values at 25°C for (a) PACM_1:2_Fx, (b) 2143_1:2_Fx and (c) 2432_1:2_Fx. All values are in MPa. Modulus value for PACM_1:2_F0 coating may have been inaccurate and is, therefore, not shown.

Figure 7 shows tan delta curves for the select coatings. In general, all the peaks appeared narrow and uniform, indicating the presence of homogeneous phases in the bulk of the coatings. In the polyamine-cured coatings, minor peaks in the low temperature regions may be indicative of a separate soft PDMS phase, with 2432_1:2_Fx exhibiting a more prominent secondary phase. For coatings cured using PACM, T_g values decrease with the addition of APT-PDMS, from 95°C for F1 to 85°C for F3. For coatings cured using the polyamines, APT-PDMS resulted in increase in T_g values from 79°C at 0% APT-PDMS to close to 90°C with increasing amount of APT-PDMS.

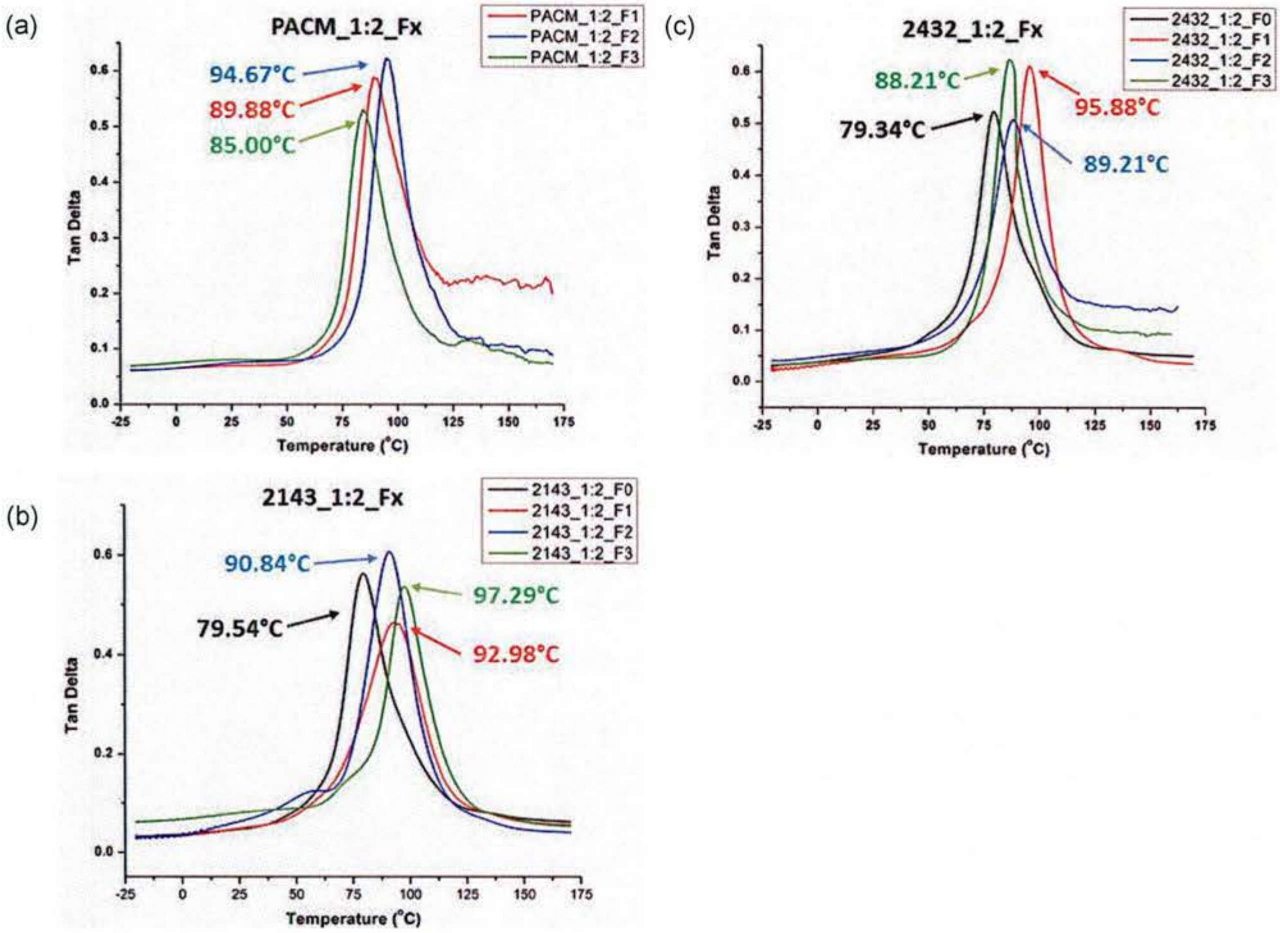


Figure 7: Tan delta curves for (a) PACM_1:2_Fx, (b) 2143_1:2_Fx and (c) 2432_1:2_Fx. Coating film sample for PACM_1:2_F0 failed before determination of T_g. The sample will be retested using DMA.

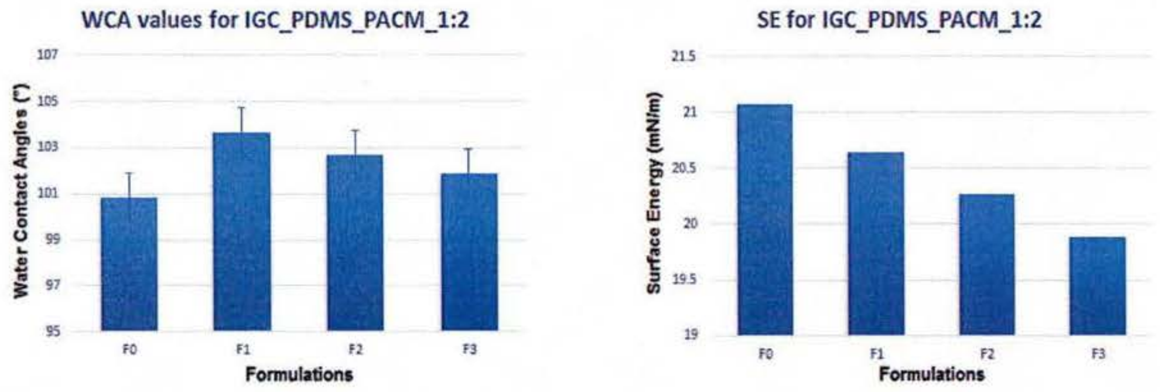
Table 5 shows the calculated crosslink density values for PACM_1:2_Fx, 2143_1:2_Fx and 2432_1:2_Fx coatings. *E'* values shown in Table 5 indicate storage modulus of the coatings in the rubbery region. 2432_1:2_F0 and 2432_1:2_F1 showed highest values for v_e, while PACM cured coatings showed lower v_e. For PACM_1:2_Fx coatings, addition of APT-PDMS resulted in an increase in v_e values, indicating tightening of the crosslink network with increasing APT-PDMS. Conversely, for the polyamine cured coatings, v_e decreased with the incorporation of APT-PDMS. For Ancamine 2143 cured coatings, v_e decreased for 0.71 mol/L for 0% APT-PDMS to 0.59 mol/L for 2% APT-PDMS. The v_e increased to 0.72 mol/L again at 3% additional APT-PDMS. Ancamine 2432 coatings were most affected by the presence of additional APT-PDMS in the coating formulations. At 0-1% APT-PDMS, the network was highly crosslinked with v_e = ~0.90 mol/L. But above 1% APT-PDMS, v_e dropped drastically to ~0.30 mol/L.

Table 5: Results from DMA for the select coatings.

Amines_ratio	F%APT-PDMS	E' (MPa)	T_g (°C)	v_e (mol/L)
PACM_1:2[a]	F1	1.80	89.88	0.17
	F2	4.03	94.67	0.38
	F3	6.59	85.00	0.63
2143_1:2	F1	7.34	79.54	0.71
	F2	6.68	92.98	0.63
	F3	6.28	90.84	0.59
	F4	7.69	97.29	0.72
2432_1:2	F1	9.29	79.34	0.90
	F2	9.58	95.88	0.89
	F3	2.98	89.63	0.28
	F4	3.83	88.21	0.36

[a] PACM_1:2_F0 coatings failed during the experiment.

Understand the FR properties of a coating involves determination of the surface energy. Commercially available FR coatings are typically based on silicone elastomers. Low surface energy coatings cause slippage of fouling organisms, like barnacles and mussels, from the surface, resulting in poor attachment of the macrofoulants. Surface energy values between 20-25 mN/m are desirable for coatings to be successfully used in marine applications. To determine if IGC_PDMS coatings can be used as viable FR coatings, contact angles and surface energies of select coatings were determined. Figure 8(a) shows WCA for PACM_1:2_Fx, up to 3% additional APT-PDMS. WCA for the four formulations were greater than 90°, indicating formation of hydrophobic surfaces after curing. Figure 8(b) shows surface energy (SE) data for the four coatings. SE was calculated using the Owen-Wendt method. Increasing % APT-PDMS resulted in slight decrease in SE, from ~21 mN/m for 0% APT-PDMS to ~19.75 mN/m for 3% APT-PDMS. Formation of a low surface energy surface indicates successful stratification of PDMS.



(a) (b)

Figure 8: (a) Water contact angles and (b) surface energy values for PACM_1:2_Fx coatings, up to 3% APT-PDMS. Coatings with %APT-PDMS amount over 3% will be characterized.

Conclusion

Siloxane modified glycidyl carbamate (IGC_PDMS) resin was synthesized using HDI trimer, glycidol and dicarbinol PDMS. Formulations were made using the resin and different amines like PACM, Ancamine 2143, Ancamine 2432, Ancamide 2634 and Ancamide 2767. Different formulations were made by varying the ratio of epoxy: AHEW as 1:1, 1:2 and 2:1. Additional APT-PDMS was added in varying amounts to the different formulations. The amount of APT-PDMS was varied as 0, 1, 2, 3, 4, 5, 10, 15, 20 and 30% weight of resin solids. After curing, all the coatings were tested for their solvent resistance, hardness and flexibility. MEK double rub test showed that the resin shows potential to be crosslinked under ambient conditions.

Epoxy: AHEW ratio of 1:2 resulted in coatings with higher hardness and flexibility amongst all formulations. PACM containing coatings formed uniform surface, probably due to increase in compatibility between phases at higher temperatures. On the other hand, curing the coatings at room temperature resulted in the formation of non-uniform, non-glossy, oily coatings. 4% APT-PDMS appeared to have caused reinforcement of the coating networks, which then resulted in improved hardness values. All coatings at epoxy: AHEW = 1:2 showed similar degradation behavior, with degradation temperatures of ~250°C. Higher initial weight loss with coatings cured using Ancamine 2143 and Ancamine 2432 may be due to the presence of solvents in the coating film. In case of PACM cured coatings, most of the solvent may have volatilized during oven-curing at 80°C. Results from DSC showed that 2143_1:2_Fx coatings showed the highest T_g values between 85-90°C, followed by the PACM cured coatings between 76-80°C and Ancamine 2432 coatings between 63-68°C. Tan delta curves for the coatings appeared narrow, indicating formation of homogeneous coating network. Incorporation of APT-PDMS increased T_g of the coatings. PACM_1:2_Fx coatings showed increase in v_e with addition of APT-PDMS, while the density values dropped for the polyamine cured coatings. Stratification of PDMS resulted in WCA values greater than 90° for the PACM cured coatings. Surface energy of the coatings lied in the range from 19-21 mN/m, indicating the formation of a hydrophobic surface, which can be potentially used to make marine FR coatings.

Acknowledgements

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Appendix H

Amphiphilic Glycidyl Carbamate Coatings for Marine Applications

Objective

To develop amphiphilic coatings based on glycidyl carbamate resin technology and to analyze their fouling release (FR) performance. The glycidyl carbamate resin system is a non-isocyanate polyurethane system that makes use of epoxy-amine curing chemistry, thus eliminating the use of isocyanates in coating application.

Synthesis

A series of amphiphilic glycidyl carbamate (AMP_GC) resins were synthesized using polydimethylsiloxane (PDMS) and polyethylene glycol (PEG) with different molecular weights and functionalities. The amounts of PDMS and PEG were varied as 5, 10 and 15% equivalents of isocyanate (HDI).

In the first step, HDI was reacted with difunctional PDMS or PEG at 80°C for ~1 hour. 1:1 by weight solvent blend of EEP: acetone was used to make resin with target 50% solids. Required amount of EEP was added to HDI-difunctional component reaction mixture. The monofunctional PEG or PDMS combined with the catalyst DBTDAc (0.05% weight of resin solids) was then added to the reaction mixture. The reaction was allowed to proceed for another hour. Before the addition of glycidol, the temperature was reduced to lower than 40°C. Glycidol solution in acetone was added to the flask. Temperature was then maintained at 45-55°C for 1-1.5 hours, until the disappearance of the isocyanate peak. The proposed reaction scheme is shown in Figure 1. Table 1 shows the different AMP_GC resins synthesized so far. In this paper, the resins have been labeled as resin label_%PDMS/PEG.

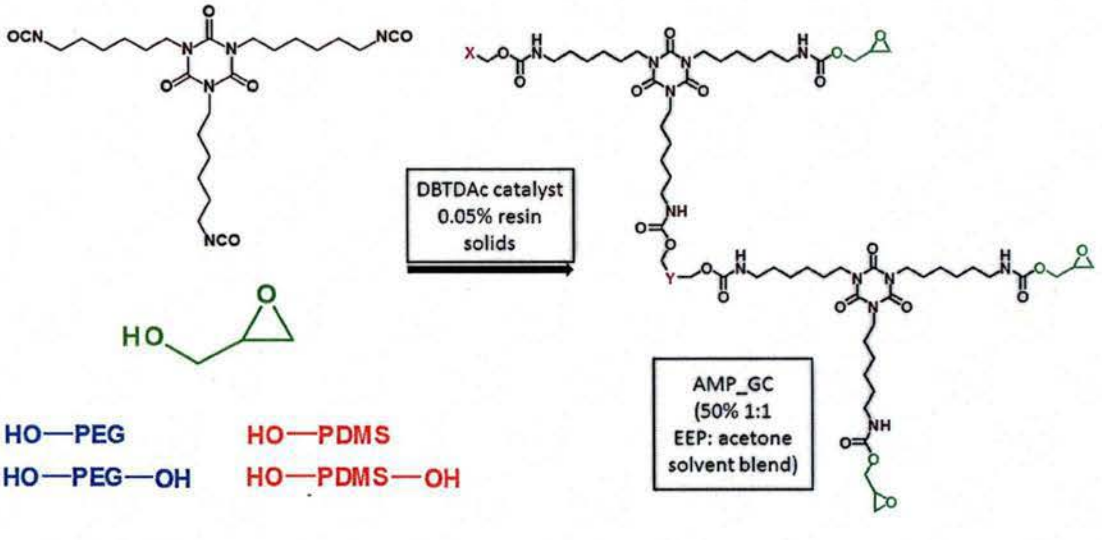


Figure 1- Reaction scheme for synthesis of AMP_GC resins. X and Y represent the monofunctional and difunctional PEG or PDMS component respectively.

Table 1- Different AMP_GC resins synthesized in this study.

Resin labels	%PDMS and PEG	MW of PDMS (gm/mol)	MW of PEG (gm/mol)
R1	5, 10, 15	1000 (d)	550
R2	5, 10, 15	1000 (m)	600
[a]R3	5	5000 (m)	1000 (d)
R4	5, 10	1000 (d)	750 (m)
[b]R5	5	4000 (d)	750 (m)
R6	5, 10	1000 (d)	2000 (m)
R7	5	1000 (m)	1000 (d)
R8	5	5000 (d)	550 (m)
R9	5	5000 (d)	750 (m)
R10	5	5000 (d)	2000 (m)
R11	5	2850 (d)	550 (m)
R12	5	2850 (d)	750 (m)
R13	5	2850 (d)	2000 (m)
R14	5	10,000 (d)	550 (m)

[a]Further study with R3 resin has been discontinued, since coatings with R3 did not cure even after 3 months of application of coating formulations.

[b]Siloxane content in the PDMS is lower than 50%, therefore, further study may be discontinued.

Resin characterization

FTIR

A Thermo Scientific Nicolet 8700 was used for FTIR measurements. A potassium bromide plate was coated with a small amount of resin sample. 32 scans were taken for each sample. Figure 2 shows a generic FTIR scan for AMP_GC resins. Peak at 2272 cm^{-1} indicating NCO disappeared completely, indicating completion of the reaction. Peaks at 910 cm^{-1} and 1030-1100 cm^{-1} wavenumbers showed presence of epoxy rings, PDMS and PEG within the resins. Peak at 1246 cm^{-1} indicated the formation of carbamate linkages (-CO-NH-).

^{13}C-NMR

Further, the synthesized resins were characterized using NMR. A dilute solution of the resin in $CDCl_3$ was analyzed using Bruker 400 ^{13}C-NMR. Figure 3 shows a sample ^{13}C-NMR spectrum for AMP_GC resins. Spectra for all AMP_GC resins were similar to the spectrum in Figure 3.

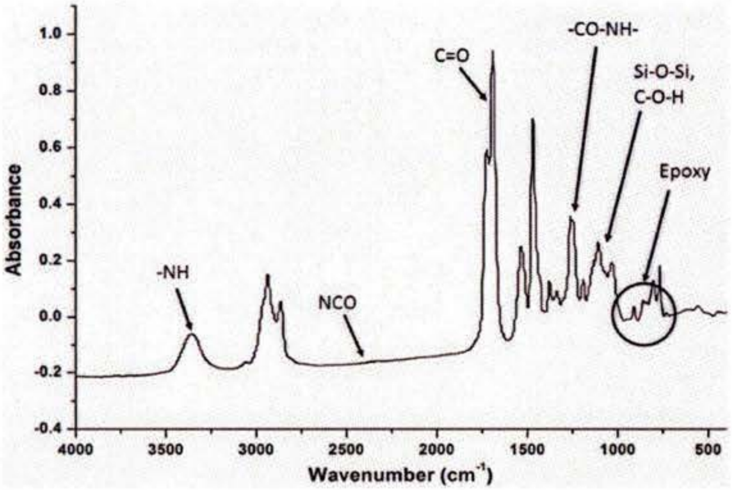


Figure 2- FTIR scans for AMP_GC resins.

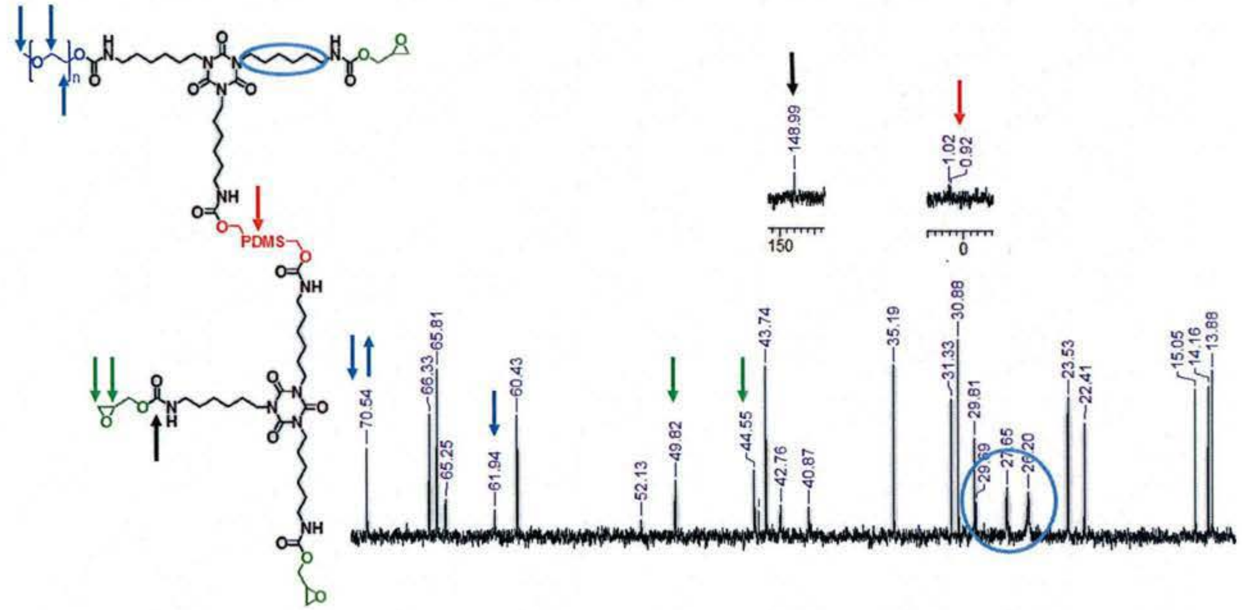


Figure 3- Sample ^{13}C-NMR spectrum for AMP_GC resins. All shifts are in ppm.

Percent solids

To determine experimental percent solids, ~1 g resin, measured accurately, was added to aluminum pans. The pans were heated in an oven at 120°C for 1 hour. Weight of the resin before and after heating were used to calculate the experimental value of percent solids. Average of three values was used for further experiments. Experimental percent solids for all resins was in the range from 48-50% (target 50%).

Epoxy equivalent weight

Epoxy equivalent weight (EEW) was determined experimentally according to ASTM D 1652. ~1 g of the resin, accurately measured up to fourth decimal place, was added to an Erlenmeyer flask. 10-15 ml chloroform was added to the flask. The resin was allowed to dissolve completely in chloroform. Crystal violet was used as the indicator. The resin solution was titrated against standardized 0.1 N HBr solution. Color change from violet to blue-green was considered to be the end point of titration. EEW titrations were conducted three times and the average of three titration values was considered to make formulations. EEW of all the resins lied in the range from 350-650 gm/eq., depending on the MW and amount of PDMS/PEG components. EEW values increased as %PDMS/PEG component was increased. Changing the MW of PDMS/PEG components also resulted in variations in the EEW values of the resins.

Coating formulations

Formulations were made using the synthesized resins and different amine crosslinkers, like Ancamine 2143 and Ancamine 2432 (polyamines) and Ancamide 2634 and Ancamide 2767 (polyamides). Ratios of epoxy: AHEW were also varied as 1:1 and 1:2.

All formulations were stirred using a magnetic stirrer for 20 min. Then, the formulations were sonicated for 10 min to remove bubbles. Steel, aluminum and glass panels were used as substrates, which were degreased using isopropanol prior to coating application. Drawdowns were made using a drawdown bar with 8 mils wet film thickness. All the coatings were cured for 2 weeks under ambient laboratory conditions.

Coating characterization

After the completion of the curing schedule, ASTM D 5402- methyl ethyl ketone (MEK) double rubs test- was conducted to assess the chemical resistance and extent of crosslinking in the coatings. A 26-oz hammer with three layers of cheesecloth was soaked in MEK. The hammer head was rewet with MEK after every 100 double rubs. The number of double rubs that caused surface changes like loss of gloss, delamination or surface mar, were noted. MEK double rubs greater than 400 indicate sufficient formation of the coating network for practical applications. Only coatings that showed MEK > 400 were further characterized for mechanical properties, impact strength and thermal behavior. Coatings with resins R1 to R6 (except R3 and R5) exhibited excellent solvent resistance, with MEK > 400. Resins R7 to R14 did not cure completely and therefore, further study has been discontinued.

Coatings with MEK > 400 were characterized for hardness, flexibility and impact strength. König pendulum hardness (ASTM 4366) was measured and reported in seconds. Reverse impact strength of the coatings was determined using a Gardener impact tester (ASTM D 2794). The maximum drop height was 43 in. and the drop weight was 3.92 lb. The results were reported as crazing or loss of adhesion or film failure in inch–pounds (in-lb). Flexibility of coatings was determined using conical mandrel bend (ASTM D 522). The results were reported as no failure or using "tear" to indicate damage to the coating film. Table 2 shows results obtained from mechanical tests. All the coatings discussed in Table 2 exhibited good solvent resistance with MEK double rub values greater than 400.

Table 2- Characterization results for AMP_GC coatings. MEK double rubs for all coatings were greater than 400.

Resins	%PDMS/PEG	E: AHEW	Amines	König pendulum hardness (s)	Pencil hardness	Reverse impact strength (in. lbs.)	Mandrel bend*	Gloss at 60°
R1_5%	5, 5	1:1	Anc.2143	115	9H	>160	ND	126.33
			Anc.2432	84	8H	>160	ND	114.00
			And.2634	119	7H	149	ND	125.00
			And.2767	80	8H	>160	ND	76.63
		1:2	Anc.2143	55	2H	>160	ND	97.13
			Anc.2432	35	8H	>160	ND	138.67
			And.2634	100	3H	>160	ND	140.00
			And.2767	43	6H	>160	ND	131.67
R1_10%	10, 10	1:1	Anc.2143	116	6H	>160	ND	134.33
			Anc.2432	104	8H	>160	ND	159.00
			And.2634	82	7H	>160	ND	149.33
			And.2767	109	7H	>160	ND	137.33
		1:2	Anc.2143	115	5H	>160	ND	138.33
			Anc.2432	44	8H	>160	ND	165.33
			And.2634	113	5H	>160	ND	165.67
			And.2767	74	H	>160	ND	141.67
R2_5%	5, 5	1:1	Anc.2143	64	4H	31	Tear	142.00
			Anc.2432	103	3H	>160	ND	134.67
			And.2634	93	2H	>160	ND	131.33
			And.2767	101	2H	>160	ND	107.03
		1:2	Anc.2143	143	6H	>160	ND	166.67
			Anc.2432	125	8H	>160	ND	172.00
			And.2634	173	9H	>160	ND	150.00
			And.2767	66	6H	>160	ND	134.00
R2_10%	10, 10	1:1	Anc.2143	45	8B	39	Tear	88.03
			Anc.2432	39	8B	63	Tear	141.67
			And.2634	76	4B	>160	ND	135.00
			And.2767	103	4B	>160	ND	100.63
		1:2	Anc.2143	110	HB	>160	Tear	85.23
			Anc.2432	59	3B	>160	Tear	128.00
			And.2634	128	5H	>160	Tear	132.67
			And.2767	105	5H	>160	Tear	69.70
R4_5%	5, 5	1:1	Anc.2143	118	9H	129	ND	108.33
			Anc.2432	84	8H	>160	ND	99.90
			And.2634	95	8H	>160	ND	106.00
			And.2767	80	8H	>160	ND	62.67
		1:2	Anc.2143	27	5H	>160	ND	69.33
			Anc.2432	24	5H	>160	ND	148.00
			And.2634	62	4H	>160	ND	77.70
			And.2767	45	3H	>160	ND	92.40
R6_5%	5, 5	1:1	Anc.2143	91	B	70	ND	17.47
			Anc.2432	69	F	86	ND	25.60
			And.2634	74	B	12	ND	33.07
			And.2767	72	B	>160	ND	15.63
		1:2	Anc.2143	86	HB	>160	ND	45.00
			Anc.2432	21	2H	>160	ND	153.67
			And.2634	74	B	>160	ND	64.77
			And.2767	48	H	>160	ND	12.17
R1_15%	15, 15	1:2	Anc.2143	31	HB	>160	ND	117.00
			Anc.2432	26	H	>160	ND	143.67
			And.2634	29	H	>160	ND	135.00
			And.2767	27	H	>160	ND	86.00

*ND indicates no damage to the coating film. MEK double rubs for Anc.2143 cured coatings were less than 400.

In general, most of the coatings appeared smooth and uniform with good glossy surfaces. Most of the coatings also showed high hardness, good impact resistance and flexibility. Among all the coatings, R6_5%_1:1 showed lowest gloss values. Glossy appearance of the coatings improved slightly with increase in amine content of the R6_5% formulations. For all the coatings, except coatings with R2_5% and R2_10%, both König pendulum hardness values and pencil hardness of the coatings decreased with increasing amount of the amine (epoxy: AHEW = 1:2). On the other hand, opposite trend was observed for coatings with R2_5% and R2_10% resins. Pencil hardness for R6_5%_1:2 was similar to or slightly better than R6_5%_1:1. Changing the epoxy: AHEW from 1:1 to 1:2 resulted in increase in pendulum and pencil hardness values. In spite of potentially complete crosslinking of the network, R2_10% coatings showed poor flexibility, with all films showing damage after mandrel bend test. This inversion in properties may be attributed to the differences in functionalities and MW of the PDMS and PEG components in the different AMP_GC resins. Coatings with R2 resin were also softer or more elastomeric compared to other resins, probably due to the presence of monofunctional PDMS. Increasing the amount of PDMS component from 5% to 10% further softened R2 coatings, making them more susceptible to damage.

Thermal behavior

Thermal behavior of the cured coatings was analyzed using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). With DSC, 5-10 mg samples of cured coatings were subjected to heat-cool-heat cycle for temperature range between -20°C-250°C. The rates of heating and curing were maintained at 10°C/min and 5°C/min respectively. Glass transition temperature (T_g) was determined as the temperature of inflection at mid-point. Degradation behavior of the cured coatings was observed using TGA. The coating samples were heated up to 800°C at s heating rate of 10°C/min. Crosslink density and storage moduli of the cured coatings was determined using DMA. T_g of the coatings was determined from tan delta peaks obtained during the experiment. DMA experiments were conducted in the multi-frequency strain mode for temperature range from -20°C-200°C. The crosslink density (v_e) was calculated using $E' = 3v_eRT$, where T is ($T_g + 60 + 273$) K, E' is storage modulus at temperature T and R is the gas constant.

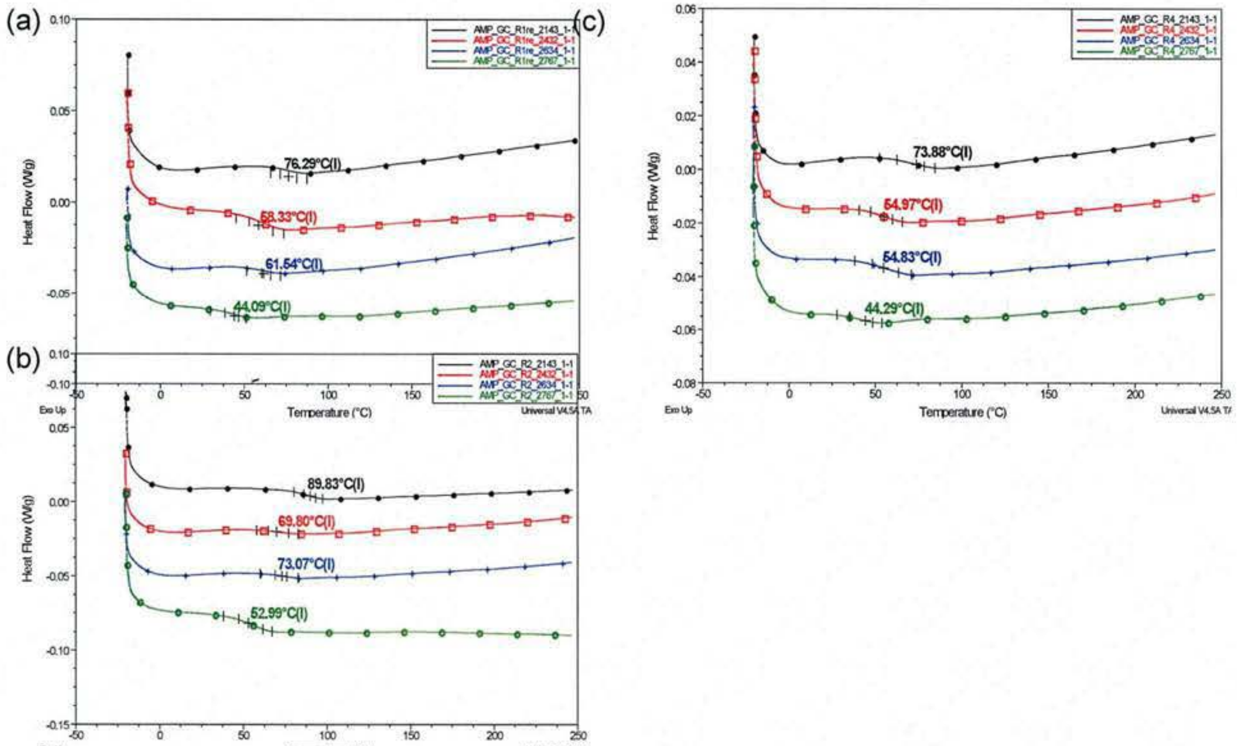


Figure 4: DSC thermograms for coatings with (a) R1_5%_1:1, (b) R2_5%_1:1 and (c) R4_5%_1:1. All legends are of the format resin label_amine_epoxy: AHEW ratio.

Figure 4 shows DSC thermograms for coatings with R1_5%, R2_5% and R4_5% resins. Coatings with R2_5% showed higher T_g as compared to R1_5% and R4_5% coatings. For all the coatings, polyamines resulted in coatings with higher T_g than polyamides as the crosslinkers. Ancamine 2143 resulted in coatings with T_g values 70°C-90°C, which is ~20°C higher than Ancamine 2432 cured coatings. Similarly, Ancamide 2634 cured coatings showed T_g values greater by ~10°C compared to Ancamide 2767.

Figure 5 shows degradation behavior of the AMP_GC coatings. All the coatings degraded at temperatures between 240°C-250°C. Initial weight loss of 1-5% for all the coatings may be due to residual solvent present in the coating films after completion of the curing schedule.

Figure 6 shows tan delta peaks for R1_5% and R2_5% coatings. Narrow, uniform peaks indicate homogeneity in the bulk of the coating films. For R1_5% coatings, polyamides resulted in coatings with higher T_g compared to polyamines, opposite to the results obtained with DSC. Ancamide 2634 and Ancamine 2143 resulted in coatings with T_g higher by ~2°C compared to Ancamide 2767 and Ancamine 2432 respectively. In spite of higher T_g with polyamides, higher crosslink density (v_e) was calculated for polyamines cured coatings, as shown in Table 8. In terms of crosslink density, Ancamine 2432 and Ancamide 2767 caused tighter crosslinking of networks compared to Ancamine 2143 and Ancamide 2634. For some coatings, a small peak was visible in the lower temperature region of ~36°C in Figure 6, indicating the presence of a minor softer phase in the coating.

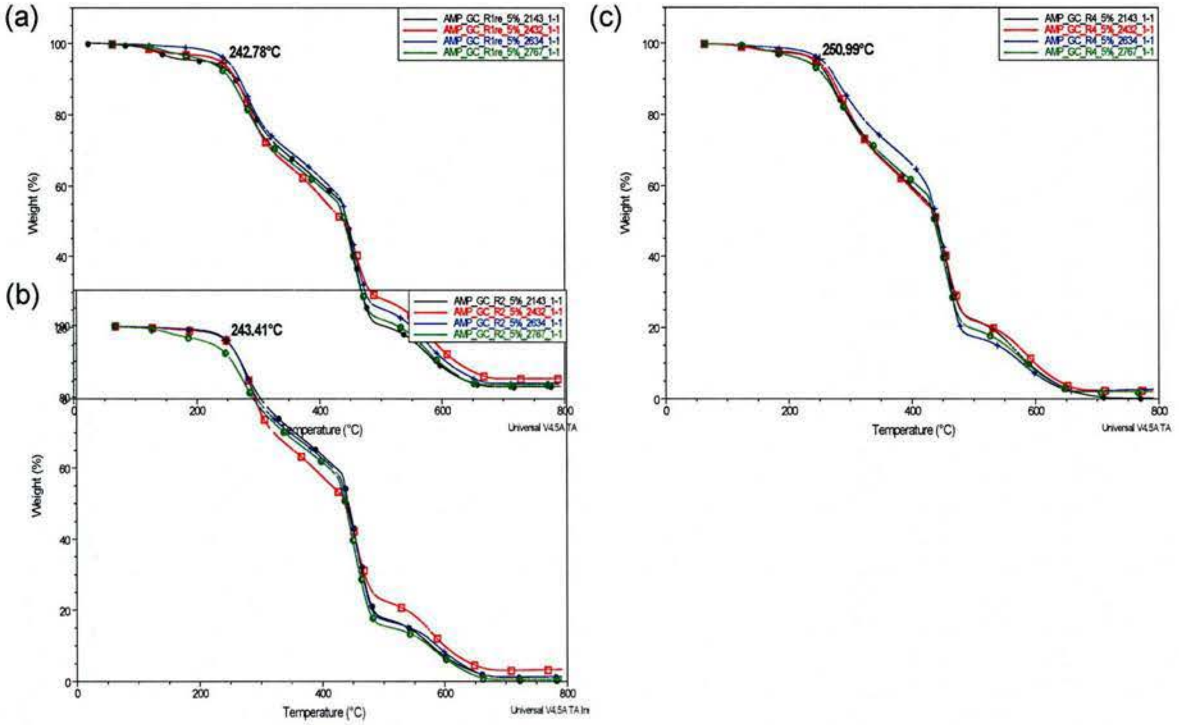


Figure 5: TGA plots for (a) R1_5%, (b) R2_5% and (c) R4_5% coatings. All legends are of the format AMP_GC_resin label_amine_epoxy: AHEW ratio.

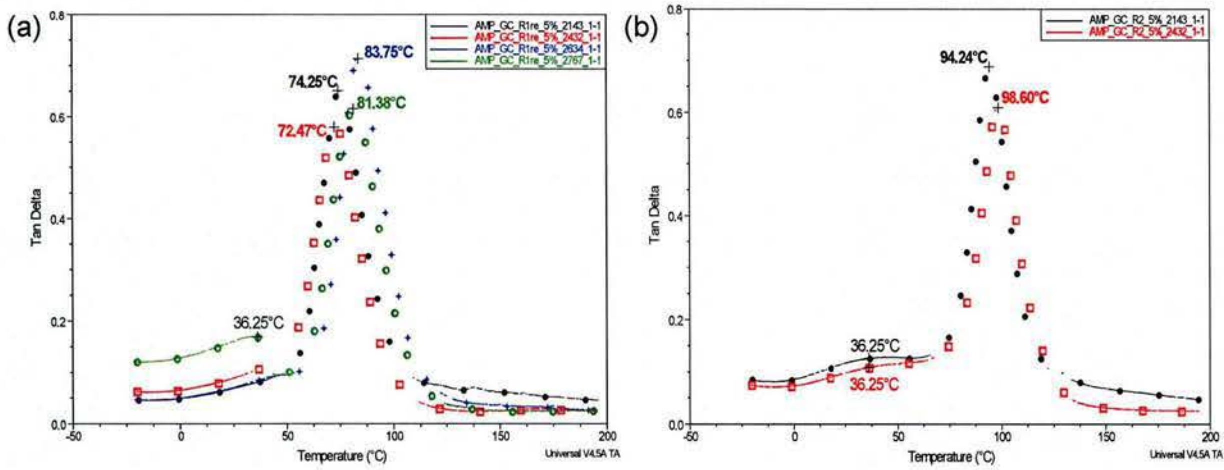


Figure 6: Tan delta peaks for (a) AMP_GC_R1_5% coatings and (b) coatings polyamine- cured AMP_GC_R2_5% coatings at E: AHEW= 1:1.

Table 8: Crosslink density of amphiphilic coatings.

Resin_E: AHEW	**Amines**	**Tg (°C)**	**E' (MPa) at *T K**	**v_e (mol/L)**
R1_5%_1:1	2143	74.60	17.61	1.73
	2432	72.48	18.28	1.81
	2634	83.57	10.97	1.06
	2767	81.92	15.55	1.50

*Temperature T= (T_g + 60 + 273) K.

Laboratory biofouling assays

Preleaching and leachate toxicity analysis

Coatings were placed in a recirculating water tank for 42 days to remove toxic leachates, impurities and catalyst before performance analysis with biological organisms. The coatings were then tested for leachate toxicity by introducing algae in artificial sea water (ASW) with nutrients. The growth of algae on the coatings was observed by obtaining extracts from each coating after 48 hours using fluorescence. The growth of the organisms on the coatings was reported as a fluorescence ratio to a positive growth control. A negative growth control (medium+ bacteria+ triclosan) was also included in the experiment. The coatings were compared to the negative control to confirm the absence of toxic leachates.

Biofilm Cellulophaga lytica (C.lytica) adhesion

Crystal violet colorimetry was used to determine *C.lytica* retention on the smooth and abraded coatings. Coating formulations were deposited into 24 well assay plates. The formulations were allowed to cure under ambient conditions for 2 weeks. After completion of 42 days of preleaching, 1 ml suspension of *C. lytica* (5% in ASW; 10^7 cells/ml) with nutrients was deposited on dried coatings in the plates. The well plates were incubated for 24 hours at 28°C to allow colonization of the biofilm on the coating surfaces. The plates were rinsed three times with deionized water to remove any unattached biofilm. Crystal violet was used to stain the samples. Extractions of crystal violet in acetic acid (33%) were observed under 600 nm absorbance, to determine amount of biofilm retained on the coatings. To determine the fouling release performance of the coatings, the plates were subjected to water jets at 10 psi and 20 psi, after 24 hours of the biofilm growth. The second and the third columns in each well plate were exposed to 10 psi and 20 psi water jet respectively for 5 seconds. The first column in each 24-well plate served as a control for bacterial growth before water jetting and was not exposed to the water jet. Finally, the biofilm adhesion was reported as the percent removal from the coating surface at the above mentioned water pressures.

Figure 7(a) shows the amount of *C.lytica* that successfully attached onto AMP_GC coatings. Compared to commercial standards like Silastic T2, Intersleek 1100SR, Intersleek 900 and Intersleek 700, AMP_GC coatings showed lower attachment of the biofilm on the surface. Coatings R1_5%_F2 and R4_5%_F2 were severely cracked after water leaching and therefore, were not tested for biofilm adhesion. Figure 7(b) shows percent removal of the biofilm from the surface of the coatings. In general, for all coatings, percent removal of the biofilm was higher at 20 psi than 10 psi. Average percent removal of 60-65% from AMP_GC coatings was significantly lower than from Intersleek 1100 SR, which showed ~98% removal of the biofilm. The amount of biofilm retained on the surface of the AMP_GC coatings (Figure 7(c)) was higher than Intersleek 1100SR. As compared to Intersleek 900 and 700, AMP_GC coatings showed similar or higher biofilm removal from the surface.

Diatom Navicula incerta (N.incerta) attachment and adhesion

N.incerta adhesion was carried out in a fashion similar to *C.lytica* adhesion explained earlier. 1 ml solution of algae in ASW was dispensed onto cured coating formulations in 24 well assay plates. The plates were incubated for 2 hours to allow diatom adhesion. Fluorescence was used to quantify the algal settlement on the coatings. Fouling release performance of the coatings was determined by exposing the well plates to water jet after 2 hours of cell settlement. Similar to *C.lytica* adhesion, the first column was used as a reference for the initial cell settlement, while the second and the third columns were exposed to water jet at 10 psi and 20 psi for 10 seconds. The results obtained are shown in Figure 8. Intersleek 1100SR showed the lowest diatom attachment among all the coatings. Although the amount of diatoms removed from Intersleek 1100SR was not as high as the AMP_GC coatings, the amount retained on the surface was extremely low. AMP_GC coatings showed similar amount of attached diatoms as Intersleek 700 and 900, Silastic T2 and regular polyurethane coatings. AMP_GC coatings facilitated easy removal of diatoms from the surface. Formulations R1_5%_F3, R2_5%_F2, R4_5%_F3 and R4_5%_F4 showed ~98% removal of diatoms, the highest removal among all the coatings (Figure 8(b)). The amount of diatoms retained on the surface of the above formulations was lower than Intersleek 1100SR.

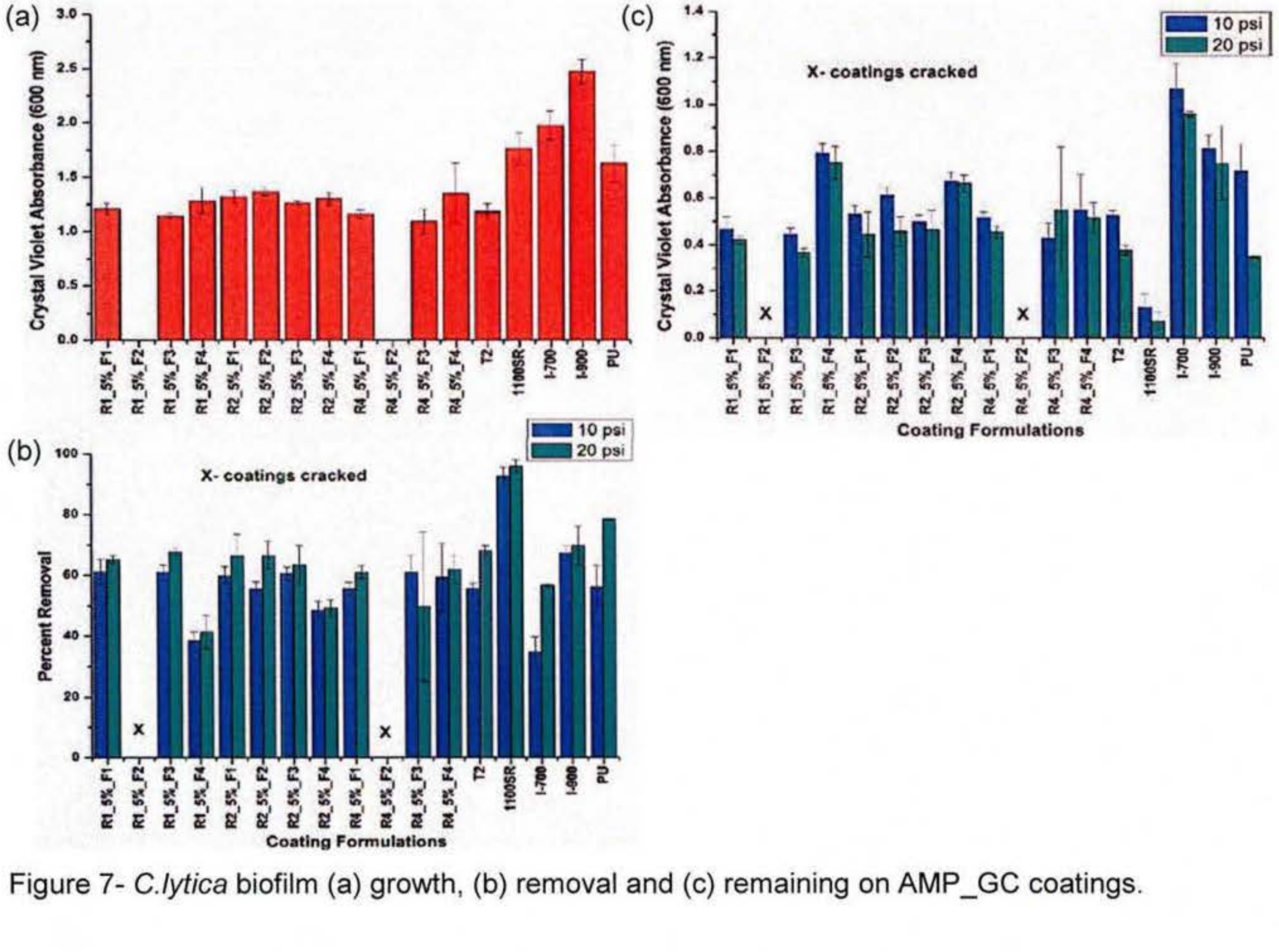


Figure 7- *C.lytica* biofilm (a) growth, (b) removal and (c) remaining on AMP_GC coatings.

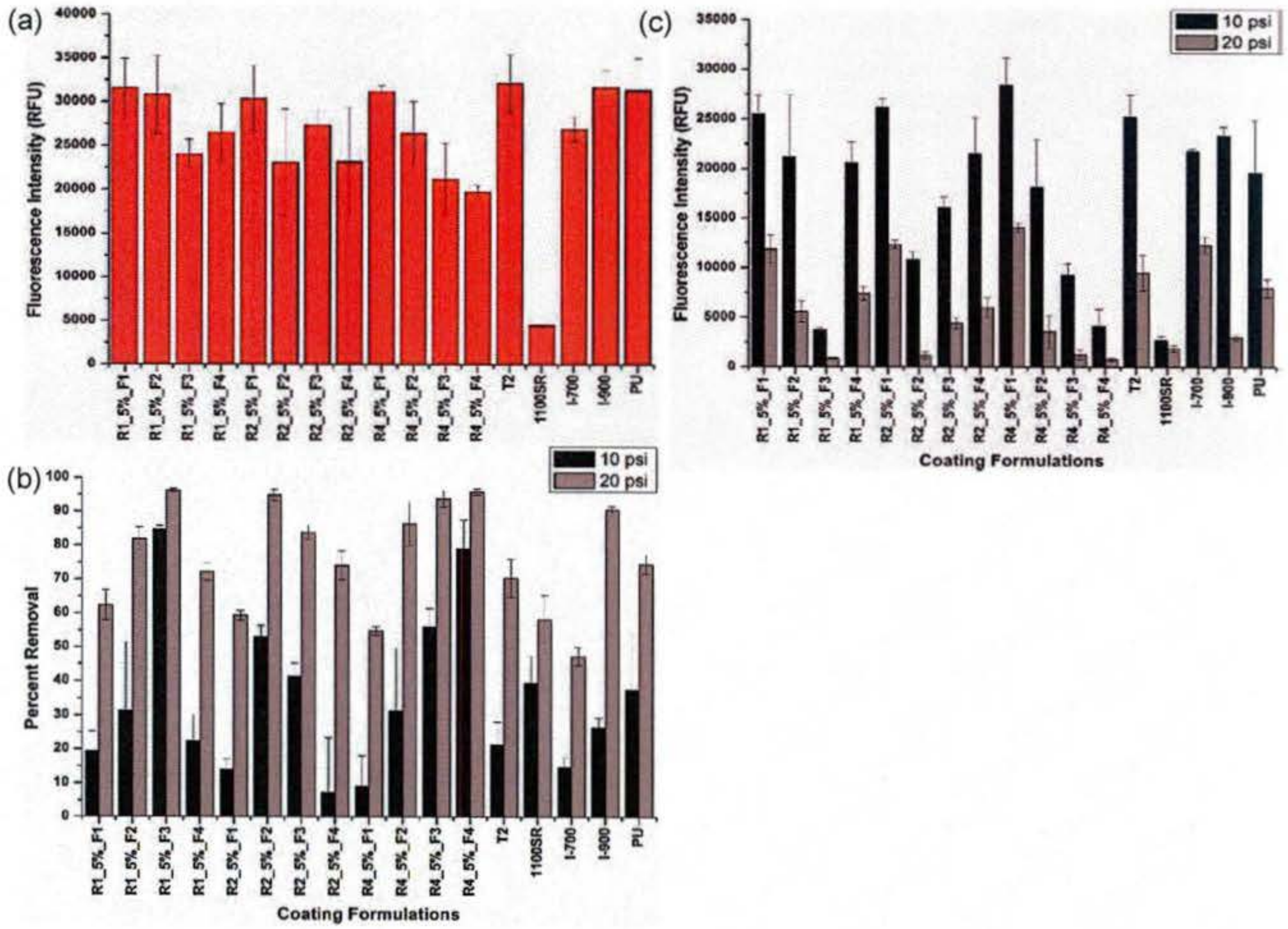
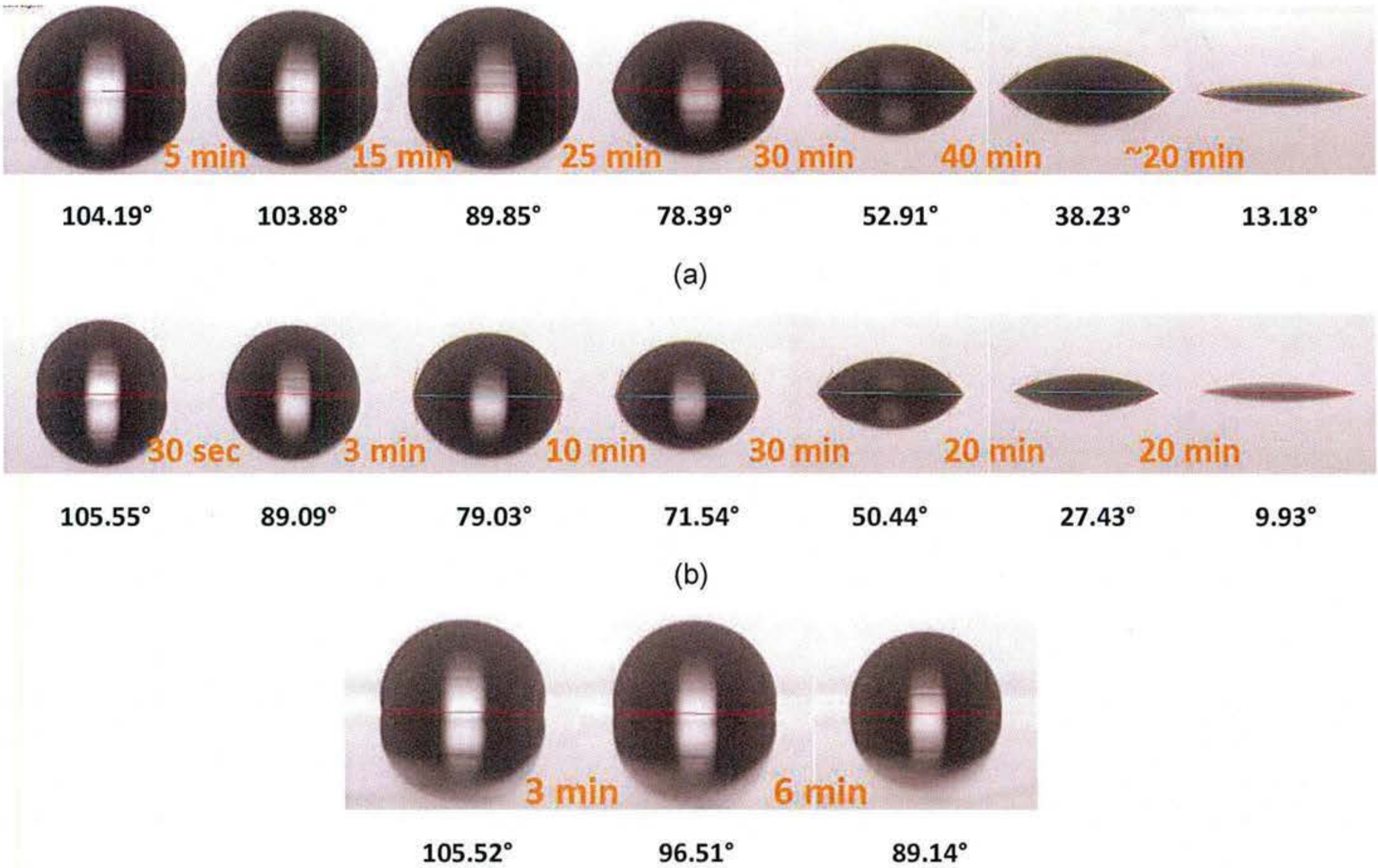


Figure 8- Diatom *N.incerta* (a) attachment, (b) removal and (c) remaining cells on the coatings.

Contact angle experiments

Figure 9 shows dynamic changes in water contact angles on the surface of AMP_GC coatings. For R1_5%_F1 and R2_5%_F1, the coating surfaces changed from hydrophobic (>90°) to hydrophilic (<90°) in ~20 min and ~10 min respectively. On the other hand, surface energy of R1_5%_F3 coating drastically within 1 min after contact with the water droplet. Dynamic changes in water contact angles may be indicative of rearrangement of chains on the surface with changing environment. Faster surface rearrangement is desired for better FR performance.



(a)

(b)

(c)

Figure 9: Dynamic changes in WCA values on (a) R1_5%_F1 coatings, (b) R1_5%_F3 and (c) R2_5%_F1 coatings. E: AHEW = 1:1 for the three coatings.

Conclusions

Amphiphilic glycidyl carbamate coatings were synthesized using HDI trimer, glycidol and PDMS and PEG of different MW and functionalities. Resins with PDMS MW = 1000 g/mol were successfully crosslinked under ambient conditions for 2 weeks. Most of the coatings appeared smooth and glossy. Hardness values of all coatings, except coatings with R2 resins, decreased with increasing amount of amine in the coating formulation. Inverse trend was observed for coatings with R2 resins, where the hardness increased with increasing amine content in the formulations. All the coatings degraded at temperatures in the range from 240-250°C. DSC thermograms showed that the coatings crosslinked with polyamines exhibited T_g values higher by

~20°C compared to the polyamide cured coatings. Tan delta peaks obtained from DMA showed the opposite behavior, in which coatings cured using the polyamides showed higher T_g values. But based on calculated crosslink density values, tighter network of coatings was observed for the polyamine cured coatings. FR experiments showed that the amount of biofilm attached onto the surface of all the amphiphilic coatings was lower than commercial standards like Intersleek 1100SR. 60-65% biofilm removal from the surface of the amphiphilic coatings at 20 psi water jet pressure was also significantly lower than Intersleek 1100SR (~98% removal). Conversely, amphiphilic coatings showed higher removal of diatoms than the commercial standards. ~98% removal of diatoms from the surface of R1_5%_F3, R2_5%_F2, R4_5%_F3 and R4_5%_F4 was higher than all the coatings. Water contact angle experiment showed a dynamic change in values, indicating rearrangement of PEG chains on the surface. Initial experiment showed faster rearrangement of chains on coatings crosslinked using Ancamide 2634, compared to Ancamine 2143.

Future work

Fouling release performance of the AMP_GC coatings against macrofoulants like barnacles and mussels is currently under investigation. Coatings are also being analyzed for their mechanical and thermal behavior. Further, effect of increasing MW of PDMS and/or PEG on FR performance and mechanical properties will be studied. AMP_GC resins will also be synthesized using IPDI trimer instead of HDI to investigate effect of changing the isocyanate on coating properties.